Rafiq Lone
Salim Khan
Abdullah Mohammed Al-Sadi *Editors*

Plant Phenolics in Abiotic Stress Management

Springer

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Dedicated to Great Teacher and Philanthropist

Mr. Peerzada Mohammad Syed Shah

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Historical Perspective of Plant Phenolics

1

Saima Hamid, Ali Mohd Yatoo, Mohammad Yaseen Mir, Shafat Ali, and Heba I. Mohamed

Abstract

The phenolic compounds in plants can be used as antioxidants, functional polymers, attractants (flavonoids and carotenoids), ultraviolet light protectors (flavonoids), flash signals (salicylic acid), and phytoalexins, and protection chemicals. Phenolic compounds are important in defense reactions from a natural physiologic point of view, such as anti-aging, anti-inflammatory, antioxidant, and anti-proliferative operations. It is therefore useful to consume crop products which have elevated levels of antioxidants, thereby reducing the occurrence of certain acute illnesses, such as arthritis, tuberculosis, and cardiac illnesses, through oxidative stress management. Based on their impacts as allelopathic compounds and plant growth regulators, small molecular weight phenolics are of excellent concern and have traditionally been regarded protection molecules in plant pathogens. Recently, its function as signal molecules has become apparent in plant microbe structures. Specific molecules, such as Agrobacterium, can function as inducers or repressors for virulent mutations on plant–pathogen structures, Rhizobium-legume, and likely other symbiosis.

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1.1 Introduction

The function of main metabolites in fundamental body activities, such as DNA formation, growth and development, breathing, transport, and breeding, has been defined for 200 years in contemporary science and physiology. In biology, Kossel can be ascribed to the notion of the secondary metabolite. Secondary compounds of plants are generally categorized as biosynthesized chemicals (Wu and Chappell 2008). There are usually three big molecular groups: phenolics, steroids, and alkaloids. Phenolics are a good example of a widespread family of metabolites, which are common to all higher plants because these molecules involve lignin structure. On the other hand, other compounds such as alkaloids, which are far more particular to the specified plant species and genus, are scarcely dispersed in the plant world. The narrow allocation of compounds forms the groundwork for chemical chemotaxonomy and ecology. Because of its great biological activity, secondary plant metabolites have been used in traditional medicine for centuries. Today, they are precious compounds such as medicines, cosmetics, fine chemicals, and nutraceuticals. They are equivalent. Recent studies have shown that aspirin (acetylsalicylate) derived from salicylate could be a nice illustration for Western countries where chemistry is the cornerstone of the medical industry, 25% of the molecules used are real vegetables (Cabras et al. 1999). Structurally and chemically secondary metabolites are much different than the main metabolites, and they relate to compounds in specific bodies which do not necessarily have vital photosynthetic and cardiovascular fundamental functioning, but are considered necessary for the preservation of crops in the setting. Plants have metabolic routes contributing to dozens of thousands of products that can efficiently respond to biotic and abiotic stress conditions. These ways, often selected after first cell duplication from vital main metabolic processes, lead to duplicate mutations displaying fresh features and optimized and diverse roles in different ways. Secondary metabolite accumulation frequently signals the beginning of evolutionary phases. The proper retention model of different secondary products is guaranteed by a rigorous spatial and temporal monitoring of gene expression. An extra standard of regulation is the necessary delivery of metabolic intermediates. Ontogene and circadian clock-controlled cell activity, together with master environmental transcription variables (Ornston and Yeh 1979; Wink 1999; Lehfeldt et al. 2000), are key characteristics of crop secondary metabolism. Secondary metabolite obviously acts as a protection against crop and signal compounds (in order to promote pollination or spreading creatures) and protects the crops against solar radiation and oxidants (for herbivores, microbes, bacteria, or conflicting crops). A particular plant secondary metabolite model is complicated; it moves in a particular tissue and organ manner; variations in evolutionary phases can be seen.

Phenolic compounds, even if the sort of compound available differs by the phylum in question, are the most commonly dispersed side-metabolites current in the plant kingdom. In bacteria, fungi and algae phenolics are rare as Bryophytes contain periodic polyphenols, including flavonoids, but the complete variety of polyphenols can be discovered in aquatic crops (Harborne 1980; Robards and Antolovich 1997). Around 2% of all plant-sized carbon photosynthesized is projected to be transformed into flavonoids or tightly associated compounds (Swain 1975). Higher crops synthesize several thousand recognized phenolic compounds, with a continuous increase in the amount of completely identified. The leaves of vascular plants comprise esters; hydroxycinnamic acid amides and glycosides; flavonoids glycosylated, particularly flavonols; and proanthocyanidins and their families. Examples of phenolic materials are lignin, suberin, and fruit sporopollenin. Certain soluble phenolics, for example chlorogenic acid, are commonly dispersed, but the allocation of many other buildings is limited to particular generations or relatives, rendering them useful biomarkers for taxonomic research. In distinct plant lines, when these compounds responded to particular requirements, the capacity to synthesize phenolic compounds is being chosen throughout evolution, allowing crops to meet the constantly evolving economic problems over moment (Noel et al. 2005). In the form of a huge “Phenolic UV Light Screens,” for instance, the effective adjustment of a few greater Charophyceae representatives, which have been considered the prototype of amphibious crops that have likely followed real crops when coming into the soil through an aquatic setting, has been mainly accomplished (Croteau et al. 2000). A prevalent collection of biochemical responses in vascular plants already existing 400 million years earlier with the development of upright vascular land plants are involved in the phenylpropanoid path contributing to lignins. In a developmental way, these metabolic backbones have increasingly been enhanced in order to adapt to various plantation households and the notable variety of biochemical products that can be seen (Payne et al. 1991). These phenolic compounds are constituted biosynthesis through either a shikimic acid pathway or the malonate-acetate process recognized as the polyketide and associated biochemical pathways, accounting for about 40% of organic carbon that circulates throughout the biosphere. In addition, the rates limiting stage in the disposal of biological material are its recovery to sulfur emissions during biodegradation (mineralization) (Chapman and Regan 1980). Generally speaking, the word “phenol” describes a phenyl band with one or more of its substituents in respect of crop phenolics. The word “polyphenol” can be used to describe naturally occurring products with, but in the sense of phenolic plant phenolic compounds, such as gossypol, phenolic carotenoid 3-hydroxyisoreniathenes (I), such concept is not adequate as it contains compounds, including gossypol and phenolic carotenoid (3). Thus, the overall principle lately suggested by Quideau et al. (2011) is that the words “phenolics of crops” be exclusively used to apply to artificial secondary metabolites biogenetically produced either by shikimate/phenylpropanoid system which offers phenyl propanoids immediately. Although the majority of these compounds have functional positions on the tissue surface, cells synthesize a large range of non-structural components which have different functions in crop development and preservation. The term “crop phenolics” therefore covers a very varied community, of the chemically recognized representatives, several thousand of whom are identifiable with a wide variety of recognized constructions: monomeric, dimeric, and polymer phenolics.

1.2 Classification of Phenolic Compounds

Three types of phenol compounds consist of (a) a benzene (C6), (b) a C6 matrix comprising a linked carbon chain of 1–4 or 7 carbon atoms (C6–C*n* category), and (c) an increased complicated skeleton with a second category of benzene (C6–C*n*–C6). Each group is classified according to the following classifications: C6–C*n*–C6 classes: C6–C1–C6, C6–C2–C6 classes; C6–C3–C6 classes; and C6–C7–C6 classes which, for instance, including the Flavonoid family.

The phenolics will be divided into three subgroups with greater difficulty. The first category is comprised of the phenol dimmers and condensation oligomerics, while the components [(C6), [(C6–C3)*n* and (C6–C3)*n*] of overall formula are mentioned under the polymer phenols. One final class called phenolic hybrids involves compounds with other kind of organic compounds such as terpenes or lipids which pretend to be phenolic hybrids.

1.2.1 C6 Phenolic Compounds

Rare parts of aromatic and medicinal plants (AMPs) contain simple phenols, such as catechol, hydroquinone, and phloroglucinol. Catechol is discovered in leaves of *Gaultheria* species according to the report of Lattanzio (Arbutin), while hydroquinone O-glycoside is discovered in leaves of multiple *Vaccine* spp. such as blueberries, cranberries, cowberries, and fruit plants (*Pyrus communis* L.) The wealthiest sources of *Bergenia crassifolia* (L.) in arbutin, among other plant species, are recorded by Pop et al. (2009), varying from 15 cents per natural plant weight to 23 tons. In the skin of different citrus fruits, phloroglucinol has been discovered as glucoside.

1.2.2 Phenolic Compounds

The category C6–C*n* is a more all-embracing category of uncommon or frequent households. The C6–C1 is a restricted class, including benzoic acid and variants of benzaldehyde. Their fundamental skull is shown in Fig. 1.1, whereas in Table 1.1 there are reports of the hydroxy and/or methoxy substitution motif. The main compounds of hydroxybenzoic acid are glucosides, and glucose esters from *p*-hydroxybenzoic, vanillic, and syringic plants are discovered occasionally only. The recognized compounds of hydroxybenzoic acid have been discovered only in relative concentration (1 ppm) in the most significant fruit and vegetable crops

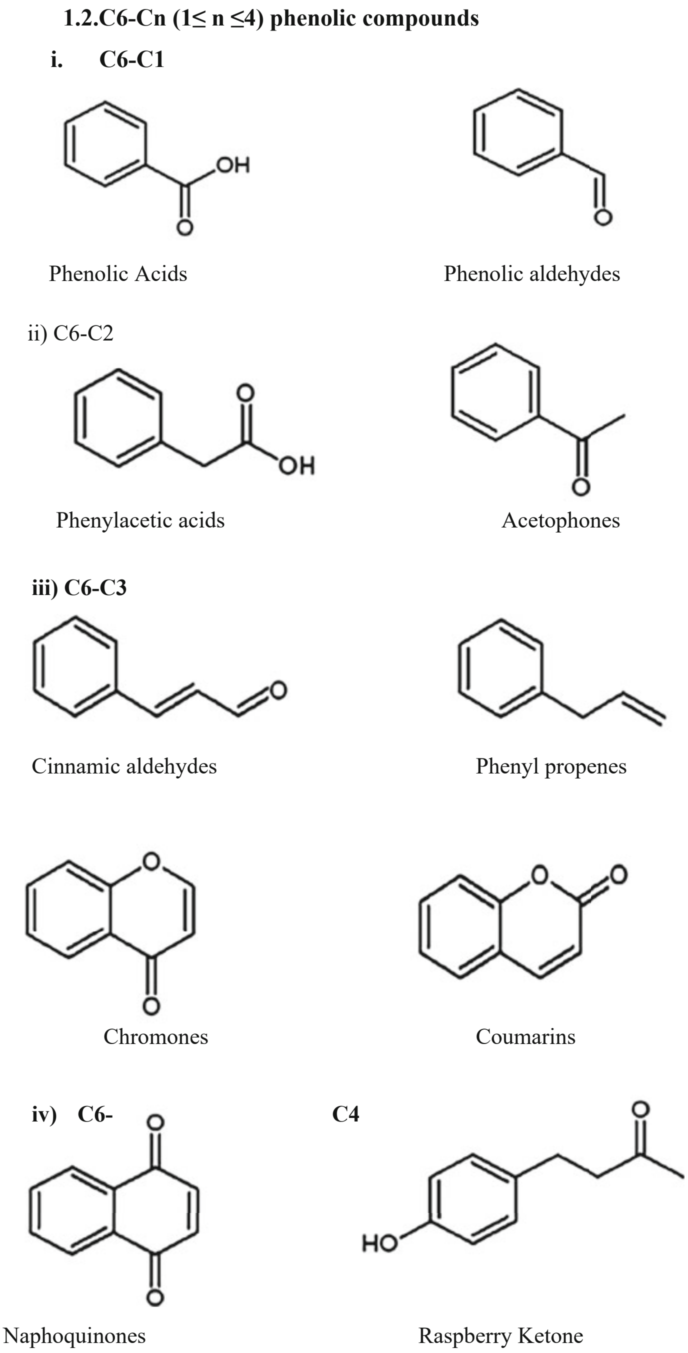
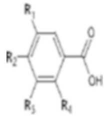
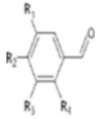


Fig. 1.1 Basic skeletons of C6–C*n* phenolic compounds

Table 1.1 Fundamental frame and substitution pattern of phenolics

	Substitute 1	Substitute 2	Substitute 3	Substitute 4	Phenolcarboxylic acids	Phenol aldehyde resin
	Hydrogen	Hydroxyl	Hydrogen	Hydrogen	4-Hydroxybenzoic acid	*p*-OH-benzaldehyde
	Hydrogen	Hydrogen	Hydrogen	Hydroxyl	2-Hydroxybenzoic acid	Salicylaldehyde
	Hydrogen	Methoxy	Hydrogen	Hydrogen	4-Methoxybenzoic acid	*p*-Anisaldehyde
	Hydroxyl	Hydroxyl	Hydrogen	Hydrogen	3,4-Dihydroxybenzoic acid	*p*-Protocatechualdehyde
	Hydroxyl	Hydrogen	Hydroxyl	Hydrogen	Dihydroxybenzoic acid	Ortho chloro benzaldehyde
	Methoxy	Hydroxyl	Hydrogen	Hydrogen	4-Hydroxy-3-methoxybenzoic acid	4-Hydroxy-3-methoxybenzaldehyde
	Hydroxyl	Hydroxyl	Hydroxyl	Hydrogen	3,4,5-Trihydroxybenzoic acid	Gallic aldehyde
	Methoxy	Hydroxyl	Methoxy	Hydrogen	4-Hydroxy-3,5-dimethoxybenzoic acid	4-Hydroxy-3,5-dimethoxybenzaldehyde

Source: Dimitrios and Basu (2012)

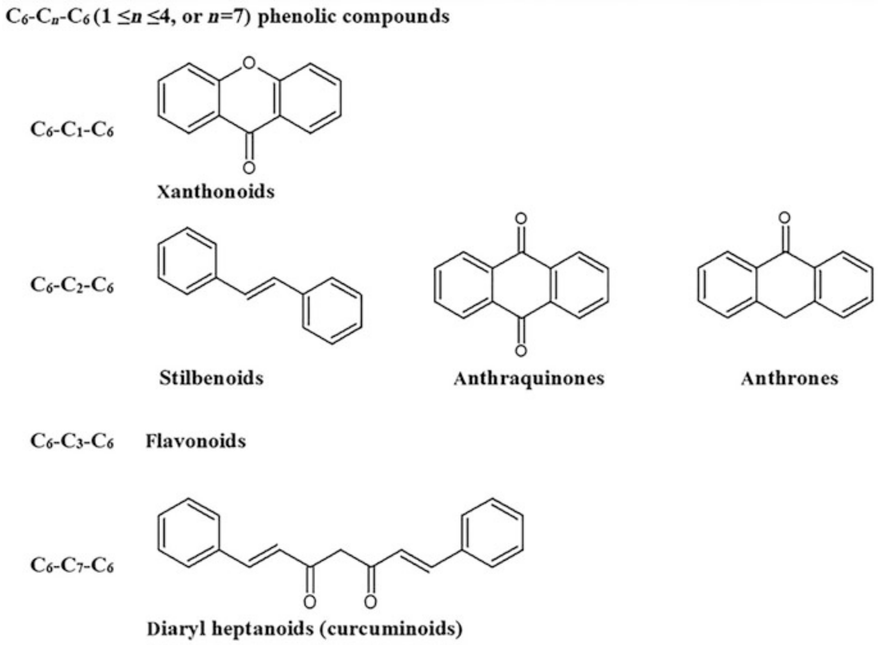


Fig. 1.2 Basic skeletons of C6–C*n*–C6 phenolic compounds (Itokawa et al. 2008)

(Herrmann 1989). Vanillin is probably the most significant phenolic aldehyde, used extensively as a flavor and aroma ingredient.

Category C6–C2 includes phenylacetic acid, acetophenone and phenethyl alcohol components, hydroxylated and/or methoxyl components known as phenylethanoids. Figure 1.2 shows the fundamental bones of the households whereas the replacement model is restricted to three or four monohydroxides or three or four dihydroxides. Homogentisic acid is rarely replaced by 2.5-dihydroxy and is recognized in strawberry and fruit (Tomás-Barberán and Clifford 2000). The important phenyl ethanol component, hydroxytyrosol, is a powerful antioxidant discovered in olive leaf and citrus juice similar to oleuropein, and the corresponding elenolic acid. The antioxidant active in different structures was shown by oleuropine and by derivatives and also by aglykon hydroxytyrosol (Gordon et al. 2001; Chimi et al. 1991). Phenylpropanoids, hydroxycinnamic substances, cinnamic aldehydes, monolignols, phenylpropenes, coumarins, isocoumarins, and chromones (Fig. 1.2) form part of the category C6–C3.

1.2.3 Xanthonoids

C6–C*n*–C6 is a wide-ranging group of phenolic compounds that include the category of xanthonoids, comprising of the stilbenoids, anthraquinones, and antrones;

the categories C6–C3–C6 which include only those of the flavonoids; and the diarylheptanoids C6–C7–C6. anthraquinone, anthrones, xanthonoids, stilbenoids, and diarylheptanoid xanthonoids are mainly connected to four genera of crops, that is, *Guttiferae*, *Gentianaceae*, *Moraceas*, and *Polygalaceae*, but xanthones of 20 species of superior crops have been separated. Simple xanthones, xanthones glycoside, Moraceae xanthones, and various xanthones (Gales and Damas 2005) monomeric and oligomeric stilbenoids have been found to be members of 33 plants species (Shen et al. 2009). They are categorized into four primary classes: monomeric xanthones. They function as wood metabolites and as inhibitors of protection (Niesen et al. 2013). Resveratrol, a blue liquor component owing to its cardioprotective impacts, is the most famous stilbenoid. However, in many other crops, beans and fruit of particular trees, the compound is also discovered (Sanders et al. 2000). Anthracene (tricyclic organic) chain with two carbonyls in the positions C9 and C10 involves a chemical structural feature of anthracene. Plants with substantial amount anthraquinones include rubiaceae, rhamnaceae, Fabaceae, polygonaceae, bignoniaceae, verbenaceae, scrophulariaceae, and liliaceae (Catalgol et al. 2012) and are commonly known in the family. The best-known part of the community is Aloe Emodin, which shows anti-induced behavior on several cancer neurons (Qing Liu et al. 2018). Anthrones are decreased types of anthraquinones that lack one carbonyl oxygen and often exist in crops in both classes (Evans et al. 1979).

1.2.4 C6–C3–C6 Phenolics: Flavonoids

The fundamental discrimination against flavonoids is focused on whether the C3 gap is closed or a fifth heterocyclic (circle C) loop. The flavonoid community thus is splitted into two communities, flavonoids with an open bridge and the flavonoids with a shut bridge; the flavonoids with five and six-member heterocyclic ring flavonoids are further differentiated in two subgroups. The six-membered heterocyclic core flavonoids are further split into two, three, and four groups. Nine kinds of phenolic compounds (flavans, phenol-3-ols, flavanones, etc.) are part of the 2-phenyl-chromanic flavonoid complex.

1.3 Biosynthetic Pathway of Phenols in Plants

The phenolic compounds are abundantly biosynthesized in plants via shikimate pathway via chloroplast. These aromatic modules perform an important part, such as lignans, pigments, antioxidants, signalers, electrons movement, and interactions (Macheroux et al. 1999). The shikimate biosynthesis process provides precursors to artificial molecules (Mittelstädt et al. 2013) as after the first highly poisonous flower in Japan, Shikimi (*Illicium anisatum*) was assigned after it was isolated (Ghosh et al. 2012). In higher crops, the biochemical mechanism is an important connection between main and secondary nutrition (Macheroux et al. 1999). The mechanism for shikimate generates in microorganism fatty amino proteins L-phenylalanine

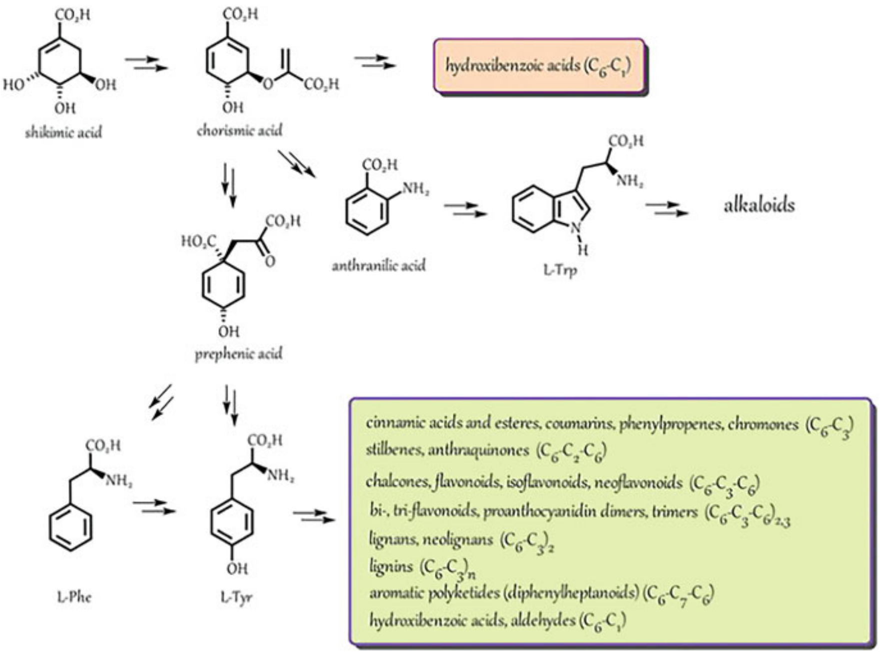


Fig. 1.3 Shikimic and chorismic acids are the common precursors for the synthesis of L-Phe, L-Tyr, and L-Trp and diverse phenolic compounds (Santos-Sánchez et al. 2019)

(L-Phe), L-tyrosine (L-Tyr), and L-tryptophane (L-Trp), molecular construction structures for the biosynthesis of protein (Figs. 1.3 and 1.4).

Phenolic compounds are allowed to express with changing environs (e.g., herbivores, pathogens, adverse temperature and pH level, salt stress, heavy metal pressure, ultrasonic, and ultraviolet rays). Factors that cause plant phenol production are divided into UVC (280–320 nm) and UVA (200–400 nm) radiation. The environment transmits UVA and UVB radiation, as all UVC and some (extremely vigorous) UVB radiation are incorporated into the coating of earth's soil. The rise in the enzyme activity in ammonia-lyase phenylalanine and chalcone synthase enzymes, among others, is responsible for this concentration (Cheynier et al. 2013). In the crops when subjected to UVB radiation, studies were carried out on the rise of phenolic compounds such as anthocyanins (Zhang et al. 2012). Another research shows that application to UVB increases the biosynthesis of anthocyanin in Cripps purple (*Malus* × *domestica* Borkh), but not in "Forelle" pears (*Pyrus communis* L.) (Marais et al. 2001). The impact can be attributed to the sensitivity to UV radiation and plant cultivars as researched while under stress, content of phenolic compounds gets influenced. The increase of phenolic compounds in plants grown in vitro exposed to aluminum (Al) and cadmium (Cd) was also studied in blueberry (*Vaccinium corymbosum*). Through the manufacturing of reactive oxygen (ROS) organisms, such heavy metals trigger elevated plant toxicity. Study writers

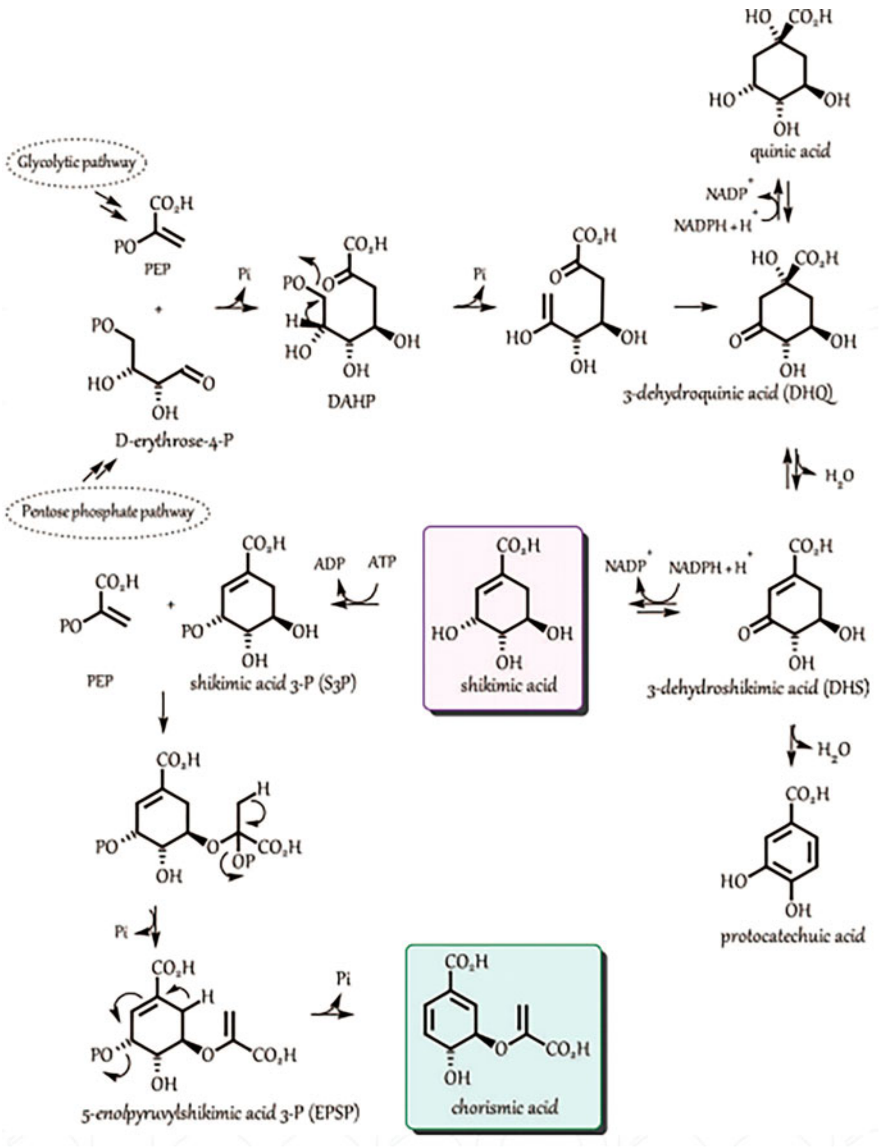


Fig. 1.4 Shikimate pathway

propose the reduction of ROS in blueberry crops by phenolic compounds, specifically chlorogenic and ellagic oils as shown in Fig. 1.5 (Manquián-Cerda et al. 2018). In 2011, an exciting survey was performed by Gutbrod et al. (2011) to explore the impact of opposition to fungus which damages leaves (*Spodoptera littoralis*) of fruit plant seedlings (*Malus* × *domestica*) (Gutbrod et al. 2011). The researchers discovered that there was a considerable herbivore bias in the most apical leaf for

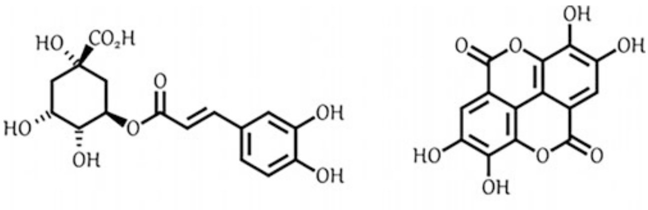


Fig. 1.5 Chlorogenic (C6–C3) and Ellagic (C6–C1) acids with their chemical outlines

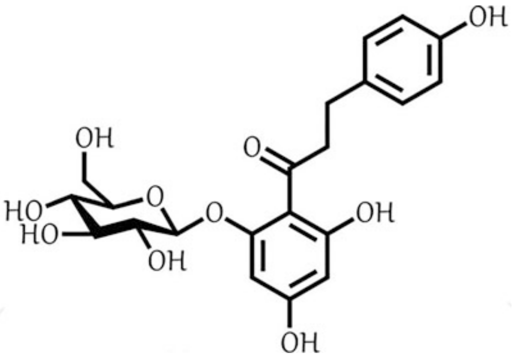


Fig. 1.6 Chemical structure of phlorizin (C6–C3)

undamaged crops (caused strength) and also the findings also indicated that flavonoid phlorizin (Fig. 1.6) was more highly concentrated in harmed crops than in undamaged crops. This shows that moth choice may be associated with phlorizin in undamaged fruit crops, which is the primary secondary phenolic metabolite in fruit leaf.

1.4 Phenols and Health Benefits

Phenolic compounds are an excellent means to prevent skin diseases, including injuries and burning owing to their normal origins and small toxicity, and are caused and influenced by them. Polyphenols also protect and assist to avoid or dim the development of certain hair disorders (e.g., wrinkles, acne) or life-threatening illnesses, including skin cancer, among which the most hazardous hair illness. Polyphenols are protective chemicals, as the skin malignancies comprise of three major illnesses: fetal cell carcinoma, malignant tissue carcinoma, and malignant melanoma. The incidence of melanoma has been shown to rise substantially in recent years, particularly for the black inhabitants (Lasithiotakis et al. 2010; Erdmann et al. 2013; Jemal et al. 2010). Phenolic compounds that have promising innate anticancer characteristics to skin cancers can affect the cell cycle. Curcumin, which functions as a pro-apoptotic compound, is one of these compounds. Studies have demonstrated that P53 does not trigger the compound that is important for the treatment of chromosome-resistant p53 melanomas. Caspase-3 and caspase-8 have an effective

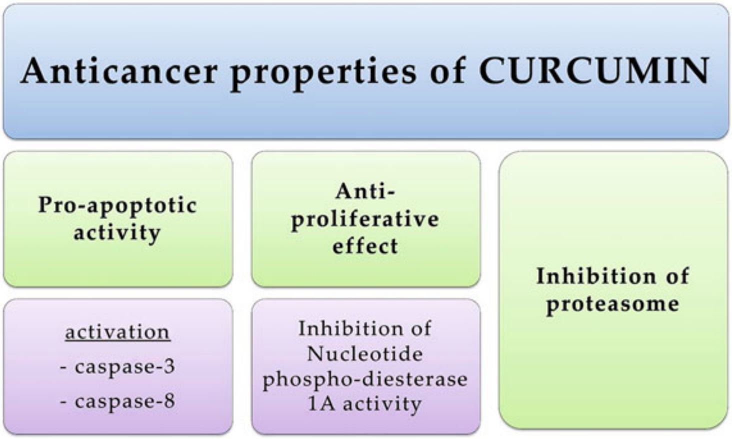


Fig. 1.7 Showing anticancer characteristics of curcumin (red areas show the curcumin characteristics, while the purple areas show specific instances of the effect of the curcumin)

impact but not caspase-9, and apoptosis is caused by a cell negotiation method (Zheng et al. 2004; Abusnina et al. 2011). In addition, curcumin had an anti-proliferative effect on a highly metastatic B16F10 murine melanoma line of nucleotide phosphodiesterase 1A attacks (Danciu et al. 2015). Induction of caspase-related apoptosis by modulation of both the internal and the external mechanisms (Attoub et al. 2011) performs a certain part in luteolin. Vitexin also exhibits proapoptotic behavior, manifested in declines in the Bcl-2/Bax proportion and in the caspase activation (Tan et al. 2012; Zhou et al. 2009). Gallic acid (accurately caspase-3) (Ji et al. 2009) is another phenol compound that can lead to apoptosis when caspase is activated (Fig. 1.7).

Caffeic acid (3,4-dihydroxycinnamic acid) is another significant phenolic with anticancer characteristics. Yang et al. (2014) noted that caffeic alcohol has a powerful inhibitor impact on the development of colony dependency of mammalian hair disease neurons and on the neoplastic conversion of HaCaT neurons induced by the epidermal development regulator (EGF) (Yang et al. 2014). Different skin diseases, including injuries and burns, may be treated with phenolic compounds. In skin tissue repair processes, phenolic antioxidants perform a significant part. They may speed up the cure and encourage the spread of ordinary skin cells in severe and permanent injuries (Thang et al. 2001). Plants wealthy in antioxidant phenolic compounds can efficiently stop the oxidative damage in the inflammatory stage of the cells, thereby encouraging the cure (Albaayit et al. 2015; Pessoa et al. 2015; Geethalakshmi et al. 2013). A number of products promoting the healing process are available on the emerging pharmaceutical industry.

1.5 Phenols as an Antioxidative Agent

The significant elements of fruit, vegetables, and beverage are simple phenolics such as hydroxycinnamic acid conjugates and flavonoid products. They demonstrate a broad variety of antioxidant activity in vivo (Rice-Evans et al. 1996) which is intended to protect against serious illnesses like pulmonary and leukemia (Boudet 2007). Phenolic compounds have a variety of physiologic characteristics such as antiallergy, anti-atherogenic, anti-inflammatory, antimicrobial, antioxidants, and vasodilatory (Middleton et al. 2000; Puupponen-Pimiä et al. 2001). Recent studies have shown that tea polyphenols can safeguard against various phases of cancer (Khan and Mukhtar 2010). EGCG, the leading green tea catechin, is the chemical-preventing drug (pulmonary, heart, gastrointestinal, hair, and prostate disease) and antiobesity and cardiac safety compound (Khan and Mukhtar 2010; Klaus et al. 2005). Epigallocatechin gallate (EGCG), which is the primary polyphenol in green tea, has improved antioxidant action and positive impacts on wellness after conjugation with DHA and the tetraester so that colon can efficiently be stopped (Zhong et al. 2012). Caffeine also worked effectively to suppress body weight gain through thermogenesis stimulus, compassionate stimuli, meal intakes, and adipose volume reduction (Kobayashi-Hattori et al. 2005). Furthermore, the threat of coronary artery disease and atherosclerosis by itself was reduced by hydroxytyrosol, one important phenolic ingredient in citrus water (Tuck and Hayball 2002). An amount of crops, including grapes, pistachio, peanuts and fruits, contain the resveratrol polyphenolic compound with strong antioxidant behavior and attract enhanced exposure because of its safety advantage, particularly unusual age-related diseases such as cancer, form 2, diabetes, cardiovascular disease, and neurological conditions (Marques et al. 2009).

1.6 Antimicrobial Properties of Phenolic Compounds

Fungus and other microbial species are widely used in their setting such as land, plant, and trees, as also in the skin and other areas of the flesh. Phenolic compounds are highly antifungal, antiviral, and antibacterial. The majority is not hazardous, but some may harm the guest and may in the end jeopardize his or her lives (Brunke and Hube 2013). Due to growing demand for organ transplantation, are the cause for spreading of infectious diseases like HIV. The fourth major triggers of hematogenous diseases and the most commonly implicated bacteria are *Candida* species the commensal microorganisms found in every good person (Tsai et al. 2013) and in immuno-impaired individuals, but also in the remainder of the workforce (Raman et al. 2013; Tsai et al. 2013). Fungal infection signs and symptoms are not always visible, and the progression of systemic infection is very slow, often without any mistrust of the infected person. Several experiments were undertaken to assess the antifungal ability of crop insect excerpts enhanced with phenolic compounds such as acetone, water, ethanol, methanol dichloromethane, and methane compounds. The most researched solutions were aqueous acids, accompanied by methanol and

Table 1.2 Showing activity of plant extracts against *Candida* species

Plant source	*Candida* species	Minimum inhibitory concentration (mg/mL)	Reference
Aframomum citratum	*C. glabrata*	4.68	Dzoyem et al. (2014)
Aframomum melegueta	*C. albicans*	6.25	–
Aframomum citratum	*C. glabrata*	4.68	–
Aframomum melegueta	*C. albicans*	6.25	–
Cinnamomum zeylanicum	*C. glabrata*	3.12	–
Glycyrrhiza glabra	*C. neoformans*	0.5	Fatima et al. (2009)
Lantana fucata	*C. krusei*	0.5	Correa-Royero et al. (2010)
Mindium laevigatum	*C. albicans*	0.1	Modaressi et al. (2013)
Foenum-graecum	*C. krusei*	12.5	Darwish and Aburaji (2011)

Source: Brunke and Hube (2013)

ethanol components. For this intent, different techniques/assays were used. The most commonly used and normally conducted in accordance with the Clinical and Laboratory Standards Institute (CLSI), with certain modifications, the agar disk diffusion, and the broth dilution (microdilutions and macrodilution). The outcomes, expressed as haloinhibition areas or minimum inhibitor (MICs) or as minimal fungicidal (MFCs, respectively, are regarded antimicrobial susceptibilities studies. *Candida* was the most studied *Candida* species were *C. albicans*, *C. tropicalis*, *C. krusei*, *C. glabrata*, *C. parapsilosis*, *C. lusitaniae*, and *C. guilliermondii*. The main species associated with opportunist fungal infections is considered to be guilliermondii (Vázquez-González et al. 2013, Table 1.2).

1.7 Role of Phenols in Plants and Ecosystems

The word stress has particular connotations instead of accurate definitions in plant physiological ecology. Stress may be described as any variable (biotic and abiotic) that modifies the workings, development, or development of plants (positive or negative). During multiple phases of their cycles, the majority of crops experience some type of stress that impacts the efficiency and preservation of each plant. Defense phenolic compounds tend to help reduce reactive air organisms overall and therefore affect redox-sensitive cell procedures. Plant phenolics were also involved in more immediate relationships with the paths of travel and sensory transduction. In this association, salicylic acid (SA) is a tiny phenolic compound which performs a significant environmental function in many physiological procedures including plant immune response. Through SA-signaling and interactions with other phytohormones, crops that are subjected to microbial pathogens are able to acknowledge and react with the stimuli of damaged cells through advanced inherent immune mechanisms (Pieterse et al. 2009; An and Mou 2011). The function of flavonoids in modulating auxin flow and locally detected auxin accumulations during nodulation is a well-documented instance. Perhaps best-respected instance of flavonoid communication is the mediation of flavonoid relationships in both reactive (allelopathy/defense) and collaborative (mycorrhizal) environments between crops and other animals. Phenolic signals are not well recorded inside the crops. Intra- and intercellular signaling has been proposed as involving protein operation and cell communication (Peer and Murphy 2006; Beveridge et al. 2007; Chang et al. 2009).

1.7.1 Plant Phenolics: Signaling Molecules

By synthesizing secondary metabolites, the crop interacts heavily with its biotic locale. The exudation of the plant therefore alters the physical–chemical characteristics of plant stems which are referred to as rhizosphere (Hiltner 1904). This climate helps plant microorganisms to survive as the most common origin of nutrients in terrestrial animals is that of ions, enzymes, or organic-carbon-rich molecules (prime and secondary metabolites) (Bertin et al. 2003). The choice of the bacteria (pathogens or commensals) in the branches often leads to the exudation of secondary metabolites. This chemical landscape is conductive to multiple relationships with symbiotic microorganisms in specific.

1.7.2 Plant Phenolics as Aboveground Signaling Molecules

Regarding the position of plant phenolics as inner physiological agents or chemical transmitters within the untouched plant, the development factor auxin (IAA) has several exciting impacts. Monohydroxide B-ring flavonoids are proposed as peroxidase co-factors acting as a hormonal-destroying IAA oxidase while dihydroxide B-ring types behave as IAA-degrading agents (Stafford 1991; Mathesius 2001). Some flavonoids, like quercetin, apigenin, and kaempferol, do not interact immediately with IAA but function in the plant cell plasma membrane using a sensor of the NPA, which blocks movement of polar auxins. These impacts could affect the architecture of plants. In reality, recent trials showed that flavonoid-defeated mutants show a broad variety of changes in the root and root growth between flavonoids and vegetable architectures. It has been recognized in this association that auxin causes plant development for more than half a millennium. Regarding the relationships of phytohormones and other bioactive molecules during the engagement stage of plant creation, the in vitro plant development of the patchy legume was severely reduced by quercetin and isoflavonoid formononetin and genistein. This impact is associated with an inhibition of the auxin flow and/or a redox tissue state control (Peer and Murphy 2007; Buer and Djordjevic 2009; Imin et al. 2006). In petunia crops with antisense CHS and corn larvae without CHS, extrafunction has been noted for flavonoids in the growth of usable pollen. Lack of CHS activities in petunia and corn strains has a pleiotropical impact: soil productivity and flavonoid composition are disturbed, but by addition of flavonol kaempferol or quercetin to grow potatoes, sterility could be recovered. The active soil need for flavonol happens in monocots, dicots, and angiosperms, which indicates that it may have originated in an earlier history of soil crops (Mo et al. 1992; Ylstra et al. 1996; Taylor and Grotewold 2005).

1.8 Role of Phenols in Wood Preservation

The timber sector is concerned about biological wood decay because of financial failures in transport or transport for wood. Main wood biodegraders include bacteria, fungi, insects, termites, and sea borers. A big amount of representative phenolic compounds (flavonoids, stilbenes, quinones, and tannins), which are liable for resisting certain timber types to bio-degraders, are discovered in timber which assault various timber parts at distinct levels, leading to certain model of harm (Sirmah 2009; Toshiaki 2001; Windeisen et al. 2002). Flavonoid protective heartwood against mung-like colonization by two types of feature: fungicidal action and good radical scavenger (antioxidants) safe exercise, and flavonoids have significant effects on durability of timber (Chang et al. 2000; Wang et al. 2004) and Accord (Schultz and Nicholas 2002). Because of their position in the neutralization or breakup of free radicals (Gupta and Prakash 2009), flavonoids were normal antioxidants. Pietarinen et al. (2006) demonstrated that radical exercise in spraying is particularly essential as radicals are supposed to use to destroy cell walls both in white-red and brown-red fungi. Termite trees, like the quinones with real and toxic properties, are said to comprise allochemicals (Ganapaty et al. 2004; Dungani et al. 2012). Teak strength against fungal assault is dominated by naphthoquinone, 4,5′--dihydroxyepiisocatalponol. In vitro bioassays stated that this compound was a fungicide of the Trametes versicolor white-red mushrooms (Niamké et al. 2012). Táctek, an anthraquinone, showed high anti termite usage and is supposed to be the source of opposition to termites by teak timber (Haupt et al. 2003; Kokutse et al. 2006). According to Wolcott (1955), this material has been extremely toxic to underground Reticulitermes Flavipes as a dry-wood termite *Cryptotermes brevi*s (Walker) and Sandermann and Dietrichs (1957) condensed tannins, discovered in elevated concentration in bark and wood of some tree species, are normal preservatives and antifungal agent (Zucker 1983). Most pathogens excrete extracellular proteins such as cellulases and lignases, which participate in the entry and propagation of bacteria. The most probable effects of condensed tannins are to complex and block the activity of such enzymes as antibiotics (Peter 2018). Extracts from different tannin-rich forests and barks have been used for a long time as sticking materials and wood-preserving agents (Toussaint 1997; Thevenon 1999). Most phyto paathogen excrete in the formation and dispersal of the pathogen extracellular proteins such as lignases and cellulases. The most probable effect is the complexity and the interference of condensed tannins (Peter 2018). The promoters of these enzymes are why extracts from different tannin-rich timber and barks were used for a lengthy moment as adhesives and timber preservatives (Toussaint 1997; Thevenon 1999).

1.9 Conclusions

Phenols are secondary metabolites that make up one of the most prevalent and widespread crop communities. The latter represent a broad variety of compound and enzyme compound reservoirs and a broad variety of gene regulation, metabolite, and enzyme delivery systems. Levels are both environmental and genetically regulated for phenolic compounds in crops. Despite a fundamental understanding of the primary biosynthesis mechanisms, certain issues, such as biosynthesis, intracellular movement, and plant phenolic properties, require further research. Until now, a dialog between crops and their climate has showcased the phenolic models of higher plants in the interests of crops and their stronger adjustment to internal circumstances. Plants tailor their phenolic models to altering environments by emerging fresh genes caused by gene duplication and transformation and later promotion to adjust to particular tasks. Plants are also prepared to synthesize chemical compounds that may serve as toxins and detergents for pathogens/herbivores and other rivals and that also generate necessary symbionts. A key cause of precursors to the formation of secondary phenolic metabolites is primary metabolism. Central metabolism needs elevated concentrations of restricted plant assets, and phenolic metabolite synthesis may be nutrient and/or energy restricted in intense development. However, either abiotic or biotic pressures are able to move significant quantities of substrates into secondary protective product development, resulting in development limitations. The main process by which crops react to economic limitations is energy distribution adjustment. The crop allocation model describes its environmental role and is thus the significant variable in knowing the distribution and adjustment of plants. On the other side, any advance in knowing cellular pathways and legislative processes to leverage crop cell and tissue structure potential in producing additives such as antioxidant phenolics may be tackled in the creation of a fresh approach to allow for the manufacturing of helpful secondary metabolites at a business stage.

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Phenolics: Key Players in Interaction Between Plants and Their Environment

2

Rafiq Lone, Saima Hamid Baba, Salim Khan,
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Abstract

Among the several phytochemicals found in plants, phenolic compound-based research has exploded in popularity in the last decade. Despite the fact that phenolic compounds are not necessary in main plant activities such as growth and development, these secondary metabolites have attracted the interest of researchers all over the world due to their significance in a variety of plant functions. Currently, research based on phenolic compounds is focused on the role of various classes of phenols in adapting plants to different environments, including biotic and abiotic factors, their role in reproduction, interaction with other biomolecules, and the specific functions of each individual phenolic compound. The chemotactic reactions of *Agrobacterium* and *Rhizobium*, as well as those of other soil bacteria, are regulated by phenolic compounds. Their signaling and plant-microbe interactions are excellent examples.

Keywords

Phytochemistry · Plant defense · Rhizosphere · Chemotaxis · Quorum signaling

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2.1 Introduction

Phenolic compounds are the most important phytochemicals in modern plant-based chemical research because of their diverse activities. Even though these compounds are not used as main metabolites in plants, their relative amount, place of production, and type of phenolic have a significant impact in a variety of plant activities, including the following: pollinators as a chemoattractant (Nicolson et al. 2015; Zhang et al. 2016; Siqueira et al. 1991a; Baker et al. 1997; Hammerschmidt 2005; Mandal et al. 2010), and plant–animal interactions (Liu et al. 2004, 2007a, b). As a result of the functions listed above, these phenolic compounds serve as an excellent example of how plants can adjust to changing situations beneath the effect of biotic and abiotic jolts. Phenolic compounds too permit plants to create items (blossoms, natural products) with changed color, taste, tastefulness, and smell (Naczk and Shahidi 2012; Dykes and Rooney 2007) which either pull in other life forms or give financial esteem by expanding the commercial esteem of plant items (Naczk and Shahidi 2012; Dykes and Rooney 2007). Plant-based phenolics have a large influence on the end product in the agro-industrial and food sectors, exhibiting either positive or negative effects during food processing and thereby affecting the quality and economic worth of food and medicinal items (Dong et al. 2017). As a result, plant phenolic-based research has become increasingly important in the current era. Since advances in molecular biology and genomics, the gene expression patterns can be altered by CRISPR (clustered regularly interspaced short palindromic repeats) and CAS (CRISPR-associated genes) via CRISPR-mediated gene upregulation or downregulation (Gilbert et al. 2013; Shalem et al. 2014; Cheng et al. 2013) and thus one can underpin a biochemical response with respect to plant defense to synthesize plant phenolics. Researchers have recently concentrated on phenolic and polyphenolic chemical metabolic pathways to better recognize their mechanism of synthesis (Cheynier et al. 2013) and relative content in different regions of a plant (Fialova et al. 2012). In recent decades, research into the precise structures and properties of newly discovered phenolic compounds has sparked a surge in interest, with the goal of elucidating the function specialization of individual phenolic compounds.

2.2 Chemistry and Classification of Phenolics

Phenolic is a broad term that refers to a wide range of chemical substances. These substances can be categorized in a variety of ways as Harborne and Simmonds (1964) classified them on the basis of number of carbon present in a molecule. However, in 1962 where Swain and Bate-Smith adopted another classification system by putting those under two groups, i.e., common and less common while Ribéreau-Gayon (1972) classified the phenols into three groups:

1. Phenols with a broad distribution—ubiquitous in all plants or important in a single plant

2. Phenols with a smaller distribution—only a few chemicals are known
3. Polymers of phenolic components

2.3 Classification of Phenolic Compounds

2.3.1 Simple Phenols

Simple phenolics consists of isomers with different position of functional group around benzene ring as if OH group is present at 1,2 position; then, its ortho, similarly at 1,3, is meta and at 1,4 substitution pattern is the para-phenol. The changeover sample with three functional groups might be 1,3,5, which is referred to as a meta-tri-substitution pattern when all three substituents are identical, whereas the 1,2,6 substitution pattern is signified by the prefix "vic" (Fig. 2.1).

Examples include resorcinol (1,3-dihydroxybenzene; Fig. 2.2a), a meta-dihydroxylated simple phenolic, and phloroglucinol (1,3,5-trihydroxybenzene; Fig. 2.2b), a meta-trihydroxylated simple phenolic.

2.3.2 Phenolic Acids and Aldehydes

A carboxyl group replaced on a phenol distinguishes hydroxy-benzoic acids. *p*-Hydroxybenzoic acid (Fig. 2.3a), gallic acid (Fig. 2.3b), protocatechuic acid (Fig. 2.3c), salicylic acid (Fig. 2.3d), and vanillic acid are among examples

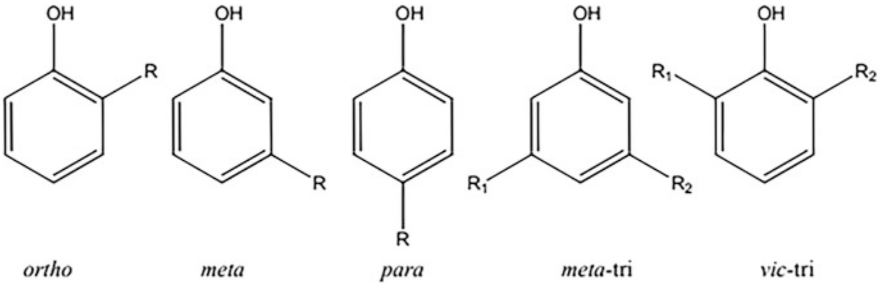
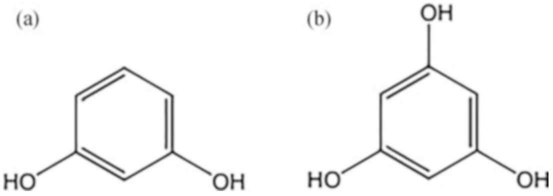


Fig. 2.1 Nomenclature for substitution patterns of phenolic compounds. R, R1, and R2 are generic substituents

Fig. 2.2 (**a**, **b**) Chemical structure of the different classes of polyphenols



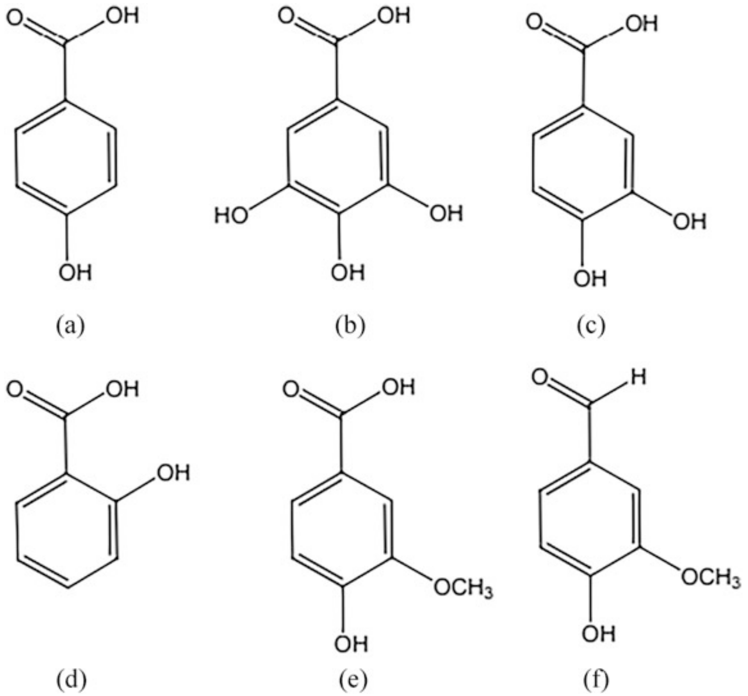


Fig. 2.3 (**a**–**f**) Chemical structure of the different classes of polyphenols

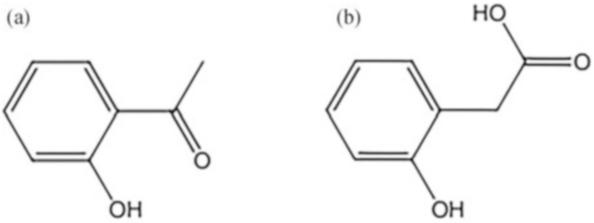


Fig. 2.4 (**a**, **b**) Chemical structure of the different classes of polyphenols

(Fig. 2.3e). Hydroxybenzoic aldehydes, such as vanillin (Fig. 2.3f), have an aldehyde group instead of a carboxyl group and are related.

2.3.3 Acetophenones and Phenylacetic Acids

Phenones are a class of C6–C2 chemicals that are uncommon in nature. 2-Hydroxyacetophenone (Fig. 2.4a) and 2-hydroxyphenyl acetic acid are two examples (Fig. 2.4b).

2.3.4 Biosynthesis, Genetics, and Metabolic Engineering

The term “plant phenolics” ought to be entirely utilized to allude to auxiliary common metabolites emerging biogenetically from the shikimate/phenylpropanoid pathway, which specifically gives phenylpropanoids (Fig. 2.5), or the “polyketide” acetate/malonate pathway, which can deliver straightforward phenols, or both, agreeing to a common scuttle the demonstration as proposed by Quideau et al. (2011). These pathways deliver stupefying differences of monomeric and polymeric structures polyphenols eludes to compounds with more than one phenolic ring that serve a wide run of physiological capacities in plants. As the fruitful adjustment to arrive of a few higher Charophyceae individuals, which are thought to be models of land and water capable plants that apparently came some time recently genuine arrive plants when they rose from an oceanic environment onto the arrive, was helped in portion by the enormous arrangement of “phenolic UV light screens.” Chemical bonds can be cleaved by the ultraviolet component of solar energy. As a result, prebiotic chemical molecules and primordial organisms could only survive in an aquatic environment, shielded by water UV absorbing oxygen. Thus, the plant phylum must have tended to the UV screen issue around half a billion a long time prior, when attacking wet conditions on the terrestrial surface, presumably through primitive bryophytes. The use of the shikimate pathway is the most noticeable chemical difference between aquatic protists and terrestrial plants. This is limited to the creation of phenylalanine and tyrosine, which have been integrated into proteins since the most punctual microscopic organisms. As it were the bryophytes, start a post-tyrosine chemistry based on cinnamic acid. Deamination of fragrant amino acids to cinnamic acids has been watched in organism and may have happened irregularly in other taxa. The allelochemistry of aerobic bacteria and algae is dominated by polyketides, which are generated by the condensation of acetyl-CoA as a starting unit and malonyl-CoA for chain extension. In bryophytes, the preliminary unit was replaced by cinnamoyl-CoA in this method, resulting in flavones and flavonols. In Bryophyta and all divisions of more recent terrestrial plants, flavonoids such as chalcones, aurones, flavones, and flavonols absorb UV

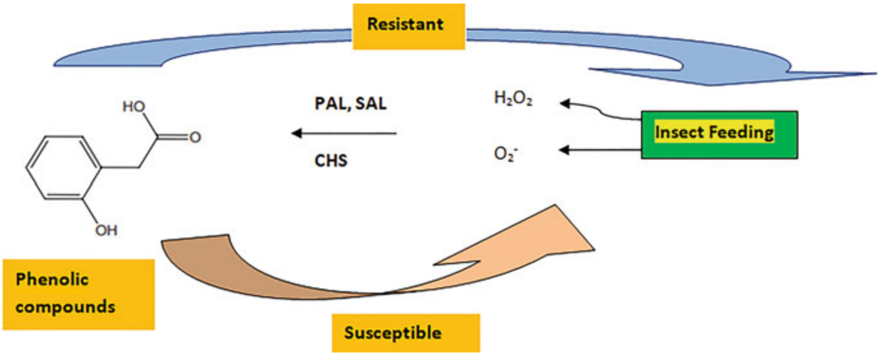


Fig. 2.5 Phenolics in plant defense

radiation and act as photoscreens (Gottlieb 1986; McClure 1975). Other occurrences in an airborne environment, such as pests and pathogens, necessitate particular plant adaptations. The adaptation to these environmental difficulties is conditioned by polyphenol chemistry yet again. Catechins are produced by reductive departure from the biosynthetic pathway that leads to anthocyanidins from leucoanthocyanidins. Condensed tannins are produced by polymerizing representatives from the two last families of flavonoid compounds. They provide crucial general defense against viruses, bacteria, fungus, insects, and herbivores (Gottlieb 1989; Gottlieb and Kaplan 1993).

2.3.5 Phenolic Transport Mechanisms

Aromatic ring structures with several phenol residues are used to represent plant phenols. Unsubstituted phenols such as polyphenols can be classified into two types: hydrolyzable tannins and condensed tannins, which are polymers of polyphenols, including phenylpropanes (C6–C3) and C6–C1 compounds, stilbenes, lignans, xanthene, flavonoids, and tannins as polymers of polyphenols. The role of flavonoids as plant phenolics, with over seven thousand different chemicals involved in plant pathogen interactions, ultraviolet radiation protection, and flower color diversity, has been extensively studied. The majority of flavonoids in plants are glycosylated, which may be required for their trafficking into vacuoles. Isovitexin (apigenin 6-C-glucoside), for example, is glycosylated. By virtue of an electrochemical gradient-dependent transport process (secondary transport), an endogenous flavonoid glucoside is carried into barley vacuoles (Klein et al. 1996). It is known that hydroxy primisulfuron-glucoside is transferred into barley vacuoles via a main transporter. In accordance with these biochemical findings, barley vacuolar transporters discriminate between exogenous and indigenous glucosides. In accordance with these biochemical findings, barley vacuolar transporters discriminate between exogenous and indigenous glucosides. A primary transporter of saponarin is recognized in Arabidopsis that produces no this flavonoid glucoside, indicating that saponarin is viewed as a xenobiotic (Frangne et al. 2002). The chalcone isomerase gene is mutated in the barley ant310 mutant, which has less than 5% of flavonoids found in wild-type plants (Reuber et al. 1996). A significant reduction in saponarin and isovitexin transport activity was observed in isolated vacuoles of 310 mutants (Marinova et al. 2007). Nonetheless, the transport activity was restored by treating the cells with the flavonoid precursor, naringenin, and the saponarin levels increased to those found in wild-type cells. When the transcriptome linkage map is examined further, bioinformatics analysis may uncover transporter genes for endogenous secondary metabolites. The anthocyanins in flowers are colored flavonoids that, according to in vivo status and derivatization patterns, are responsible for the majority of the RGB. Pollinators and UV light are protected by these substances, which are found in the vacuoles of certain plants. There have been several reports of anthocyanins being taken up by vacuoles in plants of various species; however, the mechanisms may differ based on the systems used. Anthocyanin transport across the vacuolar membrane was discovered for the first time by the bronze-2 (bz-2) mutant of maize (Marrs et al. 1995). Anthocyanin in vacuoles does not accumulate in the bz-2 mutant due to glutathione S-transferase deficiency (Smit et al. 1992). Proteins implicated in the extracellular accumulation of shikonin, on the other hand, have yet to be discovered (Kunst and Samuels 2003; Yazaki 2005).

2.3.6 Synthesis of Phenolics Against Biotic and Abiotic Stress

Clé et al. (2008) and Schmitz-Hoerner and Weissenbock (2003) found that phenolics are commonly generated and deposited in the subepidermal layers of plant tissues exposed to stress and pathogen attack. The content of a specific phenolic chemical within plant tissue varies depending on the season and during different phases of growth and development (Lynn and Chang 1990; Ozyigit et al. 2007; Thomas and Ravindra 1999). The synthesis and accumulation of phenolics are affected by a number of internal and external stimuli, including trauma, injury, drought, and pathogen attack (Kefeli et al. 2003; Zapprometov 1989). Exposure to light also boosts phenolic production in chloroplasts and their accumulation in vacuoles (Kefeli et al. 2003). Photoinhibition, as well as nutrient stressors including N, P, K, Fe, Mg deficiency, causes some plant species to produce phenylpropanoid chemicals (Dixon and Paiva 1995). Flavonoid biosynthetic pathway members could be among them (Balasundram et al. 2006; Hollman and Katan 1999).

2.3.7 Role of Phenolics in Plant Defense

Phenolics have a clone result within the plant' environment, repugnant, and attracting alternative species. Against offensive species akin to herbivores, nematodes, phytophilous insects, and fungous and microorganism diseases function as antioxidants, inhibitors, natural animal toxicants, and insecticides (Dakora and Phillips 1996; Lattanzio et al. 2006; Ravin et al. 1989). Birds are put off by simple synthetic resin acids, complex tannins, and phenolic resins on the plant surface, which migrate with the stomach flora and hinder digestion. Because of their flavor and coloring, low-molecular-weight phenylpropanol derivatives attract dependent microorganisms, pollinators, and mammals, which produce fruits (Ndakidemi and Dakora 2003; Vit et al. 1997). Adams (1989) observed phenoplasts as phytoestrogens in animals and allelochemicals for competitive plants and weeds (Xuan et al. 2005). Allelochemicals that are usually effective embrace volatile terpenoids, toxic soluble hydroquinones, hydroxybenzoates, hydroxycinnamates, and 5-hydroxynaphthoquinones. Phytoalexins, phytoanticipins, and nematicides are phenolic compounds that build up in plant tissues to protect plants against soil-borne diseases and phytophagic insects (Fig. 2.5) (Lattanzio et al. 2006).

Therefore, phenolic compounds have long been recommended as a viable alternative to chemical disease control in agricultural crops (Langcake et al. 1981). Polyphenols mainly have harmful effects on microorganisms (Cushnie and Lamb

2005; Taguri et al. 2006; Ferrazzano et al. 2009). Phytoalexins, such as hydroxycoumarins and hydroxycinnamate conjugates, are accumulated by plants in response to pathogenic infection (Karou et al. 2005; Mert-Türk 2002). Many plant defense tactics against microbial invaders are based on the synthesis, discharge, and accrual of phenolic compounds, especially SA (Lu 2009; Boller and He 2009; Tsuda et al. 2008). PAMP-induced immunity is triggered by conserved pathogen-associated molecular patterns when plant pattern recognition receptors identify potential pathogens (PAMPs). As a result, the infection takes a long time to spread before the virus completely controls the plant. (Newman et al. 2007; Ongena et al. 2007; Tran et al. 2007; Nicaise et al. 2009; Zipfel 2008) (Table 2.1).

2.3.8 Plant Phenolics in Rhizosphere

Along with other chemicals and compounds, plants do release phenolics in the rhizosphere where microorganisms of soil with other animals form a complex ecosystem and respond to every action of each living organism (Whipps 2001; Bais et al. 2006; Dakora and Phillips 1996; Bertin et al. 2003). The term rhizosphere has been involved to demonstrate the role played through phenolics in the niche of rhizospheric region of plant (Hiltner 1904). However, polyphenols which are being released by plant metabolic systems interact with other components of rhizosphere like water, carbon compounds, reactive oxygen species, enzymes, primary and secondary metabolic compounds, and also the concentration of these phenolic compounds depends on type of species, temperature, and other abiotic and biotic factors. As Hartley and Harris (1981) measured, the available quantity of phenolics in soil for dicotyledonous and monocotyledonous plants by having concentration ranges from 2.1% to 4.4% and 0.1% to 0.6%, respectively. Polyphenols initiate the oxidation and reduction reactions which affect the metabolic reactions of other soil microbial flora in the plant rhizosphere. All these factors are having cumulative effect on adjacent plants which ultimately mobilizes the phytoconstituents, hormonal equilibrium, enzymatic activity (Northup et al. 1998; Kraus et al. 2003; Hättenschwiler and Vitousek 2000). Soil structure and chemistry are strongly influenced by this dynamic and ever-changing interaction, depending on the amount and type of phenol produced from different plant species. The composition of microbial species at different root positions also changes and is formed over time. In addition, phenol binds to soil organic matter and is digested by the soil flora as it travels through the rhizosphere (Kefeli et al. 2003). Microorganisms break down phenol into components and help mineralize nitrogen in the soil to produce humus (Halvorson et al. 2009). Phenols form metal complexes and improve the mobility and availability of different elements such as Fe, Mg, Zn, C, B, and Cu to plant roots to improve soil porosity (Seneviratne and Jayasinghearachchi 2003b). $C_9H_8O_2$, $C_7H_6O_3$, $C_7H_6O_2$, 4-hydroxybenzoic acid belongs to category of phytotoxic phenolic metabolites which inhibits the seed germination and seedling growth of plants (Baleroni et al. 2000). Disruption of cell division and proper cellular enzyme function may be responsible for these effects. Both phosphatases and prolyl

Table 2.1 Phenolic acids as inducer of plant-microbe symbioses in some selected species

Phenolic acids	Functions/locations	References
Caffeic acid	Root growth inhibition	Vaughan and Ord (1990)
	Present in wall bound fraction of nodules	Chakraborty and Mandal (2008)
Cinnamic acid	Induced by rhizobia in rice and resistant to Rhizoctonia	Mishra et al. (2006)
3,4-Dihydroxybenzoic acid	Chemoattractants have an effect on the interaction's host range	Aguilar et al. (1988)
	Ferulic acid is a ferulic acid derivative	Seneviratne and Jayasinghearachchi (2003a)
	Root growth inhibition influenced by rhizobial growth concentration	Vaughan and Ord (1990)
	Induced by Rhizobia and resistant to Rhizoctonia in rice	Mishra et al. (2006)
Gallic acid	Induced by Rhizobia in rice and resistant to *Rhizoctonia*	Aguilar et al. (1988)
Gallic acid and methyl ester	Antioxidants—found in soybean nodules	Moran et al. (1997)
p-Coumaric acid	Rhizobial IAA production stimulator	Mandal et al. (2009)
	Constitutively present in root and nodule	Chakraborty and Mandal (2008)
	Influence rhizobial growth	Seneviratne and Jayasinghearachchi (2003a)
	Concentration-dependent root growth inhibition	Vaughan and Ord (1990)
4-Methoxycinnamic acid	Phytoanticipant in pea plants	Sobolev et al. (2006)
p-Hydroxybenzoic acid	Chemoattractants, influence the host range of the interaction	Aguilar et al. (1988)
	Present in soluble fraction of young nodules	Chakraborty and Mandal (2008)
4-Hydroxybenzaldehyde	Stimulator of IAA production in Rhizobia	Mandal et al. (2009)
	Concentration-dependent root growth inhibition	Vaughan and Ord (1990)
Protocatechuic acid	Stimulator of IAA production in Rhizobia	Mandal et al. (2009)
	Present in wall bound fraction of nodules	Chakraborty and Mandal (2008)
	Influence rhizobial growth	Seneviratne and Jayasinghearachchi (2003a)
Salicylic acid	Accumulation in alfalfa roots	Zawoznik et al. (2000)

(continued)

Table 2.1 (continued)

Phenolic acids	Functions/locations	References
	Exogenous application inhibits indeterminate nodulation	van Spronsen et al. (2003)
	Exogenous SA inhibits early nodulation in soybean	Sato et al. (2002)
	Auto-regulate nodulation at the step of infection thread formation	Stacey et al. (2006)
	Rhizobacteria mediated induced systemic resistance	Pieterse et al. (2001)
Syringic acids	Reported from soybean nodules	Moran et al. (1997)
Tannic acid	Induced by Rhizobia in rice and resistant to *Rhizoctonia*	Mishra et al. (2006)
Vanillic acid	Influence rhizobial growth	Seneviratne and Jayasinghearachchi (2003a)
Vanillin	*nod* gene inducer in peanut	Zawoznik et al. (2000)
Vanilly alcohol	Chemoattractants influence the spectrum of hosts in a stumble upon	Aguilar et al. (1988)
4-*O*-β-glucosides of *p*-hydroxybenzoic, protocatechuic, and vanillic acids	Identified from soybean nodules—act as antioxidants principally	Moran et al. (1997)
5-*O*-β-glucosides of gentisic acid, gallic acid, and its methyl ester	Identified from soybean nodules—act as antioxidants principally	Moran et al. (1997)

aminopeptidase, which are important for seed germination, are inhibited by phenol (Madhan et al. 2009). Phenol affects the mineral uptake mechanism of plants (Lodhi et al. 1987). In the carbon-rich rhizosphere, much of the phenolic root exudate acts as a chemotactic signal for various soil microorganisms, identifying them and migrating to plant roots (Perret et al. 2000; Taylor and Grotewold 2005). Constructive and pitiable cross-speak pathways are shaped among roots, roots and insects, and roots and bacteria, relying on the character and sort of root-derived compounds. The equal chemical sign repels or draws numerous organisms, ensuing in numerous responses in various recipients. Morris et al. (1998) have studied that isoflavones do act as chemoattractant isolated from soybean roots, the symbiotic *Bradyrhizobium japonicum* and the pathogenic *Phytophthora sojae* bacteria at the end result of root–microbe cross-interaction, the range and interest of soil microorganisms close to the foundation increases (Bais et al. 2004). As a result, root colonization continues. The growth of primary root colony-forming factors using degradable carbohydrates and organic acids is generally supported in the root elongation zone just behind the tip. Old roots, on the other hand, are home to crowded, oligotrophic-adapted fungi and bacteria, and shed cells contain woody cellulose, hemicellulose, and carbon deposits. The newly formed lateral roots and the tips of secondary non-growing roots provide relatively nutritious conditions for the invasion of mature fungal populations. With response to isoflavonoids on colonization of AMF, the overall development of plant improves due to Phosphorus is required for plant nutrition (Bagayoko et al. 2000; Siqueira et al. 1991b). When roots have a deficiency in phosphate, they make a chemical called strigolactone. At the time of the presymbiotic stage of beneficial fungal symbionts, these apocarotenoid molecules were recognized as host-derived signals (Moulin et al. 2001; Schardl et al. 2004). The beneficial bacteria that make up the rhizobacteria promote plant growth in a number of ways (Gray and Smith 2005). A number of microorganisms assist plant life to defend themselves against diseases by forming protective biofilms or antibiotics (Bais et al. 2004). While certain types of colonization result in symbiotic microbe relationships, some do results in plant infection by soil-borne diseases. When a plant is colonized by bacteria called the Rhizobium, it benefits the plant, but when it is colonized by a pathogenic called the Agrobacterium, belongs to Rhizobiaceae families. The bacteria Rhizobia have partnerships with plants which help them get more of the nutrients they need. There are many different types of bacteria that help plants, but the most well-known are the ones that help plants grow. These two bacteria, being members of the same family, have comparable and dissimilar underlying processes of symbiosis or infection, and each has its unique ecological niche.

2.4 Agrobacterium and Rhizobium Host Phenolics in Infection Cycles

As various substituted and unsubstituted phenolic compounds are being released by host plant which affects the population growth of large number of microbial populations in the soil where interaction depends on concentration and type of chemical compounds being released? However, Agrobacterium and Rhizobium hold good potential to interact either strongly or feebly (Bais et al. 2006) as both the beneficial bacteria have evolved and developed defense mechanism in order to withstand with release of phenolic chemicals (Hartmann et al. 2009; Matilla et al. 2007) (Fig. 2.6). Phenolics follow important mechanisms mainly into four categories which are discussed below:

2.4.1 Chemotaxis

Phenolics play a critical part in Agrobacterium and Rhizobium's chemotactic responses likewise as commonly occurs in soil bacteria, for routine inhibition. They are ideal for studying signal transduction and plant–microbe interactions (Palmer et al. 2004; Samac and Graham 2007). A range of plant phenolic compounds with govern *Agrobacterium* or *Rhizobium's* chemotactic migration through chemical gradients toward greater levels of nutrients and less inhibitors. Umbelliferone, vanillyl

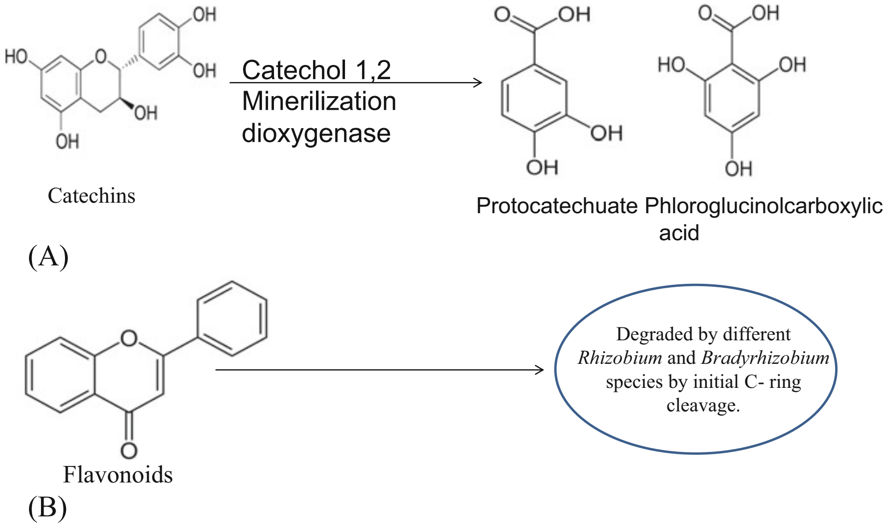


Fig. 2.6 (**a**, **b**) Rhizospheric phenolics as sources of C for *Rhizobium* spp. (**a**) Mineralization of catechins and substituted chloro-aromatics by catechol-1,2-dioxygenase into phloroglucinolcarboxylic acid and protocatechuate. (**b**) Degradation of flavonoids by C-ring cleavage into utilizable forms

alcohol, *p*-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid, and acetosyringone are all constituents of acetosyringone, e.g., apigenin and luteolin chemoattract *R. leguminosarum* bv. *trifolii* and *Sinorhizobium meliloti* (Brencic and Winans 2005). In *R. leguminosarum* bv. *viciae* and *trifolii*, however, naringenin elicits a weak to non-existent chemotactic response (Zaat et al. 1987). Luteolin also inhibits *S. meliloti's* robust chemotaxis as per the reports of Aguilar et al. 1988, with increasing concentrations of acetosyringone and umbelliferone which are known to inhibit nod gene inducers of *R. leguminosarum.* According to Djordjevic et al. (1987), some negative interactions have been found for the rhizobia when the nodule initiation gets hampered near clover root tips, which is a mandatory action in order to protect the species from pathogenic attacks due to release of Umbelliferone. As largely released, phenolic substituents directly influence the virA/G genes on the Ti plasmid of distinct *Agrobacterium* sp. As per Harighi (2009), the orf1 operon gene gets activated after manipulation of chromosomal genes such as the 8-kb chemotaxis which in turn starts with and the 7205-bp putative flagellar rods and related proteins operon (Deakin et al. 1999; Shaw et al. 1991). At very low quantities, acetosyringone and hydroxyacetosyringone secreted from plant wounds are powerful chemoattractants that also operate to trigger Agrobacterium vir genes (Escobar and Dandekar 2003). A number of additional phenolics and sugars, in addition to acetosyringone, are efficient chemoattractants. Even vanillyl alcohol, which does not induce the vir gene, is a powerful chemoattractant (Ashby et al. 1988). High doses of certain polyphenols, on the other hand, may have bacteriostatic or even bactericidal effects, limiting Agrobacterium's chemotactic migration and so preventing it from reaching plant wound sites.

2.4.2 Activation of the Bacterial Nod and Vir Gene Networks

Substituted plant phenols alter microbial gene expression after chemotaxis in a variety of ways. “Host recognition factors,” also known as “xenognosins,” are plant-derived signals (Campbell et al. 2000). Rhizobium and pathogenic Agrobacterium may also be affected due to nod and vir genes by the similar phenolics that act as chemoattractants (Djordjevic et al. 1987). Until recently, flavonoids were considered the sole chemoattractants and inducers of nod gene expression in rhizobia (Cohen et al. 2001; Stougaard 2000). D’Arcy-Lameta and Jay (1987) found that until the late 1980s, essentially every investigation on this topic focused on soybean isoflavonoids. Other chemicals, such as flavones and flavonols from broad beans, were only discovered to induce the nod gene in the late 1990s (Bekkara et al. 1998). Other organic compounds, primarily phenolics, were discovered to be effective inducers of nodABC genes over time, with the effect being contingent on the presence of a functional nodD gene (Perret et al. 2000; Subramanian et al. 2006). Distinct Rhizobium species have different nodD genes that respond best to different phenolics. Although some phenolics have a favorable impact on nod genes, others may have a negative impact. As some *Bradyrhizobium japonicum* strains are induced by daizen, genistein, and isoflavonoids from soybeans, whereas those of *S. meliloti* are inhibited by those phenols instead of induced by luteolin (Begum et al. 2001; Kosslak et al. 1987). Phenolic compounds can trigger or attract nod genes, but not both. Another phenolic compound, isoliquiritigenin (2′,4′,4-trihydroxychalcone), induces nod genes but does not attract them (Kape et al. 1992). When rhizobia enter the host cells, flavonoids impede the transport of auxins, as well as increasing Nod signal production (Brown et al. 2001). Several flavonoid-binding proteins are known to regulate auxin polar transport in Arabidopsis through homologues of the PIN gene (Subramanian et al. 2007). Inhibition of auxin transport, on the other hand, is not essential for the formation of distinct nodules, which can occur even when isoflavone levels are extremely low (Grunewald et al. 2009; Subramanian et al. 2007). A range of phenolic substances have been shown to stimulate vir gene expression in Agrobacterium, one of the most potent of which is acetosyringone (Gelvin 2009). Sensor and transducer system VirA/VirG detects these phenolics and activates all vir loci that code for the majority of protein machinery, allowing T-DNA transfer (Zupan et al. 2000). ChvE, a chromosomally expressed glucose/galactose-binding protein, senses sugar components released from wounds of susceptible hosts (He et al. 2009). As VirA binds to ChvE, it undergoes a conformational shift, allowing it to interact with a number of poor vir gene inducers including $\mathbf{C_8H_8O_2}$, $C_9H_8O_3$, and C_6H_6O (Peng et al. 1998). A specific structure of phenolic compounds is needed for induction of the vir gene. A few other structural characteristics, as well as the aromatic hydroxyl group, are absolutely necessary. The unsaturated side chain of phenolics is more likely to activate the vir gene than saturated side chains (Joubert et al. 2002). In contrast to the derivatives without these methoxy substitutions, the monomethoxy compounds are more active. There are monomethoxy compounds that are more active than phenol ring derivatives without these methoxy substitutions. The dimethoxy derivatives are always the most active of the three phenolic classes. It is also necessary to have a chiral carbon at the center of the phenolic molecule to induce vir gene expression. An increase in induction potential is correlated with the polarity or acidity of the aromatic hydroxyl group attached to the hydrogen bond in the para position (McCullen and Binns 2006). Several novel types of phenolic chemicals, including three phenol amides, are able to induce vir gene expression when they have an amide group added to syringic acid (Dye et al. 1997). With regard to the vir gene-inducing activity, ethylsyringamide rankd first followed by propylsyringamide, carbethoxyethylensyringamide and syringic acid itself. Researchers have recently observed that benzene rings with positions 4, 3, and 5 of a methoxy groups greatly enhanced the induction of the vir gene in a phenolic molecule (Brencic and Winans 2005). The vir gene is also stimulated by dextro-isomers (D) of glucose in addition to phenolics (Wise et al. 2005).

2.5 Xenobiotic Detoxification and Biotransformation to Inert and/or Utilizable Form

Hirsch et al. (2003) observed that phenolic compounds have the capability to inhibit the transport mechanism of bacterial membranes as they have quality of antimicrobial properties. In bioremediation, some microbes can utilize polyphenols as source for breakdown of hazardous substances (Dua et al. 2002; Lovely 2003; Wackett et al. 1987). The ways in which phenol is detoxified are often related to the ways plants and bacteria interact. The genes for the phenolic detoxification system are located inside the genes for the phenolic-inducible vir regulon of the Ti plasmid of Agrobacterium. The regulator has a switch which will not turn on until the phenolic metabolism or inactivation has started. The enzymes in the body that are involved in the process of getting rid of foreign chemicals are similar to the enzyme called VirH2. The xenobiotic detoxification enzymes cytochrome P450-dependent mixed-function oxidases have a lot of similarities to a protein called VirH2. Through various metabolic processes plus energy or nutrition, VirH2 quenches or detoxifies the plant phenols released by the wound. Changes in xenobiotics due to the transfer of polar or reactive groups are the most common method of detoxifying xenobiotics (Brencic et al. 2004; Guengerich 2001).

Most rhizobia and bradyrhizobia species convert phenols into forms that can be utilized as C, N, or energy sources (Vela et al. 2002). This provides the bacteria with a selective advantage in terms of saprophytic and symbiotic survival in the soil and host.

2.6 Quorum Signaling (QS) for Attaining Infection

QS is an important technique for Rhizobiaceae members to monitor their environment (Bjarnsholt and Givskov 2007; Gonzalez and Marketon 2003). The detection of quorums is based on the production, release, and detection of homoserine lactones

(HSLs) or their acylated equivalents (Parsek and Greenberg 2000; Steidle et al. 2001). Quorum sensing enables bacteria to interact with one another and promotes a favorable lifestyle for pathogenic or symbiotic partnerships to live and thrive in a range of situations (Joint et al. 2002). Cell density-dependent gene expression in quorum sensing helps bacteria to coordinate some adaption processes that a single germ cannot finish. Rhizobia employ quorum sensing to synchronize themselves to phenolic cues on a population-wide scale and to operate as multicellular creatures in order to have a successful symbiosis. QS promotes nodulation efficiency, symbiosome development, exopolysaccharide synthesis, nitrogen fixation, and stress tolerance in Rhizobium (Danino et al. 2003; Gonzalez and Marketon 2003). *R. leguminosarum* bv. *viciae* possesses four quorum sensing operons that have been extensively studied. Only the cin operon, which comprises cinr/i, is located on the chromosome and directs the synthesis of long-chain quoromones such as AHL (Lithgow et al. 2000). Out of the four operons involved in quorum sensing, these AHLs only trigger the rai and tra operons on two different plasmids. Along with transfer gene M, the products of the attKLM operon on Agrobacterium's cryptic plasmid specifically decrease quorum sensing, whether the population density is low or large, and there is C and N starvation. In times of food shortage, AttM, AttL, and AttK employ other rhizospheric quoromones, such as g-butyrolactones produced by other soil bacteria, as additional nutrition and energy sources. Salicylic acid (SA) suppresses quorum sensing in Agrobacterium by upregulating the attKLM operon, which destroys the bacterial hormone N-acylhomoserine lactone (Yuan et al. 2008). According to transcriptome research, salicylic acid functions additively with indole-3-acetic acid and g-aminobutyric acid (GBA) in the quorum quenching action of *A. tumefaciens* (Yuan et al. 2008). A recent study of the Arabidopsis transcriptome highlighted the roles of Salicylic acid and indole-3-acetic acid, as well as ethylene, in Agrobacterium infection defense (Lee et al. 2009). Salicylic acid anti-Agrobacterium properties extend beyond QQ.

2.7 Understanding of the Basic Processes in the Polyphenol Biosynthesis

Plant cells release a wide variety of chemicals that help them grow, but are not actually necessary for their health. This "chemical diversity" is particularly developed in terrestrial plants; they must deal with various environmental problems, especially vascular plants; and they must also maintain valuable metabolite transport, structural rigidity, and fine homeostasis regulation (Caputi et al. 2012). Aside from methylation, which is performed by *O*-methyltransferases, acylation and glycosylation of secondary metabolites, such as phenylpropanoids and related phenolic compounds, are important chemical changes. The polarity, volatility, chemical stability in cells and solution, ability to interact with other substances (copigmentation), and biological activity of such modified metabolites have all changed. Furthermore, several of the above-mentioned procedures rely heavily on these alterations. Acyltransferases (ATs) and glycosyltransferases (GTs) catalyze the modification of natural substances with glycosyl and acyl moieties, resulting in tens of thousands of molecular variants (Tanaka et al. 2008). After the biosynthesis of the corresponding aglycone is completed, both stages normally occur in a regiospecific reaction (Ono et al. 2010). Despite the fact that a large number of cDNAs encoding members of both enzyme categories have been cloned from various plant species and tissues, the catalytic function of only a small number of gene products has been documented, primarily utilizing recombinant enzymes in vitro (Caputi et al. 2012). Catalytic flexibility characterizes both groups of enzymes, making functional predictions based only on primary sequence impossible. For over a decade, our understanding of gene family organization has been restrained to the representation plant *A. thaliana* (L.) Heynh, as this species has produced the greatest number of flavonoid-related genes as a result of widespread use of multiple "omics"-based methodologies (Yonekura-Sakakibara et al. 2012). With the increasing availability of plant genomes and protein crystal structures, it is now possible to gain a more comprehensive understanding in terms of functional development and fundamental structural components dictating specificities, the families of these two significant protein groups, such as region-specificities and catalytical properties (Tuominen et al. 2011).

2.8 Acyltransferases (AT)

With ester and amide linkages, enzymatic acylation imparts aliphatic and/or aromatic acyl moieties to the nucleophile (OHe or NHe) of acceptor molecules. Aromatic acylation commonly involves coumaroyl or sinapoyl groups, resulting in molecular stability and anthocyanin color intensification. Malonylation is a common aliphatic acylation that is critical for molecular stability, as well as water solubility and enzyme protection (Luo et al. 2007). The secondary metabolism of plants has several different types of acylations. N- or O-acylation is primarily engaged in the formation and modification of substituted and unsubstituted, as well as alkaloids and terpenoids with a variety of ecophysiological effects (Yu et al. 2000). The BAHD acyltransferases, after the first members identified are a vast family of plant-specific monomeric acyl-CoA-utilizing and functionally varied enzymes with only 10–30% amino acid similarity. A genome-wide investigation of five angiosperm taxa revealed that this family can be divided into eight primary clades. Functional studies of substrate and donor specificities among distinct BAHD enzymes should be aided by newly discovered clade-specific motifs. The extension of the BAHD family in distinct lineages is closely linked to taxon-specific metabolic diversity, according to these findings (Tuominen et al. 2011). Aside from alcohol acetyltransferases, anthocyanin/flavonoid acyltransferases such as hydroxycinnamoyltransferases and malonyltransferases engaged in polyphenol modification represent the second functional subfamily within BAHD acyltransferases (Yu et al. 2000). As no transit peptide for translocation to other subcellular locations has been identified, these proteins are thought to be found in the cytosol. Modified anthocyanins, tiny green-leaf volatile esters, lignin, suberin, and defensive chemicals, as well as phytoalexins, were among the products generated (Auria 2006). In vitro tests show that some members have a more limited preference for substrates while others have a more broad preference. However, because of the diversity of their substrate specificities, predicting function only based on structural knowledge is difficult, and hence, the vast majority of BAHD acyltransferases have yet to be described in terms of substrates and products (Luo et al. 2007).

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Genetic Basis of Phenolics in Abiotic Stress Management

3

Aqsa Tariq and Ambreen Ahmed

Abstract

Phenolic compounds are the largest group of plant secondary metabolites. Plants synthesize phenolic compounds utilizing precursor via shikimic pathway through phenylpropanoid pathway. Among phenolic compounds, flavonoids are significant having significant function in various plant physiological processes. Formation of reactive oxygen species (ROS) is one of the strategies used by plants under stress. However, excess production of ROS has negative impact on cellular processes. In this scenario, phenolic compounds assist plants by scavenging ROS as they are excellent antioxidants. Besides their antioxidant ability, they also act as metal chelators and active screeners increasing plant tolerance against extremes of environments. Phenolic compounds act as direct shield and absorb excess light, thus providing protection from UV and damage to biological entities (mainly DNA) from photodamage. Anthocyanins are important group of phenolic compounds having important role in protecting plants from photoinhibition and protecting photosynthetic complex. Moreover, phenolic compounds like most of flavonoids and salicylic acid act as signaling molecules. Flavonoids are important rhizospheric signaling molecules targeting plant beneficial microbes to flourish and benefiting plants, and in legumes, some flavonoids initiate *nod* factor for nodulation, an important process for plant–rhizobial interaction.

Keywords

Polyphenols · Flavonoids · Anthocyanins · ROS · Antioxidants

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3.1 Introduction

During stress, plants experience reduction in the optimum physiological parameters leading to limited plant growth and development. Plants, in their ecological niches, are exposed to continuous variations in their environment, including excessive salt or water, heavy metals, drought, and high-intensity radiations (Pedrol et al. 2006). Major abiotic stresses involve temperature variations (low or high temperature), water stress (drought or flood), variation in radiations, mineral deficiency, or excess, etc. This induces the production of various reactive oxygen species (ROS) such as hydroxyl radical ($OH^{\bullet}$) superoxide ($O_2^{\bullet-}$), singlet oxygen ($^1O_2$), and hydrogen peroxide (H_2O_2) that causes oxidative damage to plants and adversely reduces crop quality and productivity (Sachdev et al. 2021). Being sessile, plants maintain certain metabolic and structural adjustments to cope up with stress conditions by changing expression of stress-related genes. This developmental plasticity involves production of different metabolites that help plants to improve their growth under unfavorable environment. Metabolic signaling is the major key to regulate multiple physiological adjustments as a defense response against external stimuli. In this regard, endogenous hormonal signaling triggers the secretion of various primary and secondary metabolites to re-program the physiological activities of cell (Ahmed et al. 2020). Plastic nature of plants in terms of their competitiveness and endurance under various environmental conditions indicates the presence of complex regulatory mechanism. This regulatory system coordinate and control the perception of external stimuli, their transduction, and synthesis of various protective metabolites such as terpenes, alkaloids, and phenolics. Accumulation of these metabolites ensures plant survival and protection against oxidative damage under unfavorable conditions (Kumar et al. 2020a; Tuladhar et al. 2021). Phenols are the key metabolites actively participating in plant defense mechanism. Antioxidant ability of phenols makes them competitive ROS scavenging agent. In addition to this, phenolics also regulate the development of plant-rhizobacterial associations that passively enhance plant immunity and competence under stress conditions. Biology of phenolics in plant system and their interactions with other molecules to regulate plant defense is the key for understanding plant developmental plasticity. Therefore, translation of these molecular signals and thoughtful knowledge of their interactions is necessary. This chapter focuses on the key aspects of abiotic stresses effecting plant biology, their response, and stress-induced activeness of phenolic compounds in plant defense.

3.2 Phenolic Biofactories

3.2.1 Phenolic Compounds

Phenolic compounds (or polyphenols) are the plant special metabolites that play significant part in plant survival and defense processes during environmental variations. They play critical role in plant development by contributing to lignin and pigment biosynthesis, hence providing structural integrity to them. Phenols are characterized as aromatic metabolites with the presence of single or multiple hydroxyl groups, elaborated with amino, methyl, glycosyl, or methoxy groups (Tyagi et al. 2020). Regarding their structure, they range from simple (salicylic acid) to complex polymers (suberin, lignin). The major phenolic groups are anthocyanins, tannins, flavonoids, and hydroxycinnamic acids (HCAs). Flavonoids are extensively distributed and most common among all phenolic compounds with four thousand known molecules having subgroups, isoflavones, flavones, and its derivatives 2,3-dihydroxyflavone (Kumar et al. 2020a; Šamec et al. 2021). Some phenolic compounds are abundantly found among kingdom Plantae such as chlorogenic acid, while others are taxonomically limited to particular genera making them biomarkers for taxonomic studies such as isoflavones which are found exclusively in legumes, and some even are restricted to specific plant organs such as anthocyanins which give bright color to fruits and flowers and protect young leaves from photodamage (Lattanzio 2013). Coumarins, styrylpyrones, stilbenes, and furanocoumarins are the phenolic compounds with restricted taxonomic distribution (Grace 2005). In addition, some polyphenols such as proanthocyanidins and hydrolyzable tannins are restricted only to early developmental stages of plants. They abundantly found only in woody plants (Lattanzio 2013). Hence, presence of phenolic compounds varies according to environmental conditions, species type, organ, and even the developmental stage of plant. This wide distribution of phenolic compounds defines their structural and functional diversity.

3.2.2 Types of Polyphenols

The heterogenous nature and structures of phenols provide various ways of classification. Several classes of phenols based on their fundamental structure and carbon chains are phenols and benzoquinones (C_6), catechol melanins $(C_6)_n$, phenolic acids (C_6–C_1), acetophenones and phenylacetic acid (C_6–C_2), isocoumarins/coumarins, phenylpropenes, chromones and hydroxycinnamic acids (C_6–C_3), lignans and neolignans $(C_6–C_3)_2$, lignin $(C_6–C_3)_n$, naphthoquinones (C_6–C_4), xanthones (C_6–C_1–C_6), stilbenes and anthraquinones (C_6–C_2–C_6), flavonoids, neoflavanoids and isoflavonoids (C_6–C_3–C_6), bi-/tri-flavonoids $(C_6–C_3–C_6)_{2/3}$, and condensed tannins $(C_6–C_3–C_6)_n$ (Ahmed et al. 2020). Phenols may also be categorized as “performed phenolics” which are usually produced during plant developmental and growth processes and “induced phenolics” which are produced because of external biotic or abiotic stress or during any mechanical or physical injury (Tak and Kumar 2020). As flavonoids are abundant in nature and frequently present in leaves and fruit peel, therefore, phenolics are also categorized as flavonoids and non-flavonoids. Flavonoids are further divided into six subgroups, i.e., flavonones, flavonols (kaempferol, isorhamnetin, myricetin, and quercetin), flavones, anthocyanidins, isoflavones, and flavan-3-ols. Non-flavonoids are divided into tannins, stilbenes, phenolic acids (gallic acid), and lignans. Among them gallic acid is important as it is the precursor for other phenolic compounds like stilbenes and hydrolyzable tannins

(Aviles-Gaxiola et al. 2020; de la Rosa et al. 2019). On the other hand, phenols can also be categorized based on their occurrence in nature, i.e., shortly distributed (simple phenols, hydroquinones, and derivatives of benzoic acid), widely distributed (coumarins, flavonoids and its derivatives, and phenolic acids), and polymers (lignin and tannins). Lastly, based on their existence in plants, phenolic substances are classified as "soluble" (mostly low molecular weight tannins, flavonoids, and phenols), and "insoluble" forms (condensed tannins and phenolic acids) (Ahmed et al. 2020).

3.2.3 Biosynthetic Pathways

Various interconnected signals participate in regulating the synthesis of phenolic compounds. These include both plant developmental and environmental signals. MYBs (V-myb myeloblastosis viral oncogene homolog) are the transcription factors (TFs) involve in multiple gene expression including biosynthesis of phenolic compounds (Tyagi et al. 2020). Various MYB TFs are involved in biosynthesis of polyphenols, as activators or repressors. One gene can regulate multiple MYB proteins. Important transcription factors involved in phenylpropanoid pathways are WRKY, MYB, bHLH, WD40, and MADS box proteins (Kołton et al. 2022). Sometimes phenolic biosynthesis is also regulated with plant growth regulators, such as ethylene and abscisic acid (ABA) trigger anthocyanin production (Koyama et al. 2018). Phenolic biosynthesis has long been associated with stress stimuli. Elevated ROS levels, under stress, trigger gene expression of various antioxidants including polyphenols. Under certain environmental conditions or during sensitive developmental stages, plant experience oxidative stress due to reduced activity of ROS scavengers. The increased ROS is due to electrons leakage to O_2 from electron transport chain (ETC) in mitochondria and chloroplast or during photorespiration in peroxisomes (Grace 2005). Polyphenols are biogenetically synthesized through shikimate/phenylpropanoid pathway, malonate/polyketide pathway, or mevalonate pathway (Fig. 3.1) (Bhattacharya et al. 2010). Majority of polyphenols (hydroxycinnamic acids HCAs) are synthesized through phenylpropanoid pathways. It involves the synthesis of cinnamic acid from phenylalanine precursor using key enzyme "phenylalanine ammonia lyase" (PAL). Synthesis of cinnamic acid is critical point during secondary metabolic process (Saltveit 2017; Ledesma-Escobar et al. 2019). HCAs also act as precursors for the biosynthesis of other phenolics including flavonoids. Flavonoid biosynthesis uses the intermediate products of both phenylpropanoid and polyketide pathways. Chalcone synthase (CHS) catalyzes the major step that connects phenylpropanoid and flavonoid pathways. Flavonoid pathway is initiated with the condensation of *p*-coumaroyl-CoA with acetate via malonyl-CoA. This involves the synthesis of various flavonoids such as flavonols, chalcones, anthocyanins, flavones, catechins, and proanthocyanidins (Kołton et al. 2022). Phenolic compounds accumulate and incorporate within cell wall to fight against stress.

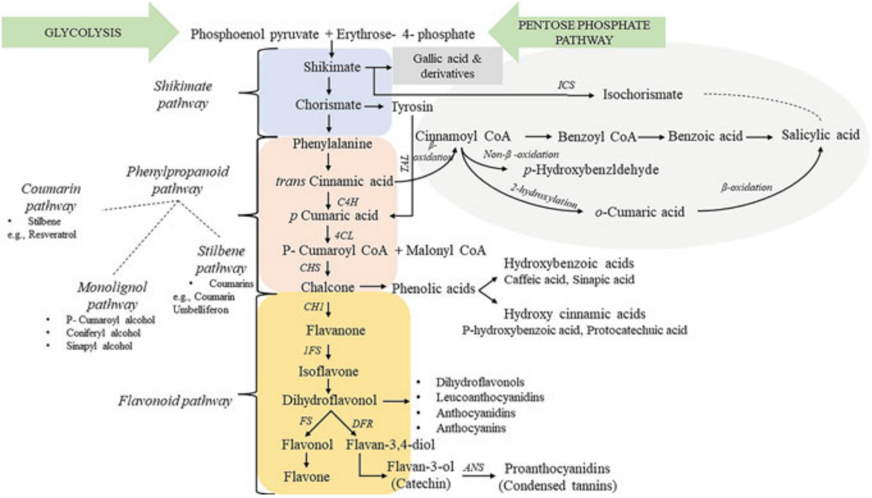

Fig. 3.1 Overview of various pathways involve in the biosynthesis of phenolic compounds showing their biosynthetic relations. *PAL* phenyl ammonia lyase, *TAL* tyrosin ammonia lyase, *ICS* isochorismate synthase, *4CL* 4-coumarate CoA ligase, *C4H* cinnamate-4-hydroxylase, *CHS* chalcone synthase, *CH1* chalcone isomerase, *1FS* isoflavone synthase, *FS* flavonol synthase, *DFR* flavan-3,4-diol, *ANS* anthocyanidin synthase

3.2.4 Phenolics in Plant Biology: Physiological Impact

Diversity of structural and distributional pattern of polyphenols defines their multi-functional properties. Phenolic compounds play principle role in various physiological processes to improve plant tolerance under sub-optimal conditions. They act as key participant in protecting plants against environmental stresses especially against ultraviolet (UV) radiations. They have antioxidant properties that improve plant adaptability. In addition, polyphenols have versatile functions such as antibiotic, antimicrobial, anti-nutritional activity, metal chelators, and signaling agents, hence provide competitive advantage to plants (Sharma et al. 2019). They greatly influence numerous physiological processes involve in developmental processes for instance synthesis of photosynthetic pigment, seed germination, flowering, senescence, and cell division (Tanase et al. 2019). Phenolic substances also possess significant taxonomic and evolutionary importance besides their key role in various metabolic and physiological processes. Metabolomic studies of various phenolic pathways display evolutionary diversification of plants (Delgoda and Murray 2017). Furthermore, some phenolics have ecological importance as they maintain and modulate fauna diversity. Polyphenols also regulate soil nutrient mineralization by effecting the activity of decomposers. Moreover, phenolic compounds present in root exudates alter soil physiochemical properties and increase nutrient uptake by plants. They increase soil porosity and absorption site which enhance nutrient mobilization. Various phenolic compounds (flavonoids, gallic acid, or ferulic acid) control spore germination, fungal growth, and plant microbial associations (both bacterial and mycorrhizal) (Lattanzio 2013). In addition, polyphenols are also involved in signal transduction and act as signaling molecules (e.g., salicylic acid (SA) and flavonoids) during several plant physiological processes. Flavonoids act as chemoattractant as well as chemorepellent for a variety of rhizopheric microbes and initiate nodulation process. In the same way, SA stimulates root development, induces flowering and stomatal closure, reduces transpiration, regulates geotropism, and inhibits fruit ripening (Mohamed et al. 2020). SA triggers signaling pathways that regulate gene expression of phenylpropanoid biosynthesis-related genes (Fig. 3.1). SA triggers CHS activity, hence, regulating phenolic compounds biosynthesis (Mohamed et al. 2020). Furthermore, SA also interacts with signaling pathways of phytohormones such as ethylene, auxins, and jasmonic acid (Vlot et al. 2009).

3.3 Plant Metabolic Adjustments Under Abiotic Stress

Plants have highly efficient mechanism to sense, response, and adapt according to varying environmental conditions. Regulation of various mechanisms at cellular and molecular level enables plants to tolerate and survive through uncomfortable conditions. Initiation of various stress-induced transcriptional factors regulates complex network of stress-related genes to synthesize proteins involved in various plant defensive mechanisms (Fraire-Velázquez and Balderas-Hernández 2013). The stimulus of abiotic stress received by cell receptors initiates series of various interconnected responses at multiple levels of cellular organization. These responses include signal sensation, transduction, RNA processing, biosynthesis of respective proteins, and its post-translational modifications (PTMs). PTMs play central role in stress signaling as they regulate protein activity at various cellular levels. Stress stimulus is sensed in various cellular compartments including cell membrane, cell wall, cytoplasm, mitochondria, and nucleus. Stress signal is sent to regulatory proteins (Ca^{2+}, protein kinases) that trigger alternative gene transcription and protein translation resulting in the production of modified proteins having key role in stress response (Zhang et al. 2022). Stress encourages ROS production which transduce signal to nucleus via mitogen-activated protein kinases (MAPKs) to initiate stress-related pathways and gene expression (activates TFs including WRKY, MYB, bHLH) leading to expression of stress-related genes including formation of polyphenols (Naing and Kim 2021). However, under certain conditions, overproduction of ROS becomes difficult to control by scavengers leading to oxidative damage. Peroxisomes, mitochondria, and chloroplasts are the primary ROS-producing bodies. ROS causes irreversible oxidation of amino acids, reduces CO_2 fixation, and interacts with photosynthetic apparatus. ROS react with chlorophyll and form chlorophyll triple state that rapidly generates singlet oxygen and damage photosynthetic system especially PSII that ultimately reduces photosynthetic efficiency and in longer term, cause cell death (Sharma et al. 2019). Plants have established natural ROS scavenging systems (enzymatic and non-enzymatic) to maintain cellular redox homeostasis and reduce cytotoxic effect of ROS.

Polyphenols especially phenolic acid, anthocyanins, and flavonoids play an important role in balancing cellular redox levels (Martinez et al. 2016).

Plant stress response involves re-allocation of resources between growth and defense systems. Metabolic adjustments and phenolic pattern of plants have been defined by resource allocation via dialogue between plant and its environment. Accumulation of secondary metabolites by activation of secondary metabolism during stress conditions is due to shifting of energy from primary to secondary metabolic pathways. Suppression of primary metabolism leads to suppressed primary growth but enable plant to acclimatize to the environment and make them more competent during unfavorable conditions. Carbon flux from primary to secondary metabolic pathways increases secondary metabolite production, and as a result, cells accumulate various metabolites and growth regulators such as jasmonic acid, abscisic acid (ABA), and ethylene (Lattanzio 2013). ABA synthesis is the first defensive strategy used by plants which play central role in stress signal management in plants. It converts adverse environmental stress signals into gene expression and transmits stress stimuli from source to the whole plant for its respective response (Pedrol et al. 2006). ABA also interacts with other stress-related transcriptional factors including those involved in phenolic biosynthesis especially anthocyanin (González-Villagra et al. 2019). Anthocyanins have antioxidant activity and are the key photoprotective agents that protect photosynthetic apparatus (PS II) of plants during radiation stress (Liu et al. 2018). Moreover, stress-induced metabolic switching also leads to the accumulation of low molecular weight osmolytes especially proline. Accumulation of compatible solutes during osmotic stress helps plants to maintain cell turgidity, restore redox metabolism, and protect and stabilize cellular proteins. Proline accumulation transfers energy toward biosynthetic pathways of phenolic compounds through OPP pathway (Lattanzio 2013). Oxidation of NADPH during proline synthesis boosts oxidative pentose phosphate (OPP) pathway activity by providing precursors for the biosynthesis phenolic compounds. Hence, oxidation of NADPH and production of NADP+ during proline synthesis by pentose phosphate pathway cause interaction and facilitation of simultaneous polyphenol biosynthesis (Lattanzio 2013).

3.4 Phenolics Are Strong Antioxidants

Presence of OH group attached to six carbon aromatic ring makes phenols a weak acid. Electron donating ability of phenols makes them strong antioxidants, hence excellent ROS scavengers. Lower electron reduction ability of phenolic radicals and their lesser reactivity than oxygen radicals make them strong scavengers. Most of the plant phenolics have radical scavenging properties; however, flavonoids, HCAs, and anthocyanins have efficient radical scavenging ability. Among flavonoids, the strongest scavenging ability is present in anthocyanidins cyanidin, flavonol quercetin, epigallocatechin gallate, delphinidin, and flavan-3-ols epicatechin gallate. Moreover, phenolics with *ortho*-dihydroxy structures readily donate electron because of additional OH group at *ortho* position (catechol structure) as compared to monohydroxy structures, thereby, are least efficient antioxidants (Grace 2005). This additional OH group lowers electron reduction potential by 300–400 mV and increases stability of respective phenoxyl radical. Phenolics with catechol structures are readily oxidized and hence have better scavenging ability. Furthermore, in flavonoids 2,3 double bond and OH group at position 3 in C ring and presence of OH at 3 and 5 positions in A ring enhances antioxidant property. In the same way, chlorogenic acid, gallic acid, and its methyl esters also possess antioxidant property, but salicylic acid do not have significant antioxidant property. Higher molecular phenolics like tannins also possess strong antioxidant ability. Beside strong antioxidants, phenolic compounds directly protect DNA and lipids from ROS, hence acting as shield against oxidative damage. Phenolic compounds mostly flavonoids and HCAs are highly efficient against lipid peroxidation and low-density lipoprotein oxidation as they are active chain breaking antioxidants and metal chelators (Grace 2005). Moreover, flavonoids also oxidize alkyl peroxyl radicals. Hence, flavonoids present near surfaces protect lipids from oxidation. Anthocyanins are the most potent antioxidants with higher abilities to quench free radical species. Anthocyanins are water soluble phenolic compounds that give characteristic colors (blue, purple, or red) to flowers and fruits. Anthocyanins act as antioxidants as well as screening agents which protect plants from visible light and shield photosynthetic apparatus from extreme lights (Liu et al. 2018). The antioxidant ability of anthocyanins mainly based on the extent of hydroxylation at B ring. This hydroxylation increases the antioxidant capacity of anthocyanins. Moreover, glycosylated forms of anthocyanins have reduced metal chelating, electron donating, and delocalizing ability due to which they have reduced radical scavenging ability as compared to aglycone form. Sugar units at 3 and 5 positions lower antioxidant ability (Zhao et al. 2014).

3.5 Plant Phenolics Under Variable Environmental Conditions

3.5.1 Osmotic Stress

Osmotic stress is the most significant among all abiotic stresses affecting plant physiological activities. Water deficiency (drought) and excess (flood) both cause the generation of ROS in plant cells. As a result, synthesis of polyphenols is enhanced due to de novo synthesis of the enzymes involved in phenylpropanoid pathway. The concentration of phenolic compounds may increase up to 10 mM in some cells. Increased activity of PAL, CHS, CH1, and flavanone 3-hydroxylase (F3H) enzymes due to overexpression of TFs is the key reason for aggregation of various phenolic substances, e.g., anthocyanin, flavonol, caffeic acid, ferulic acid, cinnamic acid, quercetin, kaempferol, and asp-coumaric acid in plant cells (Wang et al. 2018). Anthocyanins and other flavonoids accumulate in vacuole, close to ROS production sites and inhibit the chain reaction by deactivating radicals with their OH groups to avoid ROS accumulation. Thereby, reducing stress and maintaining osmotic balance within cell (Zhang et al. 2019; Kumar et al. 2020b), overexpression of key genes involved biosynthesis of anthocyanin such as dihydroflavonol

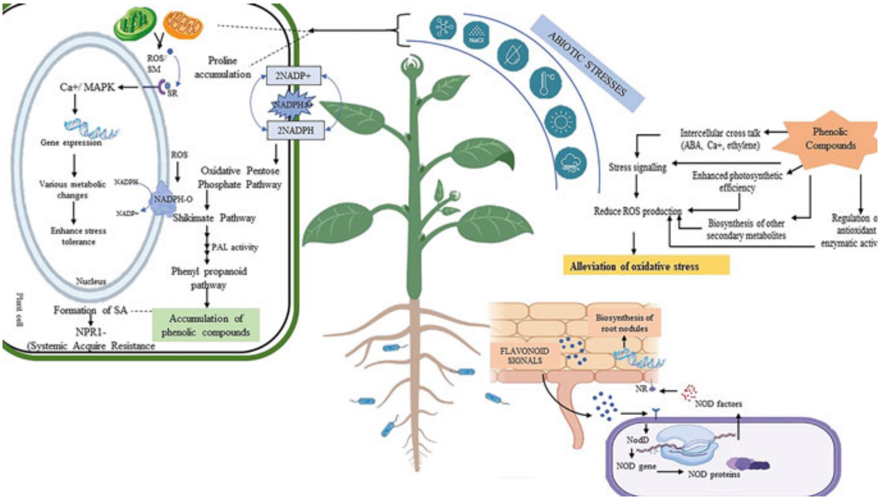

Fig. 3.2 Various abiotic stress stimuli activating stress signal to alleviate oxidative stress and enhance stress tolerance in plants. *SM* signaling molecule, *SR* signal receptor, *NADPH-O* NADPH oxidase, *PAL* phenylalanine ammonia lyase, *NR* nod receptor, *ROS* reactive oxygen species

4-reductase and and MYB TFs such as Myeloblastosis 5A and Myeloblastosis A1 (MybA1) boost anthocyanin UDP-glucose: flavonoid 3-*O*-glucosyl transferase (UFGT) production (González-Villagra et al. 2019). Anthocyanins act as antioxidants in maintaining cellular oxidative homeostasis to ensure osmotic balance. Thus, there exists a positive association between anthocyanin aggregation and osmotic homeostasis (Waseem et al. 2019; Naing and Kim 2021). Similarly, upregulation of 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase (key enzyme in shikimate pathway) leads to accumulation of catechin, vanillic acid, ferulic acid, chlorogenic acid, gallic acid, rutin, and benzoic acid in some plants under drought (Ghimire et al. 2017). Drought stress induces alteration in various gene expressions involved in biosynthesis of phenolic compounds and their overexpression causing phenolic accumulation under stress that acts as antioxidants and prevents redox damage (Fig. 3.2).

3.5.2 Temperature Stress

Deviation from optimum temperatures (chilling/freezing or high temperature) results in alteration of physiological activities in plants affecting various developmental processes and causes stress. Temperature below freezing point causes freezing injuries and formation of intracellular ice crystals that disrupt cellular activities and create osmotic potential gradient. Similarly, heat stress affects photosynthetic activities and causes oxidative stress (Kumar et al. 2020a; Jan et al. 2021). Also, high temperature causes reduction in enzymatic activities. Thermal interruptions liberate cytosolic ATP into extracellular matrix which is then received by receptors present on plasma membrane of other cells, as a result, increase in cellular Ca^{2+} concentrations occurs that trigger NADPH oxidase, thus activating ROS production (Jacobo-Velázquez et al. 2011). Hence, temperature stress affects plant photosynthetic activities and causes generation of ROS. Thermal alterations cause increased activity of PAL that accumulate phenolics which get incorporated in plant cell wall (lignin and suberin) and protect plants by inducing tolerance against cold stress (Chalker-Scott and Fuchigami 2018). Cell wall-associated phenolics have great influence in cold stress resistance in plants. Suberin and lignin act as barrier and maintain osmotic potential gradient. Similarly, accumulation of farinose in aerial parts of leaves minimizes formation of ice crystals in plant cell. Hence, change in composition of phenolic content would increase plasma membrane adhesion to cell wall, thus reducing membrane disruption during stress. Coumaric acid and caffeic acid protect microfilaments of cytoskeleton, thus protecting cell from disruption during heat stress (Commisso et al. 2016). Increased accumulation of various other phenolic substances, e.g., chlorogenic acid, anthocyanins, gallic acid, and ferulic acid significantly acts as stress protectants and improves plant resistance against temperature stress (Kumar et al. 2020c). Low temperature causes photoinhibition of photosynthesis by inhibiting assimilatory reactions and affecting electron transport resulting in overexcitation of photosynthetic apparatus, thus affecting plant photosystems especially PSII and causing photoinhibitory damage. Overexpression of PAL, CHS, and upregulation of TFs regulates anthocyanin accumulation in plant epidermis that acts as photobarrier and protects photosynthetic apparatus. Both HCAs and anthocyanins protect plant cell under low temperature by protecting chlorophyll and maintain plant photosynthetic capacity by regulating photosynthetic genes (Grace 2005). Hence, low temperature induces upregulation of anthocyanin-producing TFs. Moreover, anthocyanins also scavenge stress induce ROS to maintain normal cellular oxidation levels. Association between low temperature stress tolerance, ROS scavenging, anthocyanin accumulation, and upregulation of TFs is also found existing (Jiang et al. 2019). In addition, C-repeat binding factor 1 (CBF1) is also involved in upregulation of anthocyanin biosynthetic genes by regulating glycosyltransferases (genes involved in anthocyanin pathways) (Naing and Kim 2021). Similarly, during high temperatures, plants accumulate caffeoylquinic acid (Alegria et al. 2012).

3.5.3 Radiation Stress

Overexposure to radiation (visible light) also leads to photoinhibition. Plants have specialized proteins and photoreceptors to sense the intensity, quality, and duration of light. These photoreceptors perceive light of specific wavelength over a continuous spectral range with the help of chromophore (Aguirre-Becerra et al. 2021). In the same way, exposure to UV has led to photoinduction of DNA and degradation of chlorophyll. Radiation stress influences the light harvesting complex, photosystem II, electron transport chain, and acceptor sites of PSII. Moreover, long-term exposure to high light intensities leads to overproduction of intercellular ROS (Kumar et al. 2020c). Plants have various mechanisms to prevent overexcitation of photosynthetic apparatus. A strong correlation between high light intensity and phenylpropanoid biosynthesis exists. Plants synthesize phenolic compounds in response to oxidative pressure caused by overproduction of ROS. Biosynthesis of phenolic substances and expression of various genes involved in phenylpropanoid pathway have been strongly influenced by intensity and quality of light. Blue light influences the accumulation of malonyl-CoA and coumaroyl CoA that ultimately enhances phenolic production to scavenge ROS. Similarly, red light is involved in the stimulation of anthocyanin production (Liu et al. 2016; Qian et al. 2016). Light stress causes the accumulation of various phenolic compounds, for instance anthocyanins, catechins, HCAs, flavonols, chlorogenic acid, rutin, caffeic acid (Grace 2005). Light-dependent regulation of PAL, CHS, and F3H causes accumulation of anthocyanins and flavonoids. UV-B exposure has led to the upregulation of almost 121 genes involved in phenylpropanoid pathway including PAL and CHS (Rodríguez-Calzada et al. 2019). Flavonoids, anthocyanins, and HCAs have high UV absorbing capacity, hence act as screening agents. Anthocyanins, flavonoids (kaempferol derivatives), phenolic acid esters accumulate in epidermal cells and protect mesophyll from extreme light (Naikoo et al. 2019). Besides this, flavonoids also protect DNA from photodamage. Plant primary and secondary metabolic pathways are coordinated in response to UV stress. UV-B exposure also enhances the expression of primary metabolic genes that are directly related to phenylpropanoid pathways such as that involved in pentose phosphate pathway and shikimate pathway (Aguirre-Becerra et al. 2021).

3.5.4 Salinity Stress

In the presence of salinity, plant cells start accumulating Na^+ and Cl^- that disturb cellular homeostasis and cause nutritional imbalance due to inhibition of water and nutrient uptake. This imbalance initiates the production of ROS which can act as signaling molecule in maintaining cellular redox mechanism and triggering MYB TFs that regulates anthocyanin synthesis but under severe stress, overproduction of ROS can damage chlorophyll and negatively affect photosynthetic rate. Anthocyanin acts as antioxidant agent as it can absorb and neutralize free radicals and decompose peroxides to limit the damage by ROS. Moreover, anthocyanins have ability to chelate cellular ions, hence protecting the cell from cytotoxicity caused by ionic imbalance (Naing and Kim 2021). Upregulation of key genes (PAL, CHS) associated with anthocyanin biosynthesis is the key factor in salinity-induced anthocyanin accumulation. Beside anthocyanins, the predominant phenolics that accumulate under salinity stress are *p*-coumaric acid, isoorientin, vitexin, vanillin, rutin, orientin, oleuropein, ferulic acid, and protocatechuic acid (Jamalian et al. 2013; Grzeszczuk et al. 2018). Stress hormones also trigger phenolic compound accumulation under salinity stress. For example, jasmonic acid and its derivatives also indirectly take part in phenolic accumulation in plants by enhancing activity of

PAL and other enzymes participating in phenylpropanoid pathway (Lim et al. 2012). In the same way, abscisic acid also influences phenolic accumulation in plants. Ferulic acid provides support and strength to plant cell wall and causes cell elongation (Minh et al. 2016). Furthermore, SA also participates in mitigating salinity stress in plants. SA improves photosynthetic activity and ascorbates and guaiacol peroxidase activities and accumulation of various osmolytes including proline, etc. (Mohamed et al. 2020). Under salinity stress, salicylic acid is also involved in regulation of GST gene expression and enhances antioxidant transcription and activity of enzymes involved in ascorbate-GSH pathway (Li et al. 2013). Moreover, SA also restores membrane potential and prevents salinity-induced ionic flux through GORK channel, thus improving salinity resistance in plants (Jayakannan et al. 2013).

3.5.5 Mineral Stress

Optimum concentrations of various metals are important for normal plant physiological activities; however, at higher concentrations, they negatively affect cellular activities and retard plant growth. This can also limit CO_2 fixation, thereby disrupting photosynthetic activities. Metals can also interact with mitochondrial ETC and cause the formation of ROS (Ai et al. 2018). Major metal toxicity includes production of ROS, inactivation of metabolic enzymes, and ionic substitutions (Kumar et al. 2020c). Metal toxicity in plants triggers secondary metabolite production as they have strong antioxidant and metal chelating ability, thus protecting plants from metal stress. Heavy metal stress causes regulation of various anthocyanin biosynthetic genes including F3H, CH1, DFR, CHS; these genes regulate anthocyanin production (Handa et al. 2019). Anthocyanins act as metal chelators, hence protecting plants from metal toxicity. Activation of PAL and CHS is dominant in most cases; however, some other anthocyanin-related genes such as F3H, MYBL2, and TT8 are also the reason behind stress-induced phenolic accumulation (Imtiaz et al. 2018). The predominant phenolic acids accumulating in presence of high concentrations of heavy metal are chlorogenic acid, rutin, cinnamic acid, and epigallocatechin. Moreover, excess Cu also increases various enzymatic activities such as shikimate dehydrogenase, ascorbate peroxidase, cinnamyl alcohol dehydrogenase, and polyphenyl oxidase as a result accumulation of ferulic acid, protocatechuic acid, vanillic acid, chlorogenic acid, *p*-OH benzoic, *p*-coumaric acid, and syringic acid is prominent (Aviles-Gaxiola et al. 2020). Similarly, mineral deficiency also causes cellular stress that regulates transcriptional regulatory genes involved in phenylpropanoid pathway. For example, vanillic acid, trans-cinnamic acid, and *p*-coumaric acid are prominent under K-deficiency; similarly, chlorogenic acid and rutin are dominant phenolics during nitrogen stress. The responsible genes involved in their accumulation are PAL, CHS, and F3H (Aviles-Gaxiola et al. 2020).

3.6 Phenolic Signaling

Phenolic compounds present in root exudates act as chemotactic signal for rhizospheric microbial community. Rhizobacteria can oxidize aromatic compounds released by root exudates. Phenolic acids are alternate carbon source for diazotrophs and serve as precursor for the biosynthesis of phenolic lipids. Phenolic acids are released from emerging roots in leguminous plants during seed germination and favor the soil *Rhizobium* community to accumulate near roots, thus providing competitive advantage for them (Mandal et al. 2010). Polyphenols, mainly flavonoids, can serve as chemoattractant and promote growth of selected rhizobacteria. Leguminous plants release various phenolic compounds such as flavones, flavonols, isoflavonoids, vanillin that serve as chemoattractant for rhizobia. These signals regulate *nod* genes and develop legume rhizobial symbiosis. Moreover, phenolic acids also protect growing cells of nodules from oxidative damage during developmental phase. However, some phenolic compounds act as repressor for *nod* regulation (Mierziak et al. 2014). Phenolic compounds with free OH group interact with legume rhizobia signaling and regulate nodulation factor (*nod*) to initiate nodule formation. For instance, genistein and daidzein induce *nod* in *Bradyrhizobium japonicum* but inhibit in *Sinorhizobium meliloti.* Similarly, in *Rhizobium leguminosarum*, naringenin stimulates this factor whereas quercetin represses *nod* factor (Mandal et al. 2010). Moreover, endogenous phenolics such as *p*-coumaric acid, 4-hydroxybenzaldehyde, and protocatechuic acid stimulate bacterial IAA (auxin) production efficiency, hence making plant more competent. In addition, caffeic acid, *p*-coumaric acid, and ferulic acid interact with root formation in concentration-dependent manner and inhibit growth of roots (Chamkhi et al. 2021).

3.7 Conclusion

Phenolic compounds are important for healthy plant activities under variable environmental conditions. Knowledge about various polypropanoid pathways and factors interacting with them is important to develop stress-tolerant plant species. There is a need to study the factors involved in the regulation of gene expression regarding biosynthesis of phenolic compounds. Changing environmental conditions severely affects our agricultural products. Thus, in this case, extensive study of phenolic compounds and their practical application would assist in the development of strong agricultural and horticultural systems by producing stress-tolerant plant species.

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4

Phenolic Biosynthesis and Metabolic Pathways to Alleviate Stresses in Plants

Yamini Tak, Manpreet Kaur, Chirag Gautam, Rajendra Kumar, Jyotsana Tilgam, and Suman Natta

Abstract

Phenolics are the plant secondary metabolites which play salient physicochemical roles entire lifespan. Phenolics are produced under various biotic and abiotic stresses and play key roles to alleviate stresses regulate hormonal regulation, improving photosynthetic activity, nutrient mineralization, metal-chelating property, antioxidative capacity, etc. Phenolic compounds are mainly biosynthesized by shikimic acid pathway in advanced plants and shikimate is the key central metabolite for synthesis of complex phenolics. Phenylalanine ammonia lyase is a prime enzyme for phenylpropanoid biosynthetic pathway, connecting primary metabolism to secondary metabolism. It has been seen that during harsh environmental conditions, phenolic compounds are synthesized and accumulated in host plant to emerge from that stress. This chapter furnishes knowledge about the biosynthetic pathways of different phenolic compounds and newly illuminated steps in the biosynthesis to mitigate various biotic and abiotic stresses, many of which allocate precursors.

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Biosynthesis · Flavonoids · Phenolic compound · Plant · Stress

4.1 Introduction

For survival, plant faces many hurdles during their whole life; biotic and abiotic stresses are unique vain aspects which affect their growth and development. Biotic stress comprises bacteria, virus, fungi, insect pests, and weed while abiotic stress includes drought, temperature (high or low), salinity, heavy metals, and ultraviolet radiations, etc. (Pandey et al. 2017). But plants have their own response system or mechanisms that dare them to survive even in adverse conditions by synthesizing phenolic compounds which help them to stay alive. Phenolics are the secondary metabolites, generally outspread in plant kingdom which plays pivotal role in seed germination, cell division, hormonal regulation, nutrient mobilization, attract pollinators, and protection from plant various stresses (Wink 2018; Tak and Kumar 2020). Some phenolic compounds are synthesized by modification reactions such as acylation, methylation, trans-esterification, glycosylation which alters their biological activity and function. Phenols help the plant to avoid adversity in all conditions (Castrillón-Arbeláez and Délano Frier 2016). Centered on the presently accessible studies on the catastrophic consequence of stresses on plants, in this book chapter we lighten on general overview, structure, biosynthesis and metabolism of phenols, flavonoids, and anthocyanin under biotic and abiotic stresses.

4.2 Phenolics in Response to Stresses

Due to sessile nature of plants, various environmental curtailments such as biotic and abiotic stresses deed as limiting factor for their growth, nutrient uptake, and overall development (Gull et al. 2019). Huge numbers of secondary metabolites are biosynthesized and accumulate in plant cells to coping with traumatic conditions and provide capacity to plant to endure against adversative conditions. Phenolic compounds or polyphenols are the key secondary metabolites which have benzene ring attaching with one or more –OH groups and present in plants in free or bound form (Isah 2019). Soluble phenolics are biosynthesized mainly in endoplasmic reticulum of plants and these are elated to cell wall and bound with protein and carbohydrate by a specific bond, named as bound phenolics (Shahidi and Yeo 2016). Phenolic concentration in plant tissue is a fine signal to forecast the level of infection from biotic factors and tolerance of abiotic stress. Phenolics play a decisive role in floras during adverse climatic conditions and improve plant growth and development (Akula and Ravishankar 2011). Plant polyphenols act as defensive compounds during stress and help to plant cope up with adverse climatic conditions by enhancing mineral uptake and mobilization. Soil microbes present in rhizosphere of the

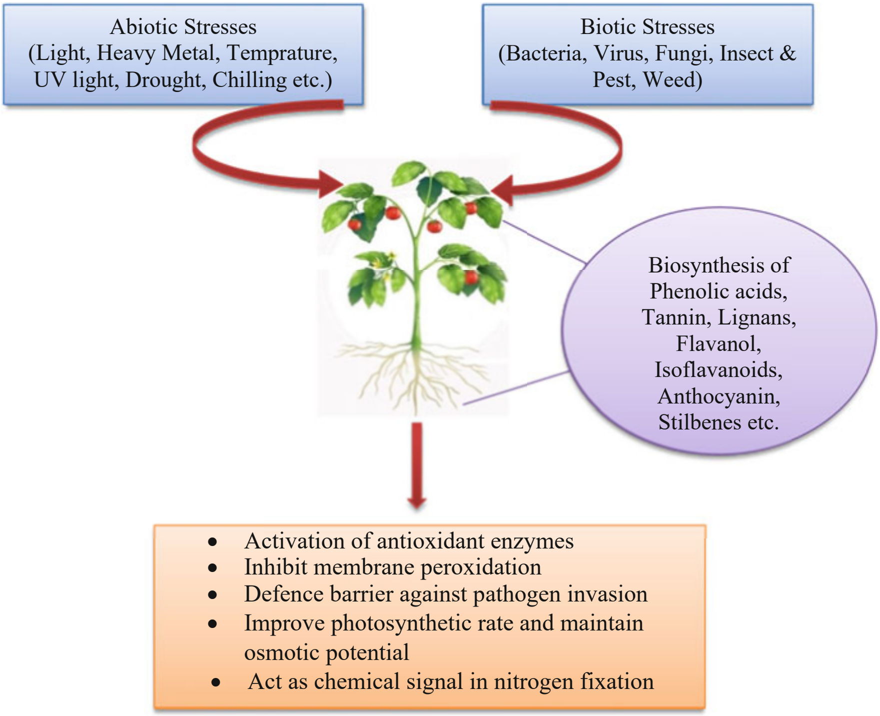

Fig. 4.1 Phenolics and their response under biotic and abiotic stresses

plant which boost up synthesis of phenol and assist for uptake of mainly N and P from soil (Backer et al. 2018). Some phenols and their derivatives help in biological nitrogen fixation, nodule formation, and hormone signaling. Phenolics act as antioxidative compounds and quench the reactive oxygen species during biotic and abiotic stress conditions (Caverzan et al. 2016). Phenolics works as allelochemicals for weed and other plants; some act as phytoalexins in opposition to the pathogen attack or sometimes these compounds are known as phytoestrogens in grazing animals (Zhao et al. 2018). Overall from seed germination to maturation, directly and indirectly phenolics help to plant for better survival capability during harsh climatic conditions. Phenylpropanoid pathway is transcriptionally upregulated by some elicitors of abiotic stresses resulting provide resistance to plant against stresses (Sharma et al. 2019b) (Fig. 4.1).

4.3 Biosynthesis, Metabolism of Phenols Under Stress Conditions

Plant phenolics are immense cluster of compounds differing from one or more aromatic ring to highly polymerized compounds. In vascular plants, phenols are chiefly synthesized by shikimic acid pathway but in bacteria and fungi malonic acid pathway is predominant act as connecting link between primary and secondary metabolites (Kumar and Goel 2019). In plants, shikimic acid is the precursor for synthesis of aromatic acids such as phenylalanine, tyrosine, and tryptophan; these amino acid plays an imperative role in production of plant phenolics (Francenia Santos-Sánchez et al. 2019). These aromatic acids are moved to cytosol for protein biosynthesis and this shikimic acid pathway also furnishes carbon skeleton for biosynthesis of auxin, salicylic acid, quinones, and plant pigments (Mérillon and Ramawat 2017). This pathway contains seven sequential enzymatic reactions and starts with condensation of phosphoenolpyruvate from glycolysis and erythrose-4-phosphate from oxidative pentose phosphate pathway to form 3-deoxy-D-arabinoheptulosonate 7-phosphate (DAHP) by DAHP synthase than this DHAP is cyclized to form 3-dehydroquinate (DHQ) with the help of DHQ synthase enzyme (Huccetogullari et al. 2019). Bifunctional enzyme 3-dehydroquinate dehydratase/ shikimate dehydrogenase catalyzes two sequential reactions and forms shikimate by DHQ. In the next step, shikimate-3-phosphate (S3P) is produced by shikimate by shikimate kinase enzyme catalytic reaction (Francenia Santos-Sánchez et al. 2019). Condensation reaction catalyzed by 5-enolpyruvylshikimate 3-phosphate synthase (EPSPS) enzyme and forms an EPSP and inorganic phosphate by S3P and one molecule of PEP. Glyphosate is a broad-spectrum herbicide helpful to control weeds; its structure is similar to PEP so binds with the enzyme-S3P complex and inhibits the pathway (De Souza and Sant'Anna 2008). In the subsequent phase, EPSP is changed into chorismate-by-chorismate synthase (CS) enzyme and finally phenylalanine is produced. Phenylalanine ammonia lyase (PAL) enzyme is the chief committed enzyme yield *trans*-cinnamic acid and ammonia by nonoxidative deamination of phenylalanine (Kong 2015). PAL activity was first quantified in protein extracts of *Sorghum bicolor* by Koukol and Conn. In some monocots and fungi, tyrosine is converted into 4-hydroxycinnamic acid by tyrosine ammonia lyase (Louie et al. 2006; Shuab et al. 2016). PAL is encrypted by single gene family to multiple gene families which are divergently expressed throughout plant growth and in comeback to various stresses. Dehghan et al. (2014) found that two major genes *Ct*PAL (phenylalanine ammonia lyase) and *Ct*CHS (chalcone synthase) in *Carthamus tinctorius* induced during wounding and salinity stress. Unusual fellow of the soybean PAL gene family, *Gm*PAL2.1 magnify resistance to *Phytophthora sojae* in transgenic soybeans (Zhang et al. 2017). Promoter analysis exhibited that PAL comprises cis-acting elements such as ABRE, ARE, HSE, TCA-elements, TC-rich repeat and GA, CGTCA, TGACG, WUN-motif in the upstream area which counter to various stress hormones and might exhibit its essential role in biotic and abiotic stresses (Valifard et al. 2015). Shikimate dehydrogenase and glucose-6-phosphate dehydrogenase are imperative enzymes in phenylpropanoid pathway. Mishra and Sangwan (2019) reported that PAL, shikimate dehydrogenase, glucose-6-phosphate dehydrogenase enzyme activities increased under high cadmium stress in *Withania somnifera*.

4.3.1 Hydroxycinnamic Acid and Their Derivatives

Phenolic acids are categorized into two sections: hydroxybenzoic and hydroxycinnamic acid. Most familiar hydroxycinnamic acids are caffeic acid, ferulic acid, sinapic acid, quinic acid, and chlorogenic acid. Structurally, phenolic compounds have a C6–C3 framework, progenitor of other typical phenolic and lignin compounds (Kumar and Goel 2019). Caffeic acid is the precursor of many polyphenols, restoring and start biosynthesize lignin in cell walls and increase its longevity under heavy metal stress and pathogen attack (Riaz et al. 2019). Caffeic acid is biosynthesize by phenylpropanoid pathway firstly *trans*-cinnamic acid is transformed into *p*-coumaric acid by the cinnamate 4-hydroxylase (C4H) enzyme after that by a hydroxylation 4-coumarate 3-hydroxylase (C3H) converts *p*-coumaric acid into caffeic acid (Berner et al. 2006). Caffeic acid intercepts oxidation of organelles and cell membrane by regulating the lipoxygenase activity in plants and oxidizes the reactive oxygen species (Gulcin 2020). Klein et al. (2015) conveyed that exogenously application of caffeic acid relieves salinity-induced growth hinderance in young branch, prevents chlorophyll loss in leaves, and elevates nitric oxide and cyclic guanosine monophosphate content in nodules of roots of soybean. Methylation of caffeic acid by *O*-methyltransferase produces ferulic acid (4-hydroxy-3-methoxycinnamic acid) (Kumar and Pruthi 2014). Ferulic acid acts as the connecting bridge between cell wall confining polymers and binds to structural proteins and lipids. Li et al. (1993) reported that 10^{-3} M of caffeic and ferulic acids helps the elongation of lettuce hypocotyls, but more than 10^{-3} M hinders germination and seedling growth. Ferulic acid is transformed into sinapic acid by two sequential reactions, in first step ferulic acid is converted into 5-hydroxyferulic acid by ferulate-5-hydroxylase (F5H) enzyme and finally sinapic acid is produced by caffeic acid/5-hydroxyferulic acid 3/5-*O*-methyltransferase (COMT) enzymatic reaction (Ruegger et al. 1999). Bi et al. (2017) found that sinapic acid or its derivatives help in plant development, protect from UV rays, and hinder with abscisic acid homeostasis throughout seed germination in *Arabidopsis thaliana* during drought stress.

CoA ligase enzyme integrates Co-A into caffeic acid and produced caffeoyl-CoA and this compound trans-esterified with quinic acid to yield chlorogenic acid (Clifford et al. 2017). Under UV stress, hydroxycinnamoyl CoA quinate transferase (HQT) enzyme increased and produced chlorogenic acid for UV protection in tomato (Sonnante et al. 2010). Moglia et al. (2008) found that dicaffeoylquinic acids was increased in foliage of globe artichoke (*Cynara cardunculus* L. var. *scolymus*) to withstand against UV-C exposure but chlorogenic acid and luteolin-7-glucoside was much less noticeable and was statistically unsignificant. Ferulic acid acts as precursor for synthesis of aromatic compounds vanillin, first step the feruloyl-CoA-synthetase enzyme changes ferulic acid to feruloyl-Co-A after that enoyl-CoA-hydratase/aldolase converts feruloyl-CoA into vanillin (Luziatelli et al. 2019).

4.3.2 Lignin and Lignans

Lignans have a significant contribution in avoiding differential stresses. Lignin reduces the pathogen invasions like a physical barrier and also protects plants from enzymatic degeneration by microorganisms (Malinovsky et al. 2014). Lignin is the second most copious organic compound in plants, constituting nearby 30% of the organic carbon in the environment. Different monolignols such as coniferyl alcohol, *p*-coumaryl alcohol, and sinapyl alcohol are consequent from caffeic and ferulic, *p*-coumaric, and sinapic acids, respectively (Amthor 2003). Monolignols are formed in the cytoplasm and shifted to the cell wall by ATP-dependent ABC-transporter and polymerized by laccases or peroxidases (Wang et al. 2013). These monolignols units are associated by a bond between locations 8 and 8′ and form a compound known as a "lignin." In vitro, this bond can be formed by blending of coniferyl alcohol and peroxidase by 8–8- and 8–5-linkages (Hatfield 2001). Dimerization of two coniferyl alcohol by peroxidases or laccases leads to the formation of the (±)-pinoresinol (Paniagua et al. 2017). Plant dirigent proteins (DIR) have important roles in biosynthesis of also lignin. Wheat dirigent (TaDIR13) y direct coniferyl alcohol coupling into (+)-pinoresinol and lignin extract from TaDIR13 improved antibacterial effects to *Pseudomonas syringae* (Ma and Liu 2014). *Fusarium graminearum* extract is a fungal elicitor which triggered the accumulation of lignin in hairy root cultures of *Linum album* by remarkably increasing the expression of crucial genes convoluted in phenylpropanoid and lignan metabolism (Esmaeilzadeh Bahabadi et al. 2014). Under water scarcity condition *Pinus radiate* shows unusual lignification within the secondary cell wall and reduces lignification in middle lamella to prevent leakage of water and enhance tolerance from various microorganisms (Donaldson 2002). Transcription factor, *Ii*WRKY34, has pleiotropic effects on biomass growth rate and lignan biosynthesis protects *Isatis indigotica* plant from salt and drought stress. *Ii*WRKY34 expression has widespread effect on primary and secondary metabolism and increases carbon flow again toward lignan and flavonoid biosynthesis (Xiao et al. 2020).

4.3.3 Benzoic Acid and Derivatives

Benzoic acid acts as a precursor for many primary and secondary metabolites; it is formed by curbing of the C_3 side chain by two carbon compounds of phenylalanine. Some secondary metabolites such as salicylic acid, hydroquinone, catechol, vanillin, gallic acid, and protocatechuic acid are the benzoic acid derivatives (Ng et al. 2016). Protocatechuic acid is a 3,4-dihydroxybenzoic acid and occurs in various plant species. It has strong antioxidant properties which ultimately prevents the plants from oxidative stress caused by different biotic and abiotic stress conditions. It is present in onion scales and provides resistance against onion smudge, a fungal disease due to *Colletotrichum circinans* (Kakkar and Bais 2014). In *Aerobacter aerogenes*, both protocatechuic and o-pyrocatechuic acids are formed at pre-aromatic stage. In *Phycomyces blakesleeanus*, *p*-coumaric acid is converted into 4-hydroxybenzoic acid and further it converted into protocatechuic acid by enzymatic catalysis (Sandmann and Hilgenberg 1982).

Gallic acid is 3,4,5-trihydroxybenzoic acid extant in many plants and precursor of gallo- and ellagitannins. It has antimicrobial, anti-inflammatory, anticancer activities and prevents reactive oxygen species generation (Chen et al. 2013). There are two possible pathways for gallic acid biosynthesis in both plants and bacteria: (1) by direct oxidation and (2) dehydration followed by hydroxylation. Dehydration of DHQ is catalyzed by the dehydroquinate dehydratase (DQD) domain of the dehydroquinate dehydratase/shikimate dehydrogenase (DQD/SDH) enzyme and produces 3-dehydroshikimic acid (3-DSH) (Muir et al. 2011). After that, $NADP^+$-dependent oxidation is catalyzed by the SDH domain of DQD/SDH and produced gallic acid from 3-DSH. Sometimes by β-oxidation of caffeic acid or by dehydration of 3-DSH, protocatechuic acid is formed, and by hydroxylation of protocatechuic acid, gallic acid is formed (Zeraik et al. 2014). Yildiztugay et al. (2017) reported that external application of gallic acid enhanced activities of superoxide dismutase (SOD), catalase (CAT), and enzyme activities in ascorbate-glutathione cycle such as monodehydroascorbate reductase and dehydroascorbate reductase and contents of ascorbate and glutathione in soybean leaves under cold stress. They also suggested that gallic acid is an influential inducer of radical scavenging activity and helpful to improve photosynthetic efficiency and water status of the plants.

Ellagic acid is a polyphenol commonly present in plant vacuoles, dimeric derivative of gallic acid and it is a principal component of ellagitannins. By esterification of gallic acid and glucose, β-glucogallin (1-*O*-galloyl-β-d-glucopyranose) is formed and by transesterification reaction, di-, tri-, tetra-, and pentagalloylglucose are formed. By the oxidation of galloyl residues, ellagitannins and gallotannins are formed (Mittasch et al. 2014). Canola cultivars (Rainbow and Oscar) seeds were drenched with diverse concentrations of ellagic acid for 6 h and salt stress was imposed on the plants for 4 weeks. Ellagic acid plays important role to overcome the consequence of salinity and enhances the overall growth of the plants (Khan et al. 2017).

Salicylic acid is a phenolic compound and plays an imperative role in plant shield responses to biotic and abiotic elicitors. SA-responsive defensive genes activate defensive responses in plants against pathogen infection, resulting in hypersensitive response in wounded or infected cells (Tripathi et al. 2019). Apart from this, SA also regulates various physicobiochemical processes in plant cell such as carbohydrate and nitrogen metabolism, osmolytes production, antioxidative enzymes which provides help to plant to withstand against abiotic stresses (Sharma et al. 2019a). Plants retain two pathways for the biosynthesis of SA (1) isochorismate pathway and (2) phenylalanine ammonia lyase pathway; both of these pathways derive from chorismate. In *Pseudomonas* species, *PmsC* gene shows similarity with isochorismate synthetase (ICS) enzyme and catalyzes chorismate into isochorismate (Chen et al. 2009). In bacteria, isochorismate pyruvate lyase (IPL) enzyme convert isochorismate to SA. The ICS1 complexes comprises PROHIBITIN (PHB) protein family, with PHB3 the most copious helps in protein complex formation and stabilization. PHB proteins have varied biological roles that comprise interim as scaffolds for. It has been reported that PHB 3 and ICS1 level decreased under UV-C stress conditions (Seguel et al. 2018). In Arabidopsis, PBS3 is a GH3 acyl adenylase-family enzyme catalyze ATP- and Mg^{2+}-dependent conjugation of L-glutamate primarily to the 8-carboxyl of isochorismate and produces SA. At the time of pathogen attack EPS1, a BAHD acyltransferase-family protein accumulate SA in plants (Torrens-Spence et al. 2019). It has been experimental that SA alleviates and regulates multiple signaling pathways like ABA-dependent or independent pathway, mitogen-activated protein kinase pathway, reactive oxygen, and nitrogen species pathways and helps to plant to mitigate the cold stress (Saleem et al. 2020). During pathogen infection or UV stress in Arabidopsis, a small amount of SA is biosynthesized by PAL pathway. PAL genes are diversely present in plant tissue and this PAL enzyme converts aromatic amino acid Phenylalanine into *trans*-cinnamic acid, and depending on plant species, this *trans*-cinnamic acid converts into SA via two possible intermediates: ortho-coumaric acid or BA (Dempsey et al. 2011). In potato and Arabidopsis, inhibitor of PAL enzyme, 2-aminoindan-2-phosphonic acid (AIP) reduced pathogen elicitor persuaded SA accumulation (Chen et al. 2009). Huang et al. (2010) revealed that in Arabidopsis *pal*1 *pal*2 double mutants were lack in anthocyanin pigments in different tissues and susceptible to UV-B stress. The two pal1 pal2 pal3 pal4 quadruple mutants had considerably decreased lignin and SA accumulation after pathogen attack (Huang et al. 2010) (Table 4.1).

4.3.4 Stilbenes

Stilbenes are plant-derived phenolic secondary metabolites, derived from phenylalanine pathway and play a vital role in protection of plant in contradiction of pathogens (Chong et al. 2009). It occurs in a plant kingdom in diverse plant families including grape (Vitaceae), *Shorea ovalis* (Dipterocarpaceae), *Gnetum latifolium* (Gnetaceae), pine (Pinaceae), Carex genus (Cyperaceae), peanut (Fabaceae), and sorghum (Poaceae). Stilbenes have many biological properties such as antimicrobial, repellent cardioprotective, antitumor, neuroprotective, and antioxidative (Pandey and Rizvi 2009). Stilbene backbone is biosynthesized via association of three molecules of acetate with malonyl-CoA and forms CoA-activated phenolic acid catalyzed by stilbene synthase (STS) enzyme; consequently, there is development of a linear tetraketide intermediate (Springob et al. 2006). STS enzyme contains two 40–45 kDa subunits with an iso-electric point (p*I*) of 4.8, relatable to chalcone synthase (CHS) enzyme which is the main crucial enzyme in flavonoid biosynthesis. STS and CHS contain a solitary essential cysteine residue (Cys 164) in the active site (Park et al. 2020). Parage et al. (2012) found that furthermost diversity of the STS

Table 4.1 Phenolic acids and benzoic acid derivatives elicited in plants and their parts by different stresses

S. no.	Phenolic compound	Plant source	Plant part	Stress condition	Biological activity/function	Reference
1.	Ferulic acid	Cucumber (*Cucumis sativus* L.)	Leaf	Dehydration	Reduced lipid peroxidation as a result of antioxidant enzyme activation, as well as an upsurge in proline and soluble sugar content in leaves	Li et al. (2013)
2.	Ferulic acid, sinapic acid, caffeic acid, and *p*-coumaric acid	Foxtail millet	Seed	Drought	Regulate stress during germination	Yu et al. (2020)
3.	Ferulic, *t*-cinnamic, sinapic, and 4-hydroxybenzoic acids	Wheat	Seed	*Fusarium* infection and chemical spray	Synergetic effect increases antioxidant content	Stuper-Szablewska et al. (2019)
4.	Caffeic, chlorogenic acid	Tomato	Leaf	Heavy metal	Inhibit oxidation of organelles and cell membrane	Kısa et al. (2019)
5.	Chlorogenic acid	Tomato	Ripe fruit	*Alternaria alternate* infection	Inhibit colonization of bacteria by halting alternariol biosynthesis	Wojciechowska et al. (2014)
6.	Lignan	Soybean	Leaf	*Phytophthora sojae*	Defense barrier against pathogen invasion	Li et al. (2017a)
7.	Lignin	Cotton	Leaf and plant	*Verticillium dahlia* fungus attack	Enhance expression of GhBOP1-GhTGA3 gene and lignin accumulation	Zhang et al. (2019)
8.	Protocatechuic acid and vanillic acid	Rice	Root and leaves	Growth attributing characters	Vigorous to endorse shoot elongation and endurance and enhance ascorbate peroxidase and superoxide dismutase level	Xuan and Khang (2018)
9.	Rutin and gallic acid	Rice (*Oryza sativa* L.)	Seed	For maximize yield	Regulate antioxidants and alleviate reactive oxygen generation	Singh et al. (2017)
10.	Gallic acid	Soybean	leaves	Cold stress	Enhanced antioxidant activity	Yildiztugay et al. (2017)

(continued)

Table 4.1 (continued)

S. no.	Phenolic compound	Plant source	Plant part	Stress condition	Biological activity/function	Reference
11.	Methyl gallate, flavonoid, and ellagic acid	Strawberry (*Fragaria* × *ananassa* Duch.)	Fruit	ABA and salinity stress	Inhibit free-radical-mediated corrosion of proteins, lipids, and DNA	Jamalian et al. (2013)
12.	Salicylic acid	Tomato	Leaf	Salt stress	Improves photosynthesis, regulation, and balance of osmotic potential and alleviating membrane damage	Mimouni et al. (2016)
13.	Salicylic acid	Rice	Leaf	Small brown plant hopper infestation	Expression of PAL gene induces peroxidase and polyphenol oxidase defensive enzyme in SBPH infestation	Duan et al. (2014)

gene family found in grapevine. When grapevine is infected with *Plasmopara viticola,* nearly 20 different STS genes are expressed. STS is encoded by a multigene family mainly containing the pinosylvin-forming STS genes from pine, resveratrol-forming STS genes from grapevine, and another three novel genes from *Pinus densiflora*. When grapevine leaves bare to downy mildew infection and UV-C acquaintance, thirty-three full-length sequences encoding VvSTS genes were expressed (Jeandet et al. 2021). Huang et al. (2016) found that *VqSTS21* was upregulated in response to powdery mildew infection and confer resistance to osmotic stress in *Arabidopsis*. In several orchid species, bibenzyl stilbenes and their tricyclic derivatives were accumulated at the time of fungal infection. R_2R_3-MYB transcription factor genes (VviMYB14 and VviMYB15) control the stilbene biosynthetic pathway in grapevine (Verma et al. 2017). Microarray and RNA sequencing data revealed that WRKY TFs correlated with STS genes expressed under different stress conditions and developmental stages. In spruce, stilbenes undergo further modified into the plant cell such as *O*-glycosylation, *O*-methylation, oligomerization, and other further modifications to yield astringin and isorhapontin (Metsämuuronen and Sirén 2019). A resveratrol *O*-methyltransferase catalyzes resveratrol methylation to produce pterostilbene both in vitro and in vivo at the time of downy mildew infection. Glycosylation of polyphenolic compounds is a very common modification in plants; addition of carbohydrate changes bioactivity of stilbenes and provides resistance to plant tissues from oxidation and enzymatic degradation. During berry maturation, mesocarp-specific glucosyltransferase expression depicted accumulation of resveratrol glucosides. Oxidative connection of resveratrol or resveratrol derivatives by horseradish peroxidase or laccase-like stilbene oxidases dimers, trimers, and tetramers of stilbenes is produced (Giacomini et al. 2016). During mildew infection or UV irradiation in grapevine leaves, peroxidases are coupled with *trans*-resveratrol oxidation to yield δ-viniferin and ε-viniferin in vacuole of plant cells (Pezet et al. 2004) (Table 4.2).

4.3.5 Flavonoids

Flavonoids are major clutch of plant secondary metabolites with distinct metabolic roles in plants such as ultraviolet-B exposure protectants, inhibit ROS production, attract pollinators for fertilization, signaling molecules under different stresses, and regulate hormonal transport (Panche et al. 2016). More than 9000 flavonoids are recognized in different plant species till now, and they contain 15 C backbone (C6–C3–C6) with two or three benzene rings (ring A, B, and C) (Kumar and Pandey 2013). They are classified into chalcones, flavones, flavanones, flavonols, flavanols, flavanones, isoflavones, anthocyanins, and aurones. Enzymes intricate in the biosynthetic pathway of flavonoids are present in endoplasmic reticulum, vacuole, plastids, and nucleus (Santos et al. 2017).

Table 4.2 Stilbenes in plants exposed with different stresses

S. no.	Stilbene	Source	Amount	Stress/ condition	Reference
1.	Resveratrol	Rice	0.697 μg/g FW in seedlings and 3.053 μg/g DW in seeds	Ultraviolet (UV-C) stress	Zheng et al. (2015)
2.	*t*-Piceatannol and *t*-resveratrol	*Gnetum parvifolium*	1.4 mg/g DW and 4.2 mg/g DW	High temp. and UV exposure	Deng et al. (2017)
3.	*t*-Arachidin	Peanut (*Arachis hypogaea*)	4.3 mg/g DW	*Aspergillus flavus* infection	Sobolev (2008)
4.	*t*-Resveratrol	Grape (*Vitis vinifera*)	11 mg/g DW	Water deficiency	Deluc et al. (2011)
5.	*t*-Viniferin and *t*-pterostilbene	European wild grape	1.2 mg/g FW	UV-C exposure	Duan et al. (2015)

4.3.5.1 Flavanones

Mainly, naringenin, hesperetin, and eriodictyol represent most of the flavanones. Flavanones are the main precursor of other flavonoid, identified by the chiral center at C2 and absence of the C2–C3 bond (Khan and Zill-E-Huma 2014). Flavanones are mainly present in Rutaceae and Lamiaceae family also reveals powerful antioxidant and radical scavenging activity. In utmost of the plants, membrane-bound P450 monooxygenase and cinnamate 4-hydroxylase converts cinnamic acid into *p*-coumaric acid. After that 4-coumaryl: CoA ligase activates *p*-coumaric acid into *p*-coumaroyl-coenzyme A (CoA). In the following step, three malonyl-CoA moieties are attached with one molecule of *p*-coumaroyl-CoA to form chalcone catalyzed by type III polyketide synthase chalcone synthase (CHS) (Wang et al. 2011). This is first committed step for flavonoid biosynthesis and finally chalcones isomerase (CHI) stereospecifically isomerized chalcone into (2S)-flavanones (Naringenin). Naringenin upregulates gene expression of superoxide dismutase, catalases, and glutathione peroxidase, stimulates DNA repair and blocks apoptosis (Kang et al. 2014). Naringenin is converted into eriodictyol by flavonoid 3′-hydroxylase (F3′H), jointly with cytochrome P450 reductase (CPR). Eriodictyol is present in mainly citrus fruits, bitter in taste, and have a very low toxicity. Deng et al. showed that in some plants naringenin is known as a potent in vitro inhibitor of 4-coumarate CoA ligase key enzyme in the monolignol synthesis (Gao et al. 2020).

4.3.5.2 Flavones

Flavones are mainly found in higher plants and show various roles in plant reconcile to stress conditions and antioxidative capacity and act as a signaling molecule for root nodulation during nitrogen fixation by bacteria (Liu and Murray 2016). Flavones have a double bond between C2 and C3, so they are structurally differ from other flavonoids. In plants, flavones are conjugated with conjugated as glycosidic, acetyl, or malonyl moieties. Flavone synthase (FNS) is a crucial enzyme for flavones biosynthesis; this enzyme transforms flavanone to flavones by instigate a double bond between C2 and C3. Zhang et al. (2007) reveled that, in *Petroselinum crispum*, a soluble 2-oxoglutarate-dependent dioxygenase (FNS I) and, in *Antirrhinum majus*, NADPH-dependent cytochrome P450 monooxygenase (FNS II) enzymes catalyze this reaction. Apigenin, tricetin, and luteolin are flavone compounds distributed in many plants which have anti-inflammatory, antioxidative, antiallergenic, and anticancerous properties (Panche et al. 2016).

4.3.5.3 Flavonols

Flavonols are most extensively found flavonoids; these are the 3-hydroxy derivatives of flavanone. Flavonols hinder the formation of reactive oxygen species due to metal-chelating property and regulate cellular redox homeostasis during environmental induced changes in the cell by redox-controlled MYB transcriptor factors (Pollastri and Tattini 2011). Flavonols have a sizeable affinity toward protein and their signaling cascade, so theaters a central role in growth and development of the cell. Flavanone 3-hydroxylase (F3H) catalyzes oxygenation at the 3-position of flavone ((2*S*)-naringenin) to form dihydrokaempferol (Hammerbacher et al. 2019). The dihydroflavonols (dihydrokaempferol) are turned into flavonols (kaempferol) by dioxygenase enzyme flavonol synthase (FLS) which requires 2-oxoglutarate, ferric ion, and ascorbate for its activity (Cheng et al. 2014). After that, flavone 3′--hydroxylase enzyme catalyzes hydroxylation at the 3′-position of either dihydrokaempferol or kaempferol and transforms them to dihydroquercetin or quercetin, respectively. Song et al. (2020) revealed that flavonol biosynthesis is nearly related to phosphorus nutritional status. Under low Pi condition PFG-type MYB gene, *NtMYB12 expression is unregulated. NtMYB12 overexpression increased expression of* flavonol biosynthetic genes (*NtCHS*, *NtCHI*, and *NtFLS*) in transgenic tobacco and also increased bioavailability of P. Xu et al. (2020) found that quercetin and kaempferol were accrued in seedlings of *Apocynum venetum* under salt stress, ensuing in a balanced content and condensed FW. Quercetin and kaempferol protect the plant against various oxidative stresses; in *Nigella arvensis,* content of glaucine, quercetin, and kaempferol was increased against nanoparticles (TiO_2, Al_2O_3, and NiO NPs) exposure. Flavones and flavonols defend oxidative destruction to DNA and proteins and deprivation of the photosystem II against UV-B exposure (Modarresi et al. 2020).

4.3.5.4 Isoflavonoids

Isoflavonoids are mainly legume peculiar to have 3-phenylchromen-4-one backbone involved in rhizosphere microbe interactions or in root nodulation. Isoflavones are mainly present in roots, seedlings, and flowers, being particularly copious in leaves and seeds of plant (García-Calderón et al. 2020). Isoflavones are synthesized from flavanone intermediates (naringenin and liquiritigenin) by 2,3 aryl ring migration from 2-hydroxyisoflavanone (isoflavone synthase, IFS) synthase enzyme. In cytosol, 2-hydroxyisoflavanone is dehydrated or glucosylated or malonylated spontaneously or via 2-hydroxyisoflavanone dehydratase, UDP-glucose: isoflavone 7-*O*-

glucosyltransferase, malonyl-CoA: isoflavone 7-*O*-glucoside 6″-*O*-malonyltransferase, respectively, to form daidzein and genistein and accrued in vacuoles (Akashi 2005). In soybean, R1 MYB transcription factor GmMYB176 modulates isoflavonoid biosynthesis by activating chalcone synthase gene expression. Sprouted soybean restrain mainly genistein, genistin, daidzein, daidzin, glycitein, and glycitin. In leguminous family, CHS gene is more in number may be related to more isoflavonoids in this family (Vadivel et al. 2019). In *Lotus japonicus,* CHS6 (LjCHS1) nonleguminous type of gene is present for isoflavonoid biosynthesis. *L. japonicus* IFS probably has a burly preference or liquiritigenin, as compared to naringenin as a substrate under UV-B stress (García-Calderón et al. 2020). Kisiel and Kępczyńska (2016) found that in the leaves of *Medicago truncatula* constitutive expression of *GmIFS1* solitary effect in ectopic accumulation of the daidzein and more in the levels of the genistein, formononetin, and biochanin A. Coexpression of *GmIFS1* with *GmCHS7* and *GmCHI1A* escalates the isoflavone biosynthesis.

4.3.5.5 Anthocyanins and proanthocyanidins

Anthocyanins are glycosylated flavonoid pigments that are soluble in water and pervasively present in the plant kingdom. Anthocyanins are found in the epidermis of flowers and fruits deliver color to then to fascinate pollinators and kernel dispersers and defense in opposition to various abiotic and biotic stresses (Khoo et al. 2017). Anthocyanins act as antioxidant, defend photosynthetic tissues and metal-chelating agents, act as nutraceuticals, and prevent against cancer and cardiovascular diseases. The color and constancy of these colors are impacted by pH, temperature, light, and structure (Liu et al. 2018). Dihydrokaempferol produced by FLS converted into leucoanthocyanidins by dihydroflavonol 4-reductase enzyme. In the next step, leucoanthocyanidins are transformed into colored anthocyanidins compounds (e.g., cyanidin, pelargonidin, delphinidin) by leucocyanidin oxygenase: LDOX (anthocyanidin synthase). Primary anthocyanidins (pelargonidin, cyanidin, and delphinidin) vary from each other by the numeral of hydroxyl groups at their B-rings. These anthocyanidins further furnished by methyltransferases (OMT) and acetylases and further modified by 3-*O*-glycosyltransferases (UDP-glucose: flavonoid-3-*O*-glycosyltransferase: UFGT) to form anthocyanidin-3-*O*-glucosides compounds which are chemically steady and water-soluble pigments and stored in vacuoles (Li et al. 2017b). By *O*-methylation of cyanidin, peonidin is formed similarly, single or double methylation of delphinidin form petunidin and malvidin, respectively. MYB transcription factors from the R2R3-MYB family regulate anthocyanin biosynthetic pathway in plants (Xie et al. 2020). Zheng et al. (2019) revealed that by posttranslational regulation of the MYB-bHLH-WD40 (MBW) protein complex, HAT1 regulated anthocyanin accumulation. Anthocyanin-enriched transgenic petunia lines (PM2, PM6, and PM8) expressing *RsMYB1* could mitigate low pH stress in plants (Naing et al. 2018). To encounter low temperature stress in the red leaves of *Mikania micrantha,* anthocyanins are accumulation near the plant surface and ameliorate photoprotection by filtration of light or improve antioxidant status in plant (Zhang et al. 2019). Citrus Cs-UGT78D3 gene increased proanthocyanidins and anthocyanin accretion in seed coats and give out to tolerance to plant by light stress with more antioxidant potential in the transgenic Arabidopsis (Rao et al. 2019).

4.3.6 Tannins

Tannins are the polyphenols which bind to protein-NH_2 group and precipitate the proteins so decrease digestibility of protein in gut of the herbivores. It acts as protective shield for plants against pathogen attack and other abiotic stresses. Molecular weight of tannins ranging from 500 to 20,000 Da can be categorized into hydrolysable tannins and condensed tannins (Huang et al. 2017). Hydrolyzable tannins (gallo- or ellagitannins) are mainly polygalloyl esters of glucose, and condensed tannins (proanthocyanidins) contain polymerized flavanol units are produced through the shikimate pathway. Hydrolyzable tannins are biosynthesized by gallic acid and UDP-glucose, these two compounds are esterified by UDP-glucosyltransferase, and β-glucogallin (1-*O*-galloyl-β-D-glucose) is molded, β-glucogallin has a twin role, and it functions as an acyl acceptor and donar. Di- and trigalloylglucoses are formed by succeeding transformation of β-glucogallin (Smeriglio et al. 2016). After that, multiple acyl-CoA thioesterases convert β-glucogallin to pentagalloylglucose, and further by addition of galloyl residues, simple gallotannins (1,2,3,4,6-pentagalloylglucose) are formed. Laccase-like phenol oxidase stereospecifically oxidized pentagalloylglucose to the monomeric or dimeric ellagitannin, tellimagrandin II. After the infection of *Colletotrichum acutatum* in leaves of the strawberry, penta-esterified ellagitannin is accumulated and shows oxidative burst, callose deposition, and a transient upsurge of salicylic acid in phloem (Mamaní et al. 2012).

Condensed tannins (proanthocyanidins) are oligomeric compounds and most ever-present group of all phenolics. Maximum proanthocyanidins are derivative of flavan-3-ols (+)-catechin and (−)-epicatechin. Monomeric leucoanthocyanidins produced anthocyanidin by cleavage of a C–O bond under heating conditions. Leucoanthocyanidin reductase (LAR) separates C4 hydroxyl group from (+)3, 4-cis-leucocyanidin and converts it into catechin; similarly, anthocyanidin is converted into epicatechin by anthocyanidin reductase. VvMYBPA1 and VvMYBPA2 are MYB transcription factors, mainly expressed during seed development stage and regulate biosynthesis of proanthocyanidins by overexpression of ANR and LAR enzyme in grapevine root (Bogs 2005). Proanthocyanidins have a mineral binding property; sometimes convey negative traits for bioavailability of iron and zinc micronutrients. Proanthocyanidins deposited in endothelial layer of the seed coat and act as barrier for fungal or other pathogen outbreak (Bohn et al. 2008). Houde et al. (2006) revealed that grapeseed proanthocyanidin extract powerfully declined NO and ROS invention and inducible nitric oxide synthase by murine macrophages enthused with lipopolysaccharides. In Arabidopsis plant, citrus Cs-UGT78D3 gene helps to overexpress proanthocyanidins buildup in seed coats and provides tolerance to high light stress with better antioxidant potential (Rao et al. 2019) (Table 4.3).

Table 4.3 Flavonoids and anthocyanin in plants with response to different stresses

S. no.	Phenolic compound	Plant source	Plant part	Stress condition	Biological activity/function	Reference
1.	Kaempferol, quercetin-3-rutinoside (rutin), and dihydrokaempferol	Tomato	Plant	Salinity and heat	Act as antioxidant molecules	Martinez et al. (2016)
2.	Flavonols	Arabidopsis	Plant	Oxidative and drought	Mitigated the accretion of ROS	Nakabayashi et al. (2014)
3.	Quercetin 3-methyl ether and its glycosides	*Arabidopsis thaliana* and *Neurospora crassa*	Seed	Allelopathy	Inhibit conidial germination	Parvez et al. (2004)
4.	Naringenin	*Phaseolus vulgaris*	Leaf	Osmotic and Salinity Stress	Regulate photosynthetic machinery and increase chloroplastic antioxidant metabolism	Yildiztugay et al. (2020)
5.	Daidzein or genistein	*Lotus japonicus*	Plant	Drought and UV-B exposure	Act as defensive compounds (phytoalexins) and as biochemical signals in symbiotic nitrogen fixation with rhizobia	García-Calderón et al. (2020)
6.	Daidzein and glycitein	Soybean	Seeds	Water deficit	Enhanced expression of *PAL*, *CHS7*, *CHS8*, and *IFS2* temporally concurred with the onset of embryonic isoflavonoid accumulation	Gutierrez-Gonzalez et al. (2010)
7.	Anthocyanin	Purple wheat	Grains	Drought, temperature, light, salinity	Increase of the photosynthetic carbon assimilation	Li et al. (2018)
8.	Anthocyanin	*Arabidopsis thaliana*	Plant	Nitrogen deficiency	Activation of dihydroflavonol 4-reductase (DFR) and plant adapt to low N stress	Liang and He (2018)

9.	Proanthocyanidin	*Cucumber*	Seedling	Salt stress	Improved stress-induced oxidative injury in plant cells and augmented the activity of alternative oxidase	Zhu et al. (2017)
10.	Catechin and epicatechin	*Poplar*	Leaves	Rust infection	Overexpress the MYB134 transcription factor and provide resilient to rust contagion	Ullah et al. (2017)

4.4 Conclusion

By understanding the biosynthetic mechanisms of phenols and their derivatives, it is easy to identify the mechanism behind the stress resistance in plants and we can produce high-yielding and stress-resistant variety by transgenic or any novel approach. Shikimic acid pathway can be considered as the basic skeleton of phenol biosynthesis, and in which by some modification, other phenolic compounds are formed. During adverse environmental conditions, phenolic compound converts the substrate of primary metabolism to secondary product and maintains cellular homeostasis. It is necessary to continuing the research on phenol biosynthesis and its stress mechanism under biotic and abiotic stresses. In microorganisms, some novel PAL biosynthetic route had been came into light for phenylpropanoid production with nutraceutical properties. Definitely, it will be helpful to agriculture sector for better crop productivity and also beneficial to pharmaceuticals and food industries for better health.

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5 Antioxidant Phenolics from Vegetable By-Products

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Abstract

The increasing demand for healthy products has also increased the demand and consumption of fruits and vegetables whose supply chain generates by-products. For instance, 15–30% of fruits and vegetables processing is discarded as waste, such as: seeds, stalks, outer layers, stems, and pomace, obtained from different stages of the processing. In many cases, this waste is left on the farm and burnt which generates a problem for the environment. Also, the disposal of these by-products has a negative economic impact. Nonetheless, seeds, stalks, outer layers, stems, and pomace are valuable sources of phytochemicals with biological activity, such as fiber, proteins, and phenolic compounds. Phenolic compounds are mainly accumulated in the outer layers of the plant tissues; therefore, most food by-products are more abundant in bioactive compounds than the comestible parts. Many efforts on the identification and bioactive evaluation of by-products from vegetable sources have been made. This chapter reviews the latest studies regarding the potential bioactive effect of vegetable by-products on human health and the characterization of their antioxidant compounds.

5.1 Introduction

The global food waste increases every year because of the rise in the population and the consumer's awareness and importance of a more nutritious diet, preferring foods rich in bioactive compounds mainly from plants. The Food and Agriculture Organization (FAO) estimates that one-third of the food produced for human consumption

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is discarded as waste, and fruit and vegetables are the most significant contributors of that amount (FAO 2013). Moreover, food losses are derived from the food chain supply, such as agricultural production, processing, and packaging, which are the main contributors for fruit and vegetables waste generation (FAO 2011).

On the other hand, vegetable wastes are a valuable source of bioactive compounds, such as fiber, proteins, oligosaccharides, along with antioxidant phenolic compounds. Phenolic compound accumulates mainly in the peripheral parts of the plants, where they can exert, they function as protective agents from biotic and abiotic stress. Therefore, agricultural by-products from vegetables such as peel, hull, pomace, outer skin, leaves, and stems are great sources of phenolic compounds (Maietta et al. 2017), providing opportunity to re-valorize the vegetable by-products and handle the problem of waste disposal in addition to the demand for bioactive compounds.

Phenolic compounds have notorious physiological properties, like: antioxidant, anti-inflammatory, and antiproliferative (Zhang and Tsao 2016). The attraction of the scientific community in identifying and assessing the potential health benefits of phenolic compounds from vegetable by-products has been increasing. Phenolic compounds from vegetable by-products can be isolated or used as a whole extract and can be useful for pharmaceutical, food, animal, and cosmetic industries (Figueiredo-González et al. 2016).

This chapter explores the recent studies regarding the antioxidant compounds and identification of vegetable by-products (for example, leaves, seeds, and pomace), and the evaluation of their bioactive potential.

5.2 Vegetable By-Products: Production

In 2018, 1088.8 million metric tons (MMT) of vegetables were produced in the world. The most produced vegetables include 182.3 MMT of tomatoes, 96.8 MMT of onions, 75.2 MMT of cucumbers and gherkins, 69.4 MMT of cabbages and other brassicas, and 54.1 MMT of eggplants. The main vegetable producers are China with 549 MMT, India with 128.2 MMT, United States of America with 31.77 MMT, and Turkey with 24.1 MMT (FAOSTAT 2018). On the other hand, around 1.3 billion tons of food wastes are produced annually. These wastes include meat, cereal, fish, root and tubers, oil crops and pulses, and fruits and vegetables along with the food supply chain. Fruit and vegetables are the greatest contributors to these wastes. The FAO has estimated that most fruit and vegetable losses are higher from postharvest and distribution stages due to the ripening or deterioration of the crops. Also, the waste of fruit and vegetables in industrialized areas is higher due to their quality standards (Table 5.1) (FAO 2011).

Table 5.1 Estimated waste (%) of fruits and vegetables in each step of the world's food chain supply in the world

	Area						
Part of the food supply chain	Latin America (%)	South and Southeast Asia (%)	North Africa, West, and Central Asia (%)	Sub-Saharan Africa (%)	Industrialized Asia (%)	North America and Oceania (%)	Europe (%)
Agricultural production	20	15	17	10	10	20	20
Postharvest handling and storage	10	9	10	9	8	4	5
Processing and packaging	20	25	20	25	2	2	2
Distribution	12	10	15	17	8	12	10
Consumption	10	7	12	5	15	28	19

FAO (2011)

5.3 Antioxidants from Vegetable By-Products

Phenolic compounds are secondary metabolites distributed in all plant tissues. They act as protective agents from biotic and abiotic stress such as UV, dough, and pathogen attack. Phenolics also contribute to the organoleptic properties of vegetable foods like aroma, color, and flavor and essential for a balanced diet. The average consumption is 1 g/day (Cory et al. 2018). The phenolic compound's structures are diverse. They are distinguished by bearing at least a minimum one benzene ring with one or more –OH attached. They can be classified in phenolic acids, flavonoids, stilbenes, lignans, and others (Grosso et al. 2014). Phenolic acids are the simplest of phenolics. They are divided into hydroxycinnamic and hydroxybenzoic acids. Examples of phenolic acids present in vegetable by-products are caffeic and gallic acid. Flavonoids are the most common group of phenolics found in vegetable by-products. They can be further categorized in flavanones, flavones, anthocyanins, and flavonols. Stilbenes are less common phenolics; they have a core of 1,2-diphenylethene, and a common stilbene found in vegetable by-products is resveratrol (Manach et al. 2004).

On the contrary, carotenoids are the most studied group of terpenes. They are tetraterpene pigments present in yellow, orange, and red vegetables. Carotenoids are classified in hydrocarbon carotenoids (carotenes) and xanthophylls (Merhan 2017). The most common xanthophyll present in vegetable wastes is lutein, and β-carotene is an example of carotene. Some of the structures of antioxidant compounds found in vegetable sources are indicated in Table 5.2.

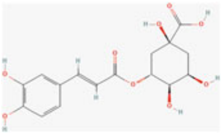
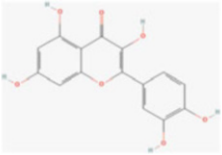
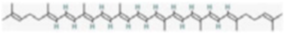
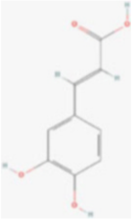
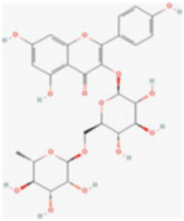
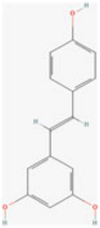
5.3.1 Vegetable By-Products

5.3.1.1 Tomato

Along the food supply chain, many vegetable by-products are produced. As an example, 20% of tomato by-products are generated from tomato processing into juice, ketchup, and paste (Andreou et al. 2020). Some of the by-products are tomato core, skin, pomace, and seeds. Tomato skin or peel is a valuable source of many bioactive compounds, and the most abundant is the carotenoid lycopene. This carotenoid is a well-known bioactive compound with many benefits for human health, such as anti-inflammatory and antioxidant potential (Caseiro et al. 2020). Tomato skin contains 7.23 g/kg of lycopene, and this by-product contains approximately 14-fold higher concentration of lycopene than the rest of the tomato tissues. Therefore, the importance of re-valorize tomato by-products is important (Martínez-Hernández et al. 2019). Conversely, owing to the nature of lycopene, it has to be encapsulated. Therefore, some studies have analyzed the optimization of lycopene encapsulation from tomato by-products (Gheonea et al. 2021).

Although tomato skin is rich in lycopene, other bioactive compounds can be obtained from this by-product, such as phenolic acids, carotenoids, and pectin. Besides, tomato leaf contains alkaloids, carotenoids, and phenolic compounds (Figueiredo-González et al. 2016). Likewise, tomato seeds have been reported for

Table 5.2 Chemical structure of the main antioxidant compounds in vegetable by-products

Compound	Structure
Chlorogenic acid	
Quercetin	
Lycopene	
Caffeic acid	
Kaempferol-3-*O*-rutinoside	
Resveratrol	

National Center for Biotechnology Information (2020)

containing condensed tannins (3.4 mg CE/g), total flavonoids 4.7 mg CE/g, and soluble phenols 1.0 mg GAE/g (Durante et al. 2017). Similarly, Di Donato et al. (2017) reported the recovery kaempferol rutinoside from the peel, seed, leaves, rotten, and unripe tomato wastes (Di Donato et al. 2017).

Furthermore, some bioactivities have been assessed in tomato by-products. For instance, the hydroalcoholic extract from tomato leaves has shown inhibitory activities against cholinesterase, lipoxygenase, α-glucosidase, and α-amylase (Figueiredo-González et al. 2016; Gheonea et al. 2021). Also, a lycopene-rich extract from tomato peel (100 μg/mL) has shown to protect rat skeletal muscle cells, L6 myoblast from oxidative damage significantly (Reshmitha et al. 2017).

Another study evaluated the application of tomato by-products as antibrowning agents, due to its antioxidant potential. Finally, the tomato by-products could be used as food colorants, functional ingredients, and natural antioxidants (Martínez-Hernández et al. 2019).

5.3.1.2 Onion

Onion (*Allium cepa*) is also a highly produced vegetable; it is the second most produced vegetable in the world. Onion bulbs are the edible part of this plant, and the nature of bulbs requires the discard of the outer layers of the skin. Therefore, the major by-products are the dried skin, the outer two fleshy leaves, the upper and lower bulbs, and bulbs that do not meet the quality standards. Around 0.5 million tons of solid onion by-products are produced per annum in Europe, mainly in Spain, the United Kingdom, and the Netherlands (Santiago et al. 2019). The by-products of onions are rich in protocatechuic acid and cyanidin-3-*O*-glucoside (Abouzed et al. 2018). Also, the concentration of quercetin, an abundant flavonoid of onion skin, is 32-fold higher than the onion's inner tissues (Munir et al. 2018). Some authors have studied the bioactivity of onion by-products. For instance, onion scale (150 and 300 mg/kg) reduced blood glucose levels in diabetic rats (Abouzed et al. 2018).

5.3.1.3 Brassicas

Broccoli by-products are particularly abundant in glucosinolates, but these by-products also contain phenolic acids, β-carotene, lutein, neoxanthin and violaxanthin, luteoxanthin, and lutein-like structures (Thomas et al. 2018). The by-products from Brassicas are derived from rejected seeds due to overripe or poor quality, low yield, poor germination rate, low grain quality and size, and yellow grains (Thomas et al. 2018). Also, stalks, leaves, and inflorescence from the broccoli frozen-food industry are generated, and accounting for 45% of the initial broccoli heads (Ferreira et al. 2020). Aires et al. (2017) reported neochlorogenic acid and chlorogenic acid, 124.7 ± 3.2 μg/g dry weight and 128.0 ± 0.5 μg/g dry weight from leaves and stems, respectively.

Cauliflower (*Brassica oleracea* var. *botrytis*) is the principal Brassicaceae crops. Around 36% of by-products, such as leaves and stems, are discarded at various stages of production chain (Amofa-Diatuo et al. 2017).

5.3.1.4 Eggplants

The peel of eggplant is one of the by-products in the food industry and has important phytochemicals with antioxidant activity such as anthocyanins. Also, microencapsulated anthocyanins from eggplant peel extract have been added as a food ingredient in gummy candies. This by-product was shown to enhance nutritional quality and antioxidant activity (Sarabandi et al. 2019). Furthermore, delphinidin-3-rutinoside is the main anthocyanin in eggplant peel extract (Ferarsa et al. 2018).

5.3.1.5 Carrots and Turnips

World production of carrots and turnip is around 40 MMT (FAOSTAT 2018). The by-products from carrots are pomace and peels, mainly generated from juice production, where 11% of the initial mass is lost (de Andrade Lima et al. 2018). Black carrot pomace (*Daucus carota* ssp. *sativus* var. *atrorubens* Alef.) has an important amount of anthocyanins. This by-product has been used as a food colorant and food additives, for instance, black carrot pomace (0–150 g/kg) was added to improve the nutritional quality of cakes. Although black carrot pomace showed good nutritional content, more sensory studies are needed (Kamiloglu et al. 2017).

In another study, the methanolic extract from *Daucus carota* L. leaves contains 11 phenolic compounds, and chlorogenic acid (458.79 mg/L) is present in the highest concentration (Eugenio et al. 2016). In contrast, carrot seed contains rutin and *p*-coumaric acid (Pavlyuk et al. 2015).

5.3.1.6 Artichokes

The edible parts of artichokes are the immature inflorescence or head, representing 15–20% of the plant. Artichokes can be consumed fresh, frozen, or processed in canned food. Processing and packaging of artichokes generate by-products constituting 80–85% of the total fresh weight of the plant and are composed of leaves, stalks, roots, receptacles, external bracts, and stems (Colantuono et al. 2018; Cassano et al. 2016). The main studied by-products from artichoke are leaves and stems, which contain phenolic compounds, flavonoids, fiber, inositol, and the sesquiterpenes lactones, being particularly rich in mono- and di-caffeoylquinic acids and flavones. Also, roots are being studied, and they are rich in inulin (Maietta et al. 2017). Chlorogenic acid is the most abundant phenolic in the leaves of globe artichokes (Stumpf et al. 2020). Also, artichoke receptacles are the richest by-product in caffeoylquinic acids and the most bioactive compared to leaves and stem (Mena-García et al. 2020).

Some researchers have evaluated the bioactive potential of the phenolic compounds from the artichoke. For instance, the addition of artichoke stem powder (3%, 6%, and 9%) in the formulation of bread, enhanced its nutritional content and showed a potential modulation of glucose metabolism through the inhibition of α-glucosidase activity (Colantuono et al. 2018).

5.3.1.7 Other Vegetables

Lentils (*Lens culinaris*) are one of the largest consumed pulses. Lentil hulls are a by-product of the de-hulling and splitting of lentils. Lentil hulls contain phenolic and condensed tannins (1.4–20.1 mg GAE/g DW and 0.2–16.1 mg CAE/g DW) (Sun et al. 2020).

Garlic (*Allium sativum*) is used as a spice and natural medicine. Another highly produced vegetable, with 28.5 MMT worldwide in 2018, is Garlic husk. “The garlic husk, which contributes 25% of garlic bulk, was regarded as agricultural waste” (Chhouk et al. 2017). Garlic by-products have shown high antioxidant activity (Jang et al. 2018).

Potato (*Solanum tuberosum* L.) is the most produced tuber globally with 365.17 MMT (FAOSTAT 2018). The processing of potato generates significant by-products, including potato peels and the outer layers of flesh. Potato peel represents 15% of waste (Gupta and Joshi 2000). Potatoes by-products contain phenolic compounds. Hsieh et al. (2016) studied the effect of a potato peel extract (1–3%) on the toxicity of cholesterol oxidation products in rats. The results showed a rise in active glutathione and Trolox equivalent antioxidant capacity levels, superoxide dismutase, catalase, and glutathione peroxidase activities. In addition, the levels of aspartate aminotransferase, alanine aminotransferase, alkaline phosphatase, blood urea nitrogen, creatinine, and cholesterol oxidation products were observed.

Spinach is a highly consumed vegetable worldwide, and its production leads to 25% of waste. Spinach by-products are rich in phenolic acids, lutein, chlorophyll, carotenoids, and contain high levels of vitamins (A, B9, and K), minerals (Fe, Mg, Mn) (Derrien et al. 2017). Also, lutein has been found in tomato, carrot, cabbage, and lettuce discards (Alzate et al. 2017).

Melon (*Cucumis melo* L.) peels, besides dietary fiber, is especially abundant in phenolic compounds and flavonoids (332.15 mg/100 g extract and 95.46 mg/100 g extract, respectively), particularly in phenolic acids, flavones, and secoiridoids (Mallek-Ayadi et al. 2017). Also, the melon peel is a great source of carbohydrates, proteins, calcium, and potassium. The main compounds are 3-hydroxybenzoic acid, apigenin-7-glycoside.

Root by-products are also sources of bioactive compounds. Asparagus roots are rich in caffeic acid. These by-products are usually discarded or burned on the farm (Zhang et al. 2019). In the case of beetroot (*Beta vulgaris* L.), it possesses phytochemical compounds that includes ascorbic acid, carotenoids, phenolic acids, and flavonoids. Beetroot ingestion offers beneficial physiological effects as co-adjuvant for several pathologies, such as type 2 diabetes, hypertension, dementia, and atherosclerosis (Clifford et al. 2015). Beetroot aerial parts are commonly cut off and discard, and the only part used is the bulb of the plant (Biondo et al. 2014), but nowadays, recent studies show the high functional value of these parts of the beetroot. The main phenolic compound in leaves was ferulic acid with 42.9%, and 57.6% resveratrol was found in stems (Battistella Lasta et al. 2019).

In Tables 5.3 and 5.4, the phenolic compounds identified in the different vegetable by-products and their bioactivities assessed, and the applications of by-products are summarized.

5.4 Conclusions

The by-products from vegetables are sources of natural antioxidants that can replace the synthetic antioxidant additives used in food products. They can also be functional ingredients, natural colorants, animal feed, and the isolation of bioactive compounds. For instance, vegetable by-products have been assessed for their antidiabetic, neuroprotective, and antioxidant properties. Nonetheless, there is a need for more studies. Phytochemicals like phenolic compounds from plant

Table 5.3 Phenolic compounds and biological activity from vegetable by-products

By-product	Bioactive/phenolic compounds (HPLC)	Biological activity	Authors
Potato peel	Chlorogenic acid Caffeic acid Isochlorogenic acid, glycoalkaloids, gallic acid, sinapic acid, vanillic acid, syringic acid, protocatechuic acid, *p*-coumaric acid, ferulic acid, ellagic acid, salicylic acid, gentisic acid, apigenin, quercetin, hesperidin, naringin, myricetin, pueranin, catechin, rutin, fisetin, 3-caffeoyl-4-feruloylquinic acid, tricaffeoylquinic acid isomer, 3,4-di-*O*-caffeoylquinic acid	Antioxidant	Friedman et al. (2017), Zhu et al. (2016), Fradinho et al. (2020), Hsieh et al. (2016), Alves Filho et al. (2020), Riciputi et al. (2018)
Potato wastes	Chlorogenic acid, 5-caffeoylquinic acid (neochlorogenic acid), 3,4-di-*O*-caffeoylquinic (isochlorogenic) acid, and caffeic acid	Antioxidant	Choi et al. (2016)
Tomato skin Tomato waste (seed and skin/peel)	Lycopene	Antioxidant	Martínez-Hernández et al. (2019), Andreou et al. (2020), Ninčević Grassino et al. (2020), Catalkaya and Kahveci (2019), Kehili et al. (2019), Coelho et al. (2019), Jurić et al. (2019), Pinela et al. (2017), Alzate et al. (2017)
Tomato skin	Lycopene	Antidiabetic	Gheonea et al. (2021)
Tomato pomace (mix of skin and seeds)	Lycopene		Amiri-Rigi and Abbasi (2019), Silva et al. (2018)
Tomato seeds and skin	Lutein, lycopene, β-carotene, caffeic acid-glucoside isomer, chlorogenic acid, quercetin glucosides, naringenin	Antimicrobial	Szabo et al. (2018)
Tomato leaves	Caffeic acid, kaempferol rutinoside	Neuroprotective and antidiabetic	Figueiredo-González et al. (2016), Aires et al.

(continued)

Table 5.3 (continued)

By-product	Bioactive/phenolic compounds (HPLC)	Biological activity	Authors
			(2017), Di Donato et al. (2017)
Tomato leaves		Antioxidant	Arab et al. (2019)
Onion skin	Glycosylated derivatives of quercetin and oxidized products, protocatechuic acid, quercetin, isorhamnetin, and keampferol	Antioxidant	Milea et al. (2019), Campone et al. (2018), Kim et al. (2019)
Onion scales	Hydoxybenzoic acids, anthocyanins, flavonols, quercetin derivatives	Antidiabetic, anti-inflammatory, antiglycation	Abouzed et al. (2018)
Onion wastes (edible outer dry layers and the apical trimmings)	Quercetin-4′-*O*-monoglucoside, quercetin-3,4′-*O*-diglucoside, quercetin, and isorhamnetin-3-glucoside	Antioxidant and antigout	Nile et al. (2017)
Onion skin	Quercetin	Antioxidant	Munir et al. (2018), Campone et al. (2018), Piechowiak et al. (2020)
Red cabbage waste	Anthocyanins	Antioxidant	Patras (2019)
Broccoli stalk and florets, and seeds	Kaempherol-3-*O*-sophoroside, quercetin-3-diglucoside-7-glucoside, caffeoyl quinic acid, sinapic acid	Antioxidant	Thomas et al. (2018), Drabińska et al. (2018)
Broccoli leaves	Neochlorogenic and chlorogenic acid	–	Aires et al. (2017)
Stalks, leaves, and inflorescence from broccoli	β-Carotene, lutein, neoxanthin and violaxanthin, luteoxanthin- and lutein-like structures	–	Ferreira et al. (2020)
Cauliflower (*Brassica oleracea* L. var. *botrytis*) by-product		Antimicrobial	Sanz-Puig et al. (2017)
Eggplant peel and pulp	Malvidin-3-rutinoside-5-glucoside, delphinidin-3-rutinoside, delphinidin-3-rutinoside-5-glucoside, petunidin-3-rutinoside, cyanidin-3-rutinoside	Antioxidant	Ferarsa et al. (2018), Sarabandi et al. (2019), Dranca and Oroian (2016), Kazemi et al. (2019)

(continued)

Table 5.3 (continued)

By-product	Bioactive/phenolic compounds (HPLC)	Biological activity	Authors
Black carrot pomace	Cyanidin-based with different sugar moieties, chlorogenic acid, ferulic acid, and caffeic acid	–	Kamiloglu et al. (2017)
Carrot waste	β-Carotene, lutein, chlorogenic acid, rutin, and *p*-coumaric acid	Antioxidant	Alzate et al. (2017), Eugenio et al. (2016), Pavlyuk et al. (2015)
Carrot peel	Carotenoids		de Andrade Lima et al. (2018)
Leaves and stems of *Brassica rapa* L. (turnip) and *Raphanus sativus* L. (radish)	Phenolic acids and flavonoids	Antioxidant	Chihoub et al. (2019)
Artichoke stalks, leaves, receptacles, external bracts, and brines	Caffeoylquinic acids, cynarine	Antioxidant	Mena-García et al. (2020), Stumpf et al. (2020), Cassano et al. (2016), Noriega et al. (2018), Colantuono et al. (2018)
Artichoke external bracts and stem	Mono- and di-caffeic acid derivatives, and apigenin-7-*O*-glucuronide	Antiglycative	Maietta et al. (2017)
Garlic husk	Caffeic acid, *p*-coumaric acid, and trans-ferulic acid, gallic acid, 4-hydrobenzoic acid	Antioxidant	Chhouk et al. (2017)
Garlic by-products	–	Antioxidant Antimicrobial	Jang et al. (2018)
Lentil hull	Condensed tannins, phenolic acids, flavan-3-ol, and carotenoids	Antioxidant	Sun et al. (2020)
Spinach discards	Lutein	–	Derrien et al. (2017, 2019)
Melon peels	Hydroxybenzoic acids and flavones	–	Mallek-Ayadi et al. (2017)
Asparagus roots	Caffeic acid	Antioxidant	Zhang et al. (2019)
Beetroot	Ferulic acid and resveratrol	Antioxidant	Battistella Lasta et al. (2019)

by-products must be encapsulated; therefore, studies regarding the optimization of encapsulation of these bioactive compounds must be performed. In addition, further information about sensory characteristics and other related quality parameters are necessary for the application as food additives. Also, there is a call for studies

Table 5.4 Applications of by-products from plant wastes

By-product	Application	Author
Tomato skin	Anti-browning agent	Martínez-Hernández et al. (2019)
Tomato leaves	Neuroprotective and antidiabetic agent	Figueiredo-González et al. (2016)
Onion waste	Food industry, improve the nutritional attributes of bread	Bedrníček et al. (2020)
Artichoke by-products	Food ingredient	Colantuono et al. (2018)

regarding the potential benefit of these by-products on human well-being, and the profitability of the extraction of bioactive compounds for further applications. Nonetheless, many studies support that the exploitation of by-products from plants, suggesting these can be an excellent solution to address the food loss problem around the world.

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Plant Phenolics: A Dynamic Compound Family Under Unfavorable Environment and Multiple Abiotic Stresses

6

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Abstract

Expeditious progress in human population and extravagant usage of natural resources for human development give rise to unfavorable environment for agricultural practices. Additionally, extreme climatic events with combine or multiple abiotic stresses at their crucial growth stages cause massive loss in food production worldwide. To diminish the catastrophic loss, agriculture scientist engaged in the findings of new approaches and achieved some breakthrough in last decades. Among the main findings, application of plant growth regulators, osmoprotectants, and some inorganic and organic chemicals showed the excellent results. It is shown that, phenolic compounds (PCs) in plants have immense role in the growth and defense machineries of a plant and making it capable of withstanding multiple stressors. In summary, PCs have capacity to improve plant performance by synthesis of pigments, secondary metabolites, structural integrity, antioxidants, defense, biochemical, and molecular equilibrium under unfavorable conditions. As described earlier the problems, this analysis compile the impacts of environmental variables on PCs. As well as in this study, we investigate the in-depth role and tolerance mechanism by PCs under these circumstances.

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Keywords

Phenolics · Abiotic stress · Climate · Osmoprotectants · Plant growth regulators

6.1 Introduction

Phenolic compounds (PCs) are extensive categories of secondary metabolites (SMs) produced in the phenylpropanoid and phenylpropanoid acetate derivative (shikimic acid pathway), showing the huge diversity in structure and functions in plants. Phenolic compounds comprised of benzene structures holding one to several OH groups and play vital roles in biotic and abiotic stress tolerance. They also serve crucial function in the growth of a plant, more notably in biosynthesis of lignin and other pigments (Tyagi et al. 2020). Moreover, the structural stability and basic framework support are provided through maintaining the conductive tissues in plants (Tsimogiannis and Oreopoulou 2019). Secondary metabolism produces a number of compounds that do not aid directly in the growth of the organism but are crucial to withstand in a particular environment. The impact of climate change and multiple abiotic stresses are well established and supposed to significantly affect the plant optimum growth by modulating physiological, biochemical, and molecular functions (Koyro et al. 2012; Singhal et al. 2017a, b; Sabagh et al. 2020; Dey et al. 2022). Therefore, the finding of new compounds is imperative to improve yield potential under these situations.

Recently significant progress has been made with the PCs and immense role under multiple abiotic stressors and unfavorable environmental conditions such as heat, drought, salt, heavy metal, UV light, and elevated CO_2 are explored (Sharma et al. 2019; Tak and Kumar 2020; Kumar et al. 2020b; Wagay et al. 2020). The environment variables have drastic effects on the production and synthesis of different PCs in plant. Under these circumstances, the gradient between ROS (reactive oxygen species) generation and scavenge gets disturbed, that causes the accumulation of ROS and damages the cell's building components like nucleic acid, protein, carbohydrate, and lipid membranes, which eventually responsible for disturbing the cell equilibrium or cell death or complete loss of functions (Kristensen et al. 2004). The accumulation of these compound is elevated during single or multiple stress situation, and triggers defensive mechanism in plants to cope with stress conditions like pathogen, herbivory; and abiotic stress like UV or light irradiation, drought, heat, cold, salinity, and others (Wu et al. 2013; Bautista et al. 2016). The biosynthesis of these protective compounds during stress conditions is related to increase in partitioning of carbon that involves in repair mechanism and biosynthesis of these compounds (Singh et al. 2010). To considering the relevance's of PCs in multiple abiotic stresses, this chapter emphasizes on the emerging functions of PCs, impact of environmental stressors on the synthesis and production of PCs, and mechanism involved in mitigation of these stresses.

6.2 Role of Phenolic Compounds in Plants

Phenolic compounds like *p*-hydroxybenzoic aldehyde, hydroxycinnamic acid, *p*-coumaric acid, *p*-vanillic aldehyde, etc. have been detected in germinated legumes (beans, pea, and lentils), and find that they are originated from seed lignin and as seed cell wall constituents via enzymes oxidations such as esterase activity (López-Amorós et al. 2006). Cytological localization of PCs in dormant seeds of *B. napus* showed that these compounds present in apoplastic compartment of the columella and during active germination, they move toward nucleus, endoplasmic reticulum (ER), protein bodies, and epidermis of root cap and associated with restoration of ER and synthesis of primary roots (Kuras et al. 1999). Further, reports suggested that cell wall contains a number of nonextractable PCs, and breakdowns during seed germination into soluble-free phenols to scavenge-free ROS. Therefore, PCs improve antioxidant property, cell division, bound to enzyme moieties for modification of protein and lipids, and generate signal and defense compounds, which are extremely important during seed germination process (Xu et al. 2020). Consequently, the PCs help in germination improvement under stressed situations by synthesis of growth inhibitors in outer layer of seed and block the premature germination. The interaction between plants and biotic or abiotic elicitors (UV-irradiation, freezing, elicitors (fungi, bacteria, viruses, nematodes) heating, wounding, chemicals) often results into the production of phytoalexins (Televičiūtė et al. 2020; Kumar et al. 2020a).

It has been well reported fact that PCs and flavonoids are the excellent antioxidants and more effective than previously known antioxidants like vitamin C, E, and carotenoids. Luteolin is one of the phenolic compounds considered as antioxidant and has free-radical scavenging activities and anti-inflammatory properties. The flavonoid flavor can attract attractant or repellent to pollinators or pests. Anthocyanins provide the color to flowers, fruits, and petals. Phenolic compounds have crucial roles in defense against biotic agents and fungi such as phototoxicity of certain coumarins called furanocoumarins. These compounds are not lethal until they are triggered by light. Flavones and flavonols safeguard cells against UV-B radiation of 280–320 nm wavelength because they accumulate in the upper layers of leaves and promote the photosynthesis.

Additionally, under excess UV-B light, synthesis of flavones and flavonols has been increased. Likewise, simple phenylpropanoid esters also play an important role in UV protection in Arabidopsis. Ultraviolet A (UV-A) region with a wavelength of 320–400 nm of sun light causes the activation of furanocoumarins, these furanocoumarins integrate into the DNA double helix and disrupt the DNA base pairs cytosine and thymine, thus blocking the transcription and repair machinery (Verdaguer et al. 2017; Corso et al. 2020).

Lignin is found in the cell walls of tracheids and vessel elements of the xylem and also deposited on the thickened secondary wall in association with cellulose and hemicellulose. The mechanical stiffness of lignin reinforces the stems and vascular tissue, enabling upward growth and allow water and minerals to be directed through the xylem under larger negative pressure without fade out of tissues. Moreover, it has considerable protective functions in plants by supporting lodging resistance. Its physical rigidity impedes feeding by animals, and its chemical endurance makes them quite distasteful to herbivores. Lignification blocks the developments of pathogens and is a habitual response to infection or wounding. Further, it can defend the seeds from unfavorable environmental circumstance, and improve seedling establishments in woody species (Liu et al. 2018). The synthesis of PCs is catalyzed by the activity of PAL with cinnamic-4-hydroxylase enzyme. PAL is a key enzyme in secondary metabolism (SM) pathways (phenylpropanoid pathway). Phenolic compound also performed as allelochemical, which has potential to inhibit the growth of competitor plants (for water and nutrients) (Darmanti et al. 2018).

In addition to discuss important functions of PCs, they also have significant role in regulation of expression of gene at the time of plant and soil microbial interaction, integral signal during plant-fungus interaction, maintain fruit quality and storage life, components of polysaccharide, suberin and cutin as primary barrier, storage substance, fruit aroma and flavor, synthesis of plant growth-promoting substances, food digestibility, nutrient uptake, bioremediation, disease resistance, as secondary metabolite, water and mineral absorption, plant growth-promoting substance, chlorophyll content, pigment composition, allochemicals, reduce photo-oxidative damage, peroxidation of lipids, and antioxidant activities in plants under normal and unfavorable conditions (Zaprometov 1992; Sharma et al. 2019).

6.3 Impact of Climate Change/Environmental Variables on Different Phenolic Compounds

The sessile nature of plant makes them capable of facing every stressor during their lifecycle (Sharma et al. 2019). A strategy of survival, cultivars, and environmental variations in various provenances, accounts for variation in >50% total plant phenolic compounds (Connor et al. 2005). Plant secondary compound groups such as flavonoids and anthocyanin may increase the possibility for chemical defense of tree species to biologically adapt to changes in the unfavorable environments such as elevated CO_2, high temperature, UV-B, etc. (Lavola et al. 2013). In Myrtaceae family climate change, foliar spray and soil nutrients impact over secondary metabolites, and studies on chemical variance have been evaluated and suggested that secondary metabolite contents associated with seasonal, collection time, and local conditions (Alcantara et al. 2012; Borges et al. 2013). The differential phenolic responses to adverse environments across different plant organs suggested that different plant organs adapt different strategies to mitigate these situations (Zhang et al. 2017). Climate change affects the quality and quantity of PCs in Iris genus species, and PCs manufacturing and aggregation in Iris species (Živkovi et al. 2015; Khapugin and Senchugova 2018).

PCs and several other secondary metabolites act as chemical interface between plants and seasonality, biological rhythm, critical stages and age, temperature, water, UV rays, soil macro and micro nutrients, altitude, atmospheric attributes, and tissue damage (Gobbo-Neto and Lopes 2007). PCs such as tannins increased in *S. jambos* leaves have also been reported under extreme environmental conditions of temperature and rainfall (Rezende et al. 2015). Edaphic variables like soil composition, precipitation, temperature, relative humidity, etc. may affect the formulation of PCs. Climate can affect the levels of phenolic content in medicinal herbs specially the flavonoids, tannins, and ellagic acid.

Tannins appear to be highly affected by adverse environment in terms of both of quantitative and qualitative variables, water resources, and nutrients (Monteiro et al. 2006; Gobbo-Neto and Lopes 2007). This has a substantial influence on the chemical makeup as well as the amount of tannins and flavonoids in plants, presumably because the development of these compounds is linked to a type of chemical plant reaction to the environment. Temperature is one of the key environmental variables impacting the synthesis and aggregation of phenolic compounds anthocyanin in grapes, and the concentration of anthocyanin dropped by up to 20% under water scarce condition (Guidoni et al. 2008). The concentrations of PCs significantly raise with warmer and anaerobic conditions, which help in diminishing microbial respiration in the peatlands (Dieleman et al. 2016). Elevated CO_2 (eCO_2), temperatures, and drought conditions reform plant communities by stimulating growth with release of PCs. For example, in reaction to increasing temperatures and eCO_2, numerous PCs in Willow leaves were decreased, implying that PCs were diluted owing to increased carbon allocation to diverse organs (Veteli et al. 2002). Elevated CO_2 increases PCs in foliage while decreasing terpenoids in foliage, but high temperature decreases phenolics in foliage while increasing terpenoids in foliage but decreasing phenolics in woody tissues of woody plants (Zvereva and Kozlov 2006; Holopainen et al. 2018). Further, the early phases in rice, elevated conditions meet the photosynthesis demands for future plant growth, but at maturity a number of resources available for PCs synthesis. Therefore, under eCO_2, phenolic compounds are less but much higher in later stages (Goufo et al. 2014). Therefore, the environment variables such as temperature, rainfall, light, and CO_2 affect the production and synthesis of different PCs in plant.

6.4 Role of PCs in Mitigation of Abiotic Stresses and Unfavorable Climatic Conditions

Plants increase the synthesis of polyphenols (PPs) such as flavonoids and phenols to compensate the negative impact of abiotic stress. During the multiple abiotic stress, biosynthetic pathway of secondary metabolites is triggered and leading to formation of different PCs, having the potential of scavenging the harmful effects. Certain genes such as phenylalanine ammonia lyase (PAL), chalcone synthase (CHS), chalcone isomerase (CHI), cinnamate 4-hydroxylase (C4H), 4-coumarate: CoA ligase (4CL), flavanone-3-hydroxylase (F3H), dihydroflavonol 4-reductase (DFR), UDP flavonoid glycosyltransferase (UFGT), flavonoid 3′,5′-hydroxylase (F3′5′H), flavonoid 3′-hydroxylase (F3′H), flavonol synthase (FLS), isoflavone synthase (IFS), and anthocyanidin synthase (ANS) regulate the PCs synthesis during these circumstances.

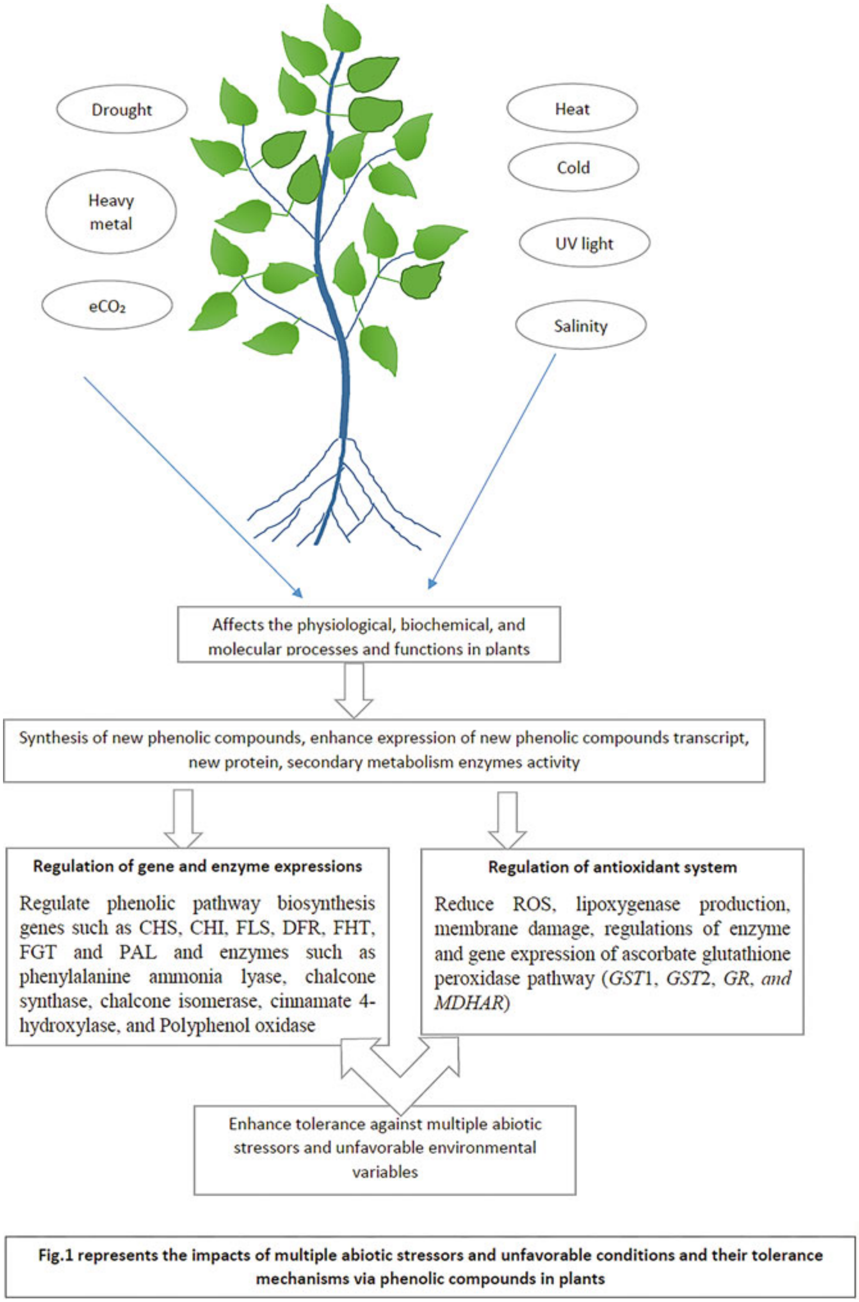
Similarly, PAL, CHS, shikimate dehydrogenase (SKDH), glucose-6-phosphate dehydrogenase (G6PDH), cinnamyl alcohol dehydrogenase (CADH), and PPO enzymes help in PCs expressions during stressful environments (Ma et al. 2014; Sharma et al. 2016, 2019). Mechanisms of PCs in mitigation of multiple abiotic stressors and unfavorable climatic factors are discussed below and represented in Fig. 6.1.

6.4.1 Drought

Climate change leads to erratic rainfall and increased the spell of drought. In plants, PCs are very pivotal to cope the constraints of water-deficit conditions. Drought stress enhances the accumulation of flavonols and phenols, which act as antioxidants and helps in mitigation of drought effects. Drought-induced PCs activation is caused by changes in phenylpropanoid biosynthesis pathways. Drought affects several key genes that encode critical enzymes of the phenylpropanoid biosynthetic pathway, bringing forth vitalizing PC production. The overall amount of phenolic acids, flavonoids, and anthocyanins in wheat (*Triticum aestivum*) plant increased, as increased the expression of genes controlling CHS, CHI, F3H, FNS, FLS, DFR, and ANS (Ma et al. 2014). Tobacco (*Nicotiana tabacum*) plant has increased in enzymatic activity of PAL and lignin content under drought stress (Silva et al. 2018). Rape mustard (*Brassica napus*) demonstrated considerable accumulation of total phenols, flavonoid, and flavonol under drought stress, as well as an increase in PAL enzyme activity associated with rapid expression (Rezayian et al. 2018). Total phenolic compounds and ferulic acid found in the leaf tissue of maize hybrids protect the inner mesophyll by sequestering light and releasing it as fluorescence. Therefore, phenolic compounds also act as photoreceptors and inhibit the excitation of chlorophyll and photodamage (Hura et al. 2008). Similarly, different polyphenols act as indicators for drought resistance in shrub plants of Patagonian shrublands by involving the antioxidant capacity, lipid peroxidation, and binding affinity with sugar enhance under varied seasons (Varela et al. 2016). Exogenous administration of salicylic acid (SA) in wheat improves the drought tolerance by influencing genes controlling ascorbate-glutathione cycle. They reported that the transcriptional expression of glutathione-*S*-transferase 1 (*GST1*), monodehydroascorbate reductase (*MDHAR*), glutathione reductase, and *GST2* increased antioxidant capacity under drought stress and reduced the peroxidation of lipids and membrane disintegration (Kang et al. 2013). Conclusively, PCs help in alleviating the impacts of drought stress by improving antioxidant capacity.

6.4.2 Salinity

Salinity causes accumulation of ROS particularly hydrogen peroxide, superoxide anions, hydroxyl ions, and requires a refined plant antioxidant system to combat ROS propagation through cell and prevent from cell death (Singhal et al. 2021;



Affects the physiological, biochemical, and molecular processes and functions in plants

Synthesis of new phenolic compounds, enhance expression of new phenolic compounds transcript, new protein, secondary metabolism enzymes activity

Regulation of gene and enzyme expressions

Regulate phenolic pathway biosynthesis genes such as CHS, CHI, FLS, DFR, FHT, FGT and PAL and enzymes such as phenylalanine ammonia lyase, chalcone synthase, chalcone isomerase, cinnamate 4-hydroxylase, and Polyphenol oxidase

Regulation of antioxidant system

Reduce ROS, lipoxygenase production, membrane damage, regulations of enzyme and gene expression of ascorbate glutathione peroxidase pathway (*GST*1, *GST*2, *GR, and MDHAR*)

Enhance tolerance against multiple abiotic stressors and unfavorable environmental variables

Fig.1 represents the impacts of multiple abiotic stressors and unfavorable conditions and their tolerance mechanisms via phenolic compounds in plants

Fig. 6.1 The impacts of multiple abiotic stressors and unfavorable conditions and their tolerance mechanisms via phenolic compounds in plants

Sabagh et al. 2021). PCs have significant antioxidant characteristics that aid in the scavenging of harmful ROS in plants. Furthermore, in response to salt stress, the phenolic biosynthetic pathway is triggered, resulting in the accumulation of several PCs with substantial antioxidative properties (Sharma et al. 2019). NtCHS1 was found to play an important role in the biochemical production of flavonoids during salt stress in tobacco plants, where accumulation directly favors ROS scavenging (Chen et al. 2019a). Likewise, the *GmFNSII-1* and *GmFNSII-2* genes in soybean control the synthesis of flavone compounds under salinity environment (Yan et al. 2014). Salinity stress enhanced the biosynthesis of phenols and oleuropein compounds in olive cultivars' leaves, and it has been observed that oleuropein works as a glucose reservoir for osmoregulation, or high energy consumption activities, and improves antioxidant activity (Petridis et al. 2012). In tomato vanillic acid is able to enhance salt tolerance by enhancing relative water contents, proline level, lowering Na^+/K^+ ratio, reduction of ROS, membrane damage, and lipoxygenase production, and inducting antioxidant defense, chlorophyll synthesis, and glyoxalase system (Parvin et al. 2020). Therefore, the PCs help in ameliorating the deleterious impacts of salinity by osmoregulation and strengthening of antioxidant system.

6.4.3 Temperature Stress (Heat and Cold)

Plants accumulate number of PCs to counteract the adverse consequences of heat stress. It is observed that some PCs such as SA also play the role of a precursor for phenol biosynthesis during high temperature stress. The accelerated synthesis of phenols such as SA helps in scavenging of ROS and provides resistance against heat stress (Godara et al. 2016). Phenols such as anthocyanins, caffeic acid, and coumaric acid have been proposed to protect against oxidative damage caused by heat stress by speeding their synthesis in carrot. During cold stress, phenolic metabolites such as suberin and lignin begin to assemble in plant cell walls, aiding in tolerance to chilling stress. The coating of the cell wall caused by phenols is advantageous in guarding against cold stress (Rivero et al. 2001; Sharma et al. 2019).

Study on high temperature tolerance plant *Heliotropium thermophilum* revealed that plant adapts through modulating membrane lipid saturation, osmotic adjustment to reduce water loss and increasing antioxidant (PCs) activities for effective scavenging the ROS (Ozturk et al. 2020). SA controls the effects of heat stress by elevating proline production, osmotic water potential, N assimilation, photosynthesis, and ethylene improvements in wheat (Khan et al. 2013). Likewise, Wen et al. (2008) found that SA mitigates heat stress in grape berry by enhancing the activity of PAL enzyme, PAL mRNA accumulation, and new PAL proteins synthesis indicating that the PCs have significant role in heat adaptation and tolerance.

6.4.4 Heavy Metal

Heavy metal (HMs) such as Hg, Cd, As, Cr, thallium (Tl), and Pb digastric for plants might be harmful at higher concentrations to bioaccumulate (accumulation in plant cell with the time) (Kumar et al. 2021b; Singhal et al. 2022). Plants take up these HMs through roots system from the soil solution and hyperaccumulation of these HMs leads to alterations in cellular redox equilibrium with excessive ROS generation (Kumar et al. 2021a). ROS propagation ultimately damages the cell organelles and manifests in ROS-promoted signaling mechanisms (Suzuki et al. 2012). The amount of flavonoids in plants is increased by excess HMs, and flavonoids augment the metal chelation process, which aids in decreasing the quantities of harmful OH* radicals in plant cells.

Heavy metals stimulate the biosynthesis pathway of phenylpropanoid by increasing the activity of key enzymes such as SKDH, G6PDH, DFR, ANS, CADH, PPO, and PAL in plants (Sharma et al. 2019). In maize (*Zea mays*), the toxicity of Cu, Pb, Cd enhanced the total phenols contents as well as some polyphenols such as chlorogenic and vanillic acid to mitigate HMs stress (Chen et al. 2019b). In the case of Mustard (*Brassica juncea*), expression of PAL and CHS enzymes regulates the Cu and Cr toxicity by increasing the total phenols, anthocyanins, kaempferol, coumaric acid, catechin, and caffeic acid (Poonam et al. 2015; Handa et al. 2019). Under Cd and Zn stress in *Kandelia obovate,* 11 different PCs viz coumaric acid, cinnamic acid, salicylic acid detected and scavenge the harmful ROS and involve in metal-ligand complex, metal detoxification, uptake and transport of Cd and Zn (Chen et al. 2020).

Conclusively, PCs have immense role in HMs toxicity tolerance by reducing the ROS species, strength antioxidant defense, and by modulation of heavy metal uptake, transport, and vacuole sequestration.

6.4.5 Ultra Violet Light

Sun light plays a major role in overall plant growth system (photosynthesis, respiration) (Kumar et al. 2017). However, from last three decades, increase in Ultra-violet rays (UV) (due to ozone hole) reaching to earth surface has increased which affects terrestrial ecosystem including plants. UV rays cause protein structural degradation, damaging mutations in DNA, cell components, and the production of hazardous ROS in plants. To counteract the harmful effects of UV-B exposure, phenolic metabolites are generated in plant cells and protect cell components by protecting the epidermal layer. By inhibiting the DNA dimerization of thymine nucleic acids, they prevent DNA damage. They also reduce the photodamage of key enzymes like Nicotinamide Adenine Dinucleotide (NAD) and Nicotinamide Adenine Dinucleotide Phosphate (NADP) (Daayf and Lattanzio 2009; Naikoo et al. 2019). Moreover, flavonoids have capability of absorbing UV radiations; hence, also act as screen layer that protects plants. The vital genes activated in plants during exposure of UV rays include CHS, CHI, FLS, DFR, FHT, FGT, and PAL. Additionally, the role of abscisic acid (ABA) during UV light stress was explained and suggested that modulations in PCs biosynthetic pathway regulate excess UV rays (Xu et al. 2017).

During an experiment, it was observed that 3 days exposure of UV in wheat (*Triticum aestivum*) plants caused the significant upsurge in vanillic acid, ferulic acid, phenolics, and *p*-coumaric acid content; however, the amount of sinapic acid, syringic acid, and *p*-hydroxybenzoic acid and modulation of PAL, C4H, 4CL, and COMT were unchanged at transcript state (Chen et al. 2019b). Therefore, PCs play crucial role during UV stress and reduce the peroxidation of cellular organ membrane, protect plant from DNA damage and photo-oxidation.

6.4.6 Elevated CO_2 (eCO_2)

Under changing climatic conditions, eCO_2 concentration is a key digastric variable that has a significant impact on plant growth and development. It was shown that eCO_2 enhanced the accumulation of phenolic acids by 25%, myricetin glycosides by 18%, catechin derivatives by 13%, and soluble condensed tannins by 19% in the leaves of silver birch trees, but decreased the accumulation of flavone glycols by 7% (Peltonen et al. 2005). Pigmentation tends to increase phenolic concentration and anthocyanic-red cultivar accumulated and maintained higher PCs such as quercetin, rutin, quercitrin, kaempferol, and quercetin-3-*O*-glucuronide as the light and CO_2 level increases, on the other hand, cyanide and its derivativeswere sensitive to mild light stress and to both ambient and increased CO_2 concentrations. The total concentration of free and bound phenolic compounds was maintained higher under all stressed environmental situations, whereas luteolin concentration was significantly increased when both the stresses applied together. Thus, the flavones and flavonoids synthesis might affect differentially and favored PCs are flavones, which are regulated by differential enzyme activity. Increase in the concentration of cyanidin derivatives in red pigmented lettuce cultivars under combined stress condition tends to protect photosynthetic apparatus (Voipio and Autio 1994), and also reduces the concentration ROS (Sgherri et al. 2015). Moreover, individually or in combination of high intensity of light and eCO_2 level to study the change of concentration of PCs in two contrastingly pigmented cultivars of lettuce (acyanic-green and anthocyanic-red leaf) and also evaluated the role of environmental condition secondary phenolic metabolite production, which consequently affecting the lettuce quality. They observed the increased phenolic compounds and antioxidant capacity by applying mid-term light stress in combination with elevated CO_2 concentration that could ultimately enhance the health promoting benefits of lettuce (López-Orenes et al. 2017). Therefore, the phenolic compound enhanced under eCO_2 conditions and helps plant to adapt well under these circumstances.

6.4.7 Under Combined Abiotic Stresses

Plant acclimatize various strategies to overcome the negative effects of different stressors. During interaction of combined abiotic stresses like elevated CO_2, temperature, and UV-B, the leaf carotenoid (+29%) and total phenolic compound (11%) were enhanced, while low content observed under alone stress conditions (UV or elevated temperature) in cowpea crop (Singh et al. 2010). Rajabbeigi et al. (2013) also observed that drought and UV interaction have potentially increased SMs like total phenolic content, flavinol quercetin, anthocyanins, and luteolin content and expression of PAL activity (Table 6.1).

Pérez-López et al. (2018) observed the increased quantities of phenolic compound like kaempferol, quercetin, quercitrin, quercetin-3-*O*-glucuronide, luteolin and rutin under light stress and eCO_2 concentration that enhanced the health promoting benefit in lettuce (Sgherri et al. 2017). Simultaneous encounter of plants to multiple stresses promote the synthesis of anthocyanins and several phenolic compounds (Balakumar et al. 1993). Accumulation of anthocyanin might delay senescence and it also serves as metal chelating agent under nutrient stress (Landi et al. 2015). The biosynthesis of phenolic compound such as flavanols, lignin, and tannin regulated by transcription factor WRKY was observed in tobacco as well as in Arabidopsis plants (Guillaumie et al. 2010; Grunewald et al. 2012). Salicylic acid (2-hydroxybenzoic acid) and its derivative such as acetyl salicylic acid (ASA), sulfosalicylic acid, benzoic acid induce tolerance to multiple stress in crops like bean (*Phaseolus vulgaris* cv Brown Beauty) and tomato (*Lycopersicum esculentum*). These compounds are very effective in elevating tolerance to heat, chilling, and drought. In these consequences, exogenous application of SA improved tolerance to drought and minerals stress like salt and boron toxicity in maize (*Zea mays* L.) (Gunes et al. 2005).

Phenolics also have pivotal role to provide tolerance to abiotic stresses in mangroves which dwell in harsh coastal environment and are excellent plant species to understand combined abiotic stress tolerance. Ravi et al. (2020) studied New Zealand mangrove (*Avicennia marina* subsp. *australasica*) under multifactorial stress condition (NSC × drought × salinity) and find accumulation of phenolic acids such as para toluic acid in the high-nonstructured carbohydrate (H-NSC) plant rather than low nonstructured carbohydrate (L-NSC) plants while the concentration of syringic acid was similar in both H-NSC and L-NSC plants under medium salinity-high drought condition.

Phenolic compounds functionally act as antioxidant, and also absorb UV radiations. These compounds help the plant to cope with environmental stresses by mitigating the harmful level of ROS and also provide protection against UV (Goleniowski et al. 2013). Sinapic and syringic acids act as antioxidant source to manage excess ROS production and also protect from harmful level of UV during combined abiotic stress particularly in summer months in mangrove (Liley and McKenzie 2006). Also, the free and bound phenolic concentration in vegetables are affected under combined postharvest wounding and extrusion stress. Viacava et al. (2020) studied accumulation of PCs when the sequential application of wound

Table 6.1 Role of some phenolic compounds under combined abiotic stressors and trait influenced and their adaptive mechanism

Sr. no.	Stress factors	Plant	Phenolic compounds	Trait influenced	Tolerance mechanisms involve
1	UV-B and drought	Chili pepper (*Capsicum annuum* L.) (Rodríguez-Calzada et al. 2019) Cowpea (Balakumar et al. 1993)	Increase in luteolin 6-C-pentoside-8-C-hexoside, flavonol Reduction in chlorogenic acid, apigenin 6-C-pentoside-8-C-hexoside, apigenin 8-C-hexoside Increase in total phenols	Large reduction in stem length, stem dry weight, number of leaves, leaf area, root dry weight, and number of floral primordia under combined stress. Reduce plant height, leaf area, plant fresh, and dry weight, increase in specific leaf weight (SLW)	Enhanced expression of Mn-SOD gene expression, scavanging ROS, and reduce oxidative stress Osmolyte, reduce membrane damage, enhance antioxidant defense
2	Cd + Zinc stress	*Kandelia obovate* (Chen et al. 2020)	Enhance expression of chlorogenic acid (Chl), pyrogallic acid (Gal), cinnamic acid (Cin), and coumaric acid (Cou)	Reduce total biomass, increase oxidative injury, damaging of physiological tissue	Scavenging free radicals and chelated with Cd and Zn and changing the bioavailability
3	Chilling + light stress	Wild marjoram (*Origanum vulgare* L.) (Szczalba et al. 2019)	Increase in total phenolic compounds	Decline in dry weight, increase in soluble carbohydrate, enhance Chl a, b and carotenoid contents and ratio, higher accumulation of H_2O_2	Osmoprotectants, maintain membrane injury, reduce photodamage, increase antioxidant enzymes
4	Cd + As	Maize (Anjum et al. 2016)	Increase in total phenolic compounds and osmolytes	Reduce activity of macro and micro elements, germination percentage, root elongation, altering sugar metabolism, protein accumulation	Higher osmolyte accumulation, higher antioxidant, osmotic adjustment, maintain cell membrane integrity
5	CO_2 + temperature + UV-B	Cowpea (*Vigna unguiculata*	Increase phenolic compounds (11%),	Reduce plant height (35%), reduction in specific leaf area, specific leaf weight, reduce	CO_2 enrichment effect, antioxidant enhancement

		[L.] Walp.) (Singh et al. 2010)		chlorophyll photosynthesis and fluorescence, modulate flower and yield traits	
6	Light + eCO_2	Lettuce (Pérez-López et al. 2018)	Increased free and conjugated fatty acid quercetin-3-*O*-glucoside, quercetin-3-*O*-glucuronide, and luteolin-7-*O*-glucoside, cyanidins, and luteolin	Higher photosynthesis, CO_2 enrichment, over excitation of pigments, formation of ROS	Increase antioxidant capacity, increase sugar content, ROS scavenging, reduce photodamage
7.	Drought + UV	Lettuce (Rajabbeigi et al. 2013)	Improvement in chlorogenic acid, chicoric acid, caffeic acid, quercetin, luteolin	Reduction in biomass production, degradation of cellular constituents, generation of ROS	Prevent oxidative damage, enhance PAL, CHS activity
8.	Salt + drought + boron toxicity	Maize (Gunes et al. 2005)	Application of salicylic acid	Improve nutrient uptake and efficiency, dry matter production, nutrient utilization	Prevention of oxidative damage
9.	UV-B + UV-C	Carrot (Formica-Oliveira et al. 2017)	3-Caffeoylquinic acid, 3,5-dicaffeoylquinic acid, 4,5-dicaffeoylquinic acid, ferulic acid	Reduce ROS accumulation, reduce oxidative stress	Increment PAL activity 115–144%, improve antioxidant capacity
10	Heat + cold	Watermelon (Rivero et al. 2001)	Total phenolic content, soluble phenolics	Reduce membrane damage, physiological injury, increase dry matter	Higher PAL activity, neutralize ROS

and extrusion was applied on carrot. Wounding alone increased total free phenolics by 288.1% and total bound phenolics by 407.6% and among them chlorogenic and *p*-coumaric acid were increased at highest level by 579.8% and 390.9%, respectively. Amalgamation of extrusion at 109 °C further increased the total free (296.6%) and bound phenolics (22.1%).

The radiations such as UV-B and C also signify its effects on production of PCs in plants by various mechanisms induced by abiotic stresses. Increase in PCs with high antioxidant capacity affects the phenylpropanoid metabolism. It is well documented in the literature that enzyme is induced by several biotic (insect and pathogen attack) and abiotic (wound, water stress, heat and chilling stress, radiation exposure, minerals, and hormonal stress) stress-induced mechanisms (Avena-Bustillos et al. 2012; Alegria et al. 2016). Thus, these postharvest abiotic stresses induce PCs accumulation, i.e., caffeoylquinic (CQA) acid, ferulic acid, and derivatives for defending plant by activating their defense system. Formica-Oliveira et al. (2017) studied the consequences of individual and combined doses of UV-B (1.5 kJ/m^2) and UV-C (4.0 kJ/m^2) on PAL, phenols, and antioxidant activities in fresh carrots. They find in increased PAL activity by nearly 760% after 72 h in UV-B radiated and controlled samples while other treatment showed 120–140% increase. Phenolic compound such as chlorogenic acid showed 70% of total phenolic compound at initial stage.

Highest phenolic accumulation 498% was achieved in UV-B treated samples after 72 h, while individual and combined UV-C treated samples showed 440% increase which was similar to control. The data of phenolic content were highly correlated ($R^2 = 0.82$) with antioxidant activity during storage. Moreover, use of UV-C treatment with UV-B radiation will not affect the bioactive compound accumulation and will be useful of sanitizing purpose.

Thus, it might be a suitable tool for food-based industries to increase antioxidant content in products by combining use of pretreatment of UV-C and UV-B and also meet the food safety issues. Light intensity, duration, temperature, and CO_2 level also influence the level of PCs in plants.

Chilling and light stresses, individually or in combination also influence the composition of phenolic plants and their shelf life. Szczalba et al. (2019) reported the combination effect of chilling and light stress on wild marjoram (*Origanum vulgare* L.), an aromatic and medicinal herb, in the juvenile stage. They used two treatments (5 °C and light irradiance of 0, 100, 250 μmol m^2/s; 18 °C and light irradiance of 0, 100, 250 μmol m^2/s) for 7 days on 10-week old plant stage. Chilling stress jeopardizes plant physiological traits such as photosynthetic ability and damages the cellular organelle by increasing ROS. They observed highest accumulation of H_2O_2 as the result of combined stress effect of 5 °C with 100 μmol m^2/s of light irradiance. To alleviate the impact of ROS, plant developed defense mechanism by accumulation of phenolic compound, peroxidase, and catalase. They observed lower level of phenols and antioxidant activity in chilled plants while high TAA and total phenol contents were observed in chilled plant with 100 μmol m^2/s of light irradiation. Chilling temperature with low level of light irradiance increases L-amino acid, antioxidant activity, and total phenolic compounds in wild marjoram.

Soil edaphic factors, deteriorated by anthropogenic led to industrial and agricultural development, also affect plant phenolics composition as a result of higher accumulation of HMs, and affect crop phenology, growth, and development. Anjum et al. (2016) studied the individual and combination effect of Cd and As on antioxidant capacity, accumulation of osmolyte and ROS at 45, 60, 75, 90 DAS in two maize genotypes (Run Nong 35 and Dong Dan 80). The concentration of Cd (100 μM) and As (200 μM) was applied at 30 DAS singly and in group. They observed increase of enzymatic activity (SOD, catalase, peroxidase, glutathione peroxidase, glutathione reductase, ascorbate peroxidase), antioxidants and nonenzymes (reduced glutathione and ascorbic acid), osmolyte accumulation, and level of ROS with time. Combined stress was more devastating for growth and development of plant, ultimately on plant yield, than individual stress in both maize genotypes. Combined stress tends to reduce ion exchange between soil and plant; therefore, reduced metal uptake by plant from soil. The tolerance level of plant against HMs also varies with genetic architecture of plant. Maize genotype Dong Dan 80 was better in performance due to more accumulation of osmolytes, lower ROS production, and higher antioxidant activities.

6.5 Conclusion

The PCs have immense role in alleviating the drastic impacts of multiple abiotic stressors and unfavorable conditions. The prime role of phenolic compounds is strengthening of antioxidant system, ROS scavenging, osmoregulation's, pigment synthesis, and enhanced expression of stress proteins under unfavorable conditions. Phenolic compounds reduce the membrane damage, oxidative stress, and activate the defense signaling mechanism of plants. By evaluating the importance of phenolic compound, it is important to deep understanding of physiological, biochemical, and molecular mechanisms of novel phenolic compounds, which give new insight into further metabolomics studies and could be a prime approach in management of multiple abiotic stresses in plants and improvement of yield production of agricultural important crops.

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Role of Plant Phenolics Against Reactive Oxygen Species (ROS) Induced Oxidative Stress and Biochemical Alterations

7

Younis Ahmad Hajam, Rafiq Lone, and Rajesh Kumar

Abstract

Plants being embedded into the environment have to develop into it and to adjust with the fluctuating environments because of the abiotic stresses. Environmental factors including adverse temperatures, flood, light, drought, salt, and heavy metals come under abiotic stressors that greatly effects plant development and crop productivity. Changes in plant growth and its natural habitat conditions can be recognized as environmental stress which interrupts its metabolic balance. Likewise, we differentiate two dissimilar kinds of environmental tension: biotic stress (brought by viruses, bacteria, or insects) and abiotic stress. Polyphenols are secondary metabolites comprising the major and the supreme predominant assembly of metabolites. These polyphenols are having significant morphological and biological significance in plants. Polyphenols impact the source and movement of organic and inorganic nutrients present in soil accessible to plant or microbes. They also respond to nutrient deficiency therefore offering means for detecting nutrients disorder before the onset of symptoms. The aim of this chapter is to summarize the updated literature about abiotic stress, and its management by polyphenols.

Keywords

Abiotic stress · Environment · Factors · Plants · Polyphenols

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7.1 Introduction

From the last 20–30 years, increased research-based proof has established in support of the fact that atmospheric and climatic deviations can promptly change the diversity of living beings (Hajam et al. 2020; Malik et al. 2020) and crop production (Kumar and Meena 2016) globally. Changes in plant growth and its natural habitat conditions can be recognized as environmental stress which interrupts its metabolic balance. Likewise, we differentiate two dissimilar kinds of environmental tension: biotic stress (brought by viruses, bacteria, or insects) and abiotic stress. Environmental factors including adverse temperatures, flood, light, drought, salt, and heavy metals come under abiotic stressors that greatly effects plant development and crop productivity (Gautam et al. 2020). During stress conditions, the "expression pattern" of the gene in the plant proteins takes place which is responsible for the regulation of the biogenesis of metabolites convoluted in communication amid plants and surroundings. Polyphenols are an essential class of specific metabolites that perform fundamental physio-biological functions during the entire life span of plants, comprising stress responses. Previous studies reported that the pathway of phenylpropanoid biosynthesis is generally stimulated during adverse environmental conditions like extreme temperatures, salinity, drought, ultraviolet radiations, and heavy metal pollution which results in various phenolic compound accumulation (Kumar et al. 2020; Mohamed et al. 2020; Sharma et al. 2019a; Linić et al. 2019). In constantly changing environmental conditions plants are revealed to multiple abiotic stresses that are inauspicious for the development and growth of the plant (Zhu 2016). These abiotic stresses are "salinity, heavy metals, excess or deficiency of nutrients, water (drought and flooding), high and low temperatures (chilling and freezing), ozone, sulfur dioxide, extreme levels of light (high and low), radiation (ultraviolet, UV-A and UV-B)," mechanical components and additional regularly arising stress conditions (Gutiérrez-Grijalva et al. 2020; Pereira 2016) (Fig. 7.1).

Plants being embedded into the environment have to develop into it and to adjust with the fluctuating environments because of the abiotic stresses and increase in phenolic compounds in plant cells are deliberated as a compatible reaction of plants towards these negative ecological situations (Hoque et al. 2020; Pereira 2016). Various chemicals are blended in plants and are characterized as primary and secondary metabolites. "Nucleic acids, fatty acids, amino acids, and sugars are the primary metabolites" which are necessary for the development of plants (Fiehn 2002; Wu and Chappell 2008). As compared to the "primary metabolites" secondary metabolites are much more divergent. These are organizationally and chemically specialized compounds and are indirectly used for the basic metabolism of the plant but are essential for the persistence of plants in the surroundings. Polyphenols groups are the extensively present secondary metabolites having significant morphological and biological significance in plants. These compounds are aromatic having more than one OH group derived from "shikimate pathway," leading to the generation of "monomeric, polymeric phenols, and polyphenols units" (Randhir and Shetty 2004). In plants, these "phenolic compounds" perform an important function in plant development, growth, and reproduction (Gautam et al. 2020). These also

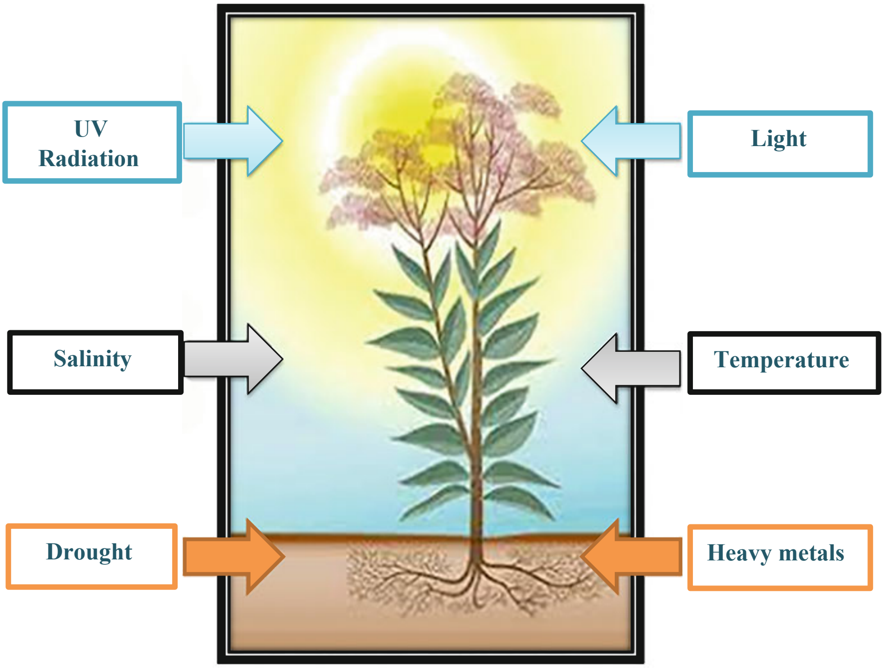

Fig. 7.1 Showing different types of abiotic stresses

impart a substantial role as defense compounds during different abiotic stresses including low temperatures, heavy metals, high light, “UV-B radiations, and nutrient deficiency”, constructing sensory and color appearances of vegetables and fruits (Alasalvar et al. 2001), fortification in contrast to predators and pathogens (Bravo 1998), further demonstrating additional important properties such as antimicrobial, antiallergenic, and antioxidant activity (Balasundram et al. 2006). Bacteria, algae, and fungi synthesize aberrant phenolic composites; however, bryophytes are producing polyphenols, such as flavonoids, on the other hand, in vascular plants a complete assortment of phenolic complexes are present (Swain 1975; Harborne and Green 1980). An approximation of around 2% of the total carbon photosynthesized by plants is transformed into “phenolic complexes” (Robards and Antolovich 1997). Numerous phenolic complexes are recognized to be produced by developed plants and the classification of these complexes is constantly growing. Plant foliage comprises “amides, esters, and glycosides of hydroxycinnamic acids (HCAs); glycosylated flavonoids, mainly proanthocyanidins and flavonols and their by-products.”

Polyphenols are the major and supreme premeditated assembly of metabolites which is plant-specific and assimilate over 8000 molecules (González-Sarrías et al. 2012). These are biosynthesized by utilizing a phenylpropanoid or shikimate pathway that yields an extensive range of monomeric and polymeric polyphenols units (Sharma et al. 2019b). Phenolic compounds organizations are fluctuating comprehensively, even if their communal property is the occurrence of a single or more hydroxyl groups, involved openly in more than one benzene ring. Conferring to their arrangements, they might be assembled into “flavonoids, stilbenoids, phenolic acids, and lignans.” Generally, phenolic complexes might exist in plants as unrestricted systems; however, further frequently, they are established in associated arrangements with a single or more sugar remains associated by “β-glycosidic links with a hydroxyl group (O-glycosides) or a carbon atom of the aromatic ring (C-glycosides).” Andreasen et al. (2000) reviewed that connected sugars may be “monosaccharides, disaccharides, or even oligosaccharides.” In the past 50 years, an estimated 1–2% per decade reduction has been observed in the production of wheat and maize, ultimately disturbing food provisions for livestock and humans (Myers et al. 2017). Therefore, global production of food must be sustained or if possible, increased in order to feed a continuously rising human population, under gradually unbalanced climatic situations and growing high temperatures (Myers et al. 2017). Novel methods are required to come across this most important agronomic problem although consuming prevailing or even condensed regions of cultivated land (Kassam and Friedrich, 2011). A significant agronomic objective is to recover the production of crops developing below stages of abiotic along with “biotic stress.” The enzyme polyphenol oxidase is located in maximum all plant species and the leaves articulated gene output might partake a function in response to stress, directed by conditional proof including localization of enzyme and its response against various “environmental factors.” Polyphenol oxidase has been described in all terrestrial plants measured to date with the exemption of Arabidopsis. Conversely, no polyphenol oxidase-like arrangements were recounted in “chlorophytes (green algae)” (Tran et al. 2012). It is hypothesized that this enzyme is associated intensely with the development of terrestrial plants signifying a function in alteration to abiotic tension linked with desiccated/nonaquatic surroundings. Though, at present, there is no convincing indication for the presence of an indispensable method clarifying the association between polyphenol oxidase and abiotic tension; certainly, it is inexact if the occurrence of polyphenol oxidase action is valuable or damaging to the plant (Mayer 2006). Although polyphenol oxidase movement is perhaps associated with accretion of ROS (Thipyapong et al. 2004; Mayer 2006) and complete redox potential standards (Webb et al. 2014), its occurrence might moreover be favorable as a suggested oxygen shield barrier (Vaughn and Duke 1984) or through dejected-modifiable photosynthesis (Trebst and Depka 1995). The present form of whatever is frequently conflicting proposed and investigational proof concerning the polyphenol oxidase latency in foliage to deliberate a benefit in crop yield, predominantly for the period of abiotic stress, including heat, cold, and drought. Polyphenol oxidase enzymes from plants consist of three provinces, such as an N-terminal plastid transport peptide, a greatly preserved type-three “copper center, and a C-terminal section” (Tran et al. 2012). Polyphenol oxidase enzymes family conduce the monophenols and *o*-di-phenols to *o*-quinones oxidation. Polyphenol oxidase are extensively scattered in “bacteria, fungi, plants, and animals” (Mayer 2006; Tran et al. 2012) but are frequently tangled with one more subclass of phenol oxidases which is the laccases “benzenediol: oxygen oxidoreductase [EC 1.10.3.2] or *p*-diphenol oxidase]," which corrode an extensive series "of *o*-, *m*-, and *p*-diphenols" (Griffith 1994). "Plant laccases are frequently extracellular proteins containing 22–45% glycosylation" (Solomon et al. 1996) while polyphenol oxidase are "intracellular proteins" (Steffens et al. 1994). Both subclasses are, conversely frequently mentioned as polyphenol oxidase (Mayer and Harel 1979; Yoruk and Marshall 2003; Marusek et al. 2006).

Polyphenol oxidase facilitated production of *o*-quinones are associated with secondary "production of reactive oxygen species as" tributary products of the reaction (Steffens et al. 1994). Even though the comprehensive procedure prevails to be recognized, the opposite unbalanced of *o*-quinones can give rise to the development of semi-quinone radicals in cytoplasm (O'Brien 1991; Thipyapong et al. 1997). Collaboration between O_2 and these free radicals will affect the superoxide anions production and the redevelopment of *o*-quinone (O'Brien 1991). Superoxide anions are immensely deranged and rapidly dismutate, either by enzyme action through superoxide or without enzymes to form H_2O_2 (Grant and Loake 2000). Accretion of cytotoxic reactive oxygen species requisites to be below constricted switch as oxidative alterations such as protein criss-cross linking "lipid peroxidation," and impairment to nucleic acids can eventually cause death of the cell (Grant and Loake 2000; Bhattacharjee 2005; Gill and Tuteja 2010; Foyer and Noctor 2012). Though, in theory, Polyphenol oxidase might also give rise to a declining quantity of oxygen nearby accessible by the O_2 reduction into water (Yoruk and Marshall 2003). Polyphenol oxidase management is multifarious and the enzyme may be existed equally as an active and a suppressed (frequently precursor or an inactive state) condition in a similar basis substance (Mayer and Harel 1979). Succeeding passage to the cavity and the breakdown of the transit N-terminal peptide bond, polyphenol oxidase is primarily present as a two-dominion biomolecule comprising a copper adhesive region and a C-terminal dominion (Flurkey and Inlow 2008). An additional comprehensive conversation, comprising deliberation of the three-dimensional construction of catechol oxidases, may originate in Gerdemann et al. (2002). The C-terminal is associated with an elastic arbitrary peptide organization which is anticipated to shield the active spot and go through structural variation due to some situations (Leufken et al. 2015). Various confirmations have been reviewed for proteolytic C-terminal handling of dormant polyphenol oxidase towards the active state and these have been verified for *Vitis vinifera*, *Vicia faba,* and *Ipomoea batatas* polyphenol oxidase (Flurkey and Inlow 2008). The amount of inactivity is not common and varies with plant types along with its tissue type. For example, polyphenol oxidase movement was identified in both the dynamic and dormant types in red clover root tissue however in white clover roots it has only observed in the dormant state (Trifolium repens); this compares with aerial tissues wherever polyphenol oxidase movement was identified in both the dynamic and dormant states in both white and red clover (Webb et al. 2013). "The perplexity of polyphenol oxidase in leaves 3573 (trypsin), acid and base shocks, mild heat, and detergents including sodium dodecyl sulfate and ammonium sulfate" (Steffens et al. 1994; Yoruk and Marshall 2003). It has been perceived that the C-terminal province regulates the optimum pH levels of polyphenol oxidase in non-proteolytic stimulated enzyme and they hypothesize that non-proteolytic stimulation as well happens in plants (Leufken et al. 2015). Winters et al. (2008) have confirmed the possibility to trigger dormant polyphenol oxidase from red clover in the occurrence of its endogenous *o*-di-phenols substratum. It has been anticipated that *o*-diphenol-facilitated instigation is an ancillary method of stimulation, along with the resultant *o*-quinones correlating with the dormant polyphenol oxidase group, by this means changing their arrangement and revealing the active regions (Winters et al. 2008). Meyer and Biehl (1981) reported that increased activity of phenolase enzyme leads to the reduction in the dormant state through foliage deteriorating in spinach (*Spinacia oleracea*). More in recent times, a recognized quinone binding region has been identified in the polyphenol oxidase enzyme, aurone synthase, from Coreopsis grandiflora, which might be accountable for the detected allosteric stimulation of dormant polyphenol oxidase (Molitor et al. 2015).

7.2 Phenolic and Abiotic Stress Management

The interaction between plants and environment contributes to the production of definite natural products. "Accumulation of phenolics" in the plant tissues provided "adaptive response" with respective continuous changes in the environment. The accumulation of phenolic compounds is major because of the "PAL (phenylalanine ammonia lyase), CHS (chalcone synthase) and other enzyme activity." Increased activity of *"Phosphoenolpyruvate* carboxylase" indicates that the process becomes reverse, i.e., production of sucrose decreases while repairing and defense processes started. Plant phenolic contributes to different physical activities like enhanced survival rate and helps plants to adapt under extreme environmental circumstances (Lattanzio et al. 2012). Any kind of environmental stress leads to the increased activity of herbivores, pathogen infection, low temperatures, high light or UV radiation, heavy metals, and nutrient insufficiency and result "in the production of free radical's species." "Plants are having the potential to combat abiotic and biotic stress conditions by neutralizing reactive oxygen species" (Khan and Khan 2017). The genes of secondary metabolites show their expression during unfavorable environmental conditions and lead to the synthesis of different signaling elements like jasmonic acid, salicylic acid, and their by-products (Winkel-Shirley 2002; Gould and Lister 2006; do Nascimento and Fett-Neto 2010; Khan and Khan 2013; Khan et al. 2013, 2014, 2015; Per et al. 2018). Abiotic stress leads to the turned off/on (Ahmad et al. 2008; Jaleel et al. 2009). Abiotic stress responsible for increased active oxygen species production inside the cells which leads to great damage to the plants (Dar et al. 2017). Phenolics such as flavonoids, tannins, hydroxyl-cinnamate esters, and lignin provide protection against biotic and abiotic stresses. Under stress conditions production of phenolic compounds increases in higher quantity under certain stress conditions as compared to the non-stressed or normal conditions (Selmar 2008). The antioxidant property of phenolic compounds helps in the neutralization of free radicals and chelation of redox-active metal ions which are able to affect the peroxidation of lipids molecules (Schroeter et al. 2002). Phyto-phenolic compounds including polyphenols contribute significantly to detoxification system which primarily includes ascorbate and also acts as a stoppage resistance machinery for vascular plants in contrast to monophenols (Yamasaki et al. 1995, 1999). Under in vitro studies, polyphenols exhibit operative antioxidant relative to ascorbate and tocopherol and have a supreme organizational interaction to perform the activity of scavenging free radicals. Due to the antioxidative property of polyphenols, they delocalize and balance the solitary electron, their raised reactivity as "electron donors and from their ability to chelate transition metal ions (termination of the Fenton reaction)" (Rice-Evans et al. 1997). It has been studied that phenolic compounds are oxidized univalently to their corresponding phenoxyl radicals by directly scavenging the free radicals or enzymatic operations (Kagan and Tyurina 1998) (Fig. 7.2).

"Plant produces phenolic compounds to endure in conditions of stress (drought, salt, UV radiation, metal, and low temperature)." A maximum number of plants produce phenyl propanoids comprising flavonoids and HCAs (hydroxy citric acid);

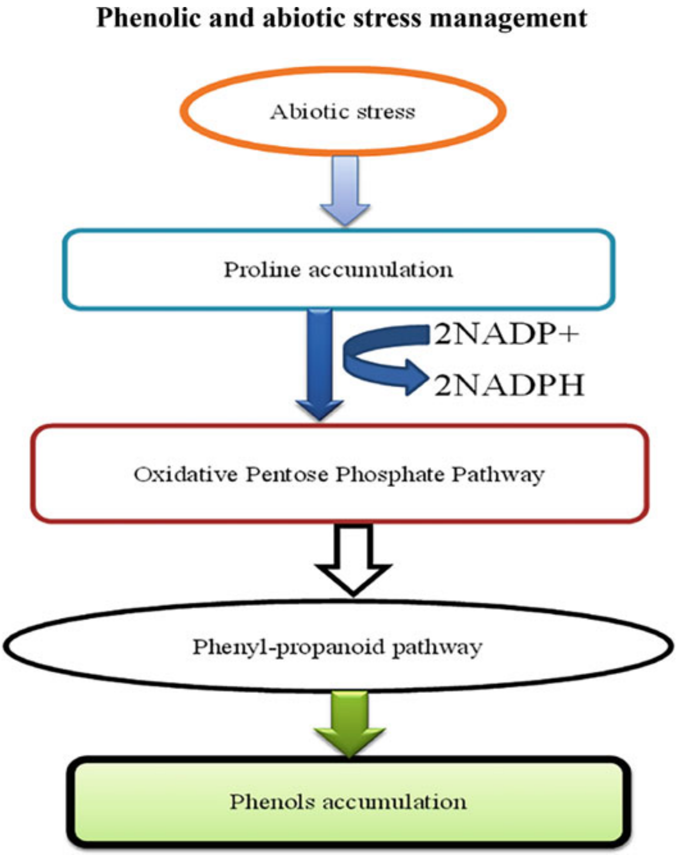

Fig. 7.2 Showing plant response towards environmental stress and accumulation of phenol

however, phenolic accretion in plants occurs only during the “abiotic and biotic stresses, including UV radiation, low temperatures, high light illumination, wounding, pathogen attack, and low nutrients” (Dixon and Paiva 1995; Yamasaki et al. 1995). Assured tributary metabolic composites are manufactured excessively during abiotic stress conditions resembling drought, where they function as antioxidants (do Nascimento and Fett-Neto 2010). “Phenolic compounds are divided into five subgroups, such as phenolic acids, flavonoids, lignins, coumarins, and tannins,” (Gumul et al. 2007) and are manufactured through chorismic acid and shikimic acid pathways (Solecka 1997). Mainly involved in defense under stress conditions but are also beneficial for other organisms such as human beings as diet supplement and alternate source of medicines (França et al. 2001; Amarowicz and Weidner 2009). Due to diverse environmental conditions, production of phenolic compounds is detected to be either overexpressed (Wróbel et al. 2005; Weidner et al. 2009) or less expressed (Weidner et al. 2007) consequently give rise to the amplified or reduced amount of the phenolic compounds in plants. Various studies have shown that under abiotic stress conditions, production of phenols was increased. In *Rehmannia glutinosa* for the period of water scarcity and chilling stress situations, total content of phenolic compounds has increased as reported by Chung et al. (2006). “Additional approval has come from the studies of Posmyk et al. (2005) in soybean subjected to chilling stress.” “Accretion of phenolic compounds caused an improved activity of PAL, CHS, and other enzymes that are convoluted in the synthesis of phenolic compounds.” “Plants reaction to abiotic stress by dehydration, hydration, and methylation of cinnamic acid, phenolic acids synthesis induces” (Dixon and Paiva 1995) numerous tributary metabolic substances in plants that display antioxidant properties related to this class of compounds. As phenolic are antioxidants, they are involved in scavenging reactive oxygen species, helps in catalyzing oxygenation reactions through complex formation with some metals, and reduces or inhibit certain oxidizing enzyme activity. “G6PDH a carbohydrate metabolism enzyme that delivers substrate to the shikimate pathway, and 3-deoxyarabinoheptulosonate 7-phosphate synthase, which is a ‘shikimate pathway enzyme is also necessary for phenylalanine synthesis’ ‘against various stress conditions.’ Researchers have interpreted that stress can stimulate increased chance of reducing parallels into synthesis of proline cytosolic.” From above points, we can conclude that different environmental disturbances around plants induce primary as well as secondary metabolic activities in them. These activities result in the deposition of bioactive components which in turn provides protection. This signaling pathway provides a connection between primary and secondary metabolic pathway, which provides a pathway for the synthesis of phenylpropanoid coupled to mass production of proline with the energy transfer through the oxidative pentose phosphate pathway (Cheynier et al. 2013). Under adverse conditions, the plants accumulate a large amount of free proline. Synthesis of proline can be “done de novo or it can be released by protein degradation with the NADPH oxidation.” Activity of oxidative pentose phosphate pathway is increased when the ratio of NADP1/NADPH is increased, generates resource to synthesize polyphenolics through the “shikimic acid pathway” (Cheynier et al. 2013; Lattanzio et al. 2009).

7.3 Phenolic as Ultraviolet Sunscreens

Somatic cells receives the light and then initiates the synthesis of metabolites in plants. Disclosure of environmental solar ultraviolet-B radiation to plants in exposed grounds badly disturbs proteins, DNA, and cell membranes, it also led to the formation of “reactive oxygen species” which modifies metabolic breakdown in the cells. However, plant phenolic work as a guard which intimate the layer of epidermal cells to protect themselves from these destructive rays and by regulating the antioxidant organizations at the cell and entire animal level, “along this interrupting gene mutation and cell death by thymine units’ dimerization in the DNA, and probable light obliteration of co-enzymes NAD (nicotinamide-adenine-dinucleotide) or NADP (nicotinamide-adenine-dinucleotide phosphate).” Flavonoids can act as good UV guards with their great absorptivity at 250–270 and 335–360 nm. Flavonoids are phenolic compounds having a substantial function in protection against UV radiation (Li et al. 1993). It has been observed that humid plants and “high-altitude plants have” a greater flavonoid percentage than plants present in temperate zones. The variation in the amount of flavonoid arrangement of plant foliage is because of excess ultraviolet rays chiefly because of the stimulation of specialized flavonoid biosynthetic genes (Kolb et al. 2001). Plants utilizing polyphenols as defense mechanisms in contrast to ultraviolet rays as a direct screen has been observed as an important function by a number of researchers. It has been found that anthocyanin (a phenolic compound) can mount up in the epidermis and can function as a blackening screen and shield the mesophyll cells from excess rays (Lake et al. 2009). According to Ryan et al. (2001) flavonoids are important in protection against ultraviolet rays utilizing Arabidopsis mutants, ultraviolet-oversensitivity. Synthesis of anthocyanin was prompted through ultraviolet light ranges between “280 and 320 nm” collectively when joined with red light in apples. It was exposed that flavonoid upgraded in barley and also observed augmented amount of poly-amines in cucumber by ultra violet-B rays. It has also been discovered that flavonoids in the pea plant roots were improved on ultraviolet revelation. Production of flavonol molecules was prompted by ultraviolet-B in leaves of silver birch and grape plant. Furthermore, in numerous species of plant, improved levels of flavonoid have been restrained at higher altitudes. “It has been demonstrated in numerous plant species that the appearance of CHS (Cannabinoid hyperemesis syndrome) is transcriptionally stimulated by ultraviolet light, which is the first enzyme in the biosynthesis pathway of flavonoid.”

7.4 Plant Phenolics and Their Role in Heavy Metal Stress

Toxicity of “heavy metal is one of the significant abiotic stresses that can change biological metabolic pathways therefore give rise to destructive impacts on plants” (Villiers et al. 2011). It has been described that heavy metal stress protection has been provided by convinced flavonoids as they display the chelation of transition metals (e.g., Zn, Cu, Fe, Ni), which produces radicals of hydroxyl utilizing Fenton’s reaction (Williams et al. 2004). In addition to this, the "chelation of these metals into the soil can be an operational state of shield in contrast to the impacts of elevated metals concentration toxins." Biosynthesis of phenolic compounds that are predecessors of lignin increases under stress conditions, let us say, in plants exposed to the stress of heavy metal as observed by Michalak (2006). "Investigation on corn plants (*Zea mays* L.) stated that these plants, when developed on soil polluted with aluminium ions and root diffusion, were observed along with high concentrations of quercetin and catechin." However, flavonoids are convoluted in plant defense, growing in topsoil that is amusing in poisonous metals say aluminum. The fabrication of betalains in *Beta vulgaris* is enthused by Cu. The hairy root systems were uncovered to metal ions to progress the production of betalains. The accretion of betacyanins in Amaranthus caudatus callus cultures is promoted by Cu. Accumulation of flavonoids was also detected in Ginkgo biloba cell cultures treated with $CuSO_4$ as related with nontreated cells. In the same way, connection between levels of flavonoid and $CuSO_4$ level in Digitalis lanata cell cultures was reported (Bota and Deliu 2011). Nickel stress gives rise to an imperative reduction in anthocyanin concentrations (Hawrylak et al. 2007). Plants with raised number of tannins, for example, tea, are capable of enduring high levels of "manganese in soil, as they are shielded by the direct ions chelation." "Heavy metal ions binding with polyphenols in Nymphaea where heavy metals such as Hg, Pb, and Cr were chelating by the polyphenols rich methanolic extract."

7.5 Plant Phenolic and Their Role in Cold Stress

Many researchers have found that nonfreezing low temperatures promote the phenolic breakdown in foliage (Akula and Ravishankar 2011). "Metabolism of phenol is promoted at an acute "low temperature, which is called as the inception temperature at which unnerving damage is also prompted" (Janská et al. 2010). "Cold stress proliferates the production of phenolic compounds into the cell wall either as lignin or suberin." Suberin deposition and lignification upsurge opposition to cold stress conditions. A proliferation in thickening of cell wall might decrease cell collapse throughout mechanical stress, "freezing-induced dehydration" and therefore given the plant freezing resistance. Apple trees are perceived to be associated with elevated chlorogenic acid levels to a commutable degree towards cold climate. Christie et al. (1994) described the "accumulation of anthocyanins during cold stress and Pedranzani et al. (2003) stated that water and cold stresses introduced variations in endogenous jasmonates in Pinus."

7.6 Mechanism of Polyphenols on Abiotic Stress Management

The proteins of foliage are immensely perilous in the progress, reproduction, and definitive grain produced out of the plants. The decrease in the amount of protein inside the leaves of plant because of salt stress is not astounding meanwhile it is well recognized that the early objectives of reactive oxygen species are proteins in biological systems. The chloroplast come under as one of the principal objectives of reactive oxygen species, which bring about noticeable modifications in an extensive diversity of proteins including thylakoid and stromal. Consequently, the concentration of leaf protein is some of the critical pointers of the cause of salt stress (Isayenkov and Maathuis 2019). Furthermore, the result bearing of salinity is a consensual problem, which changes extensively in the writings. For example, Radi et al. (2013) testified that, in wheat, whole protein gratified into the leaves of two cultivars (lenient and delicate) was reduced analogously by salt stress (Afzal et al. 2006).

Augmented accretion of harmonious solutes such as proline has been advised to improve tolerance against salt. Ultimately, proline, similarly to osmolytes, moderate redox potential by deliberating osmotic modification, shielding cellular sheaths, and alleviating enzymes beneath abiotic stress. Arabbeigi et al. (2018) recommended that developed communication of the gene accountable for biosynthesis of proline (P5CS) in *Aegilops cylindrica* may associate with salt tolerance. These findings are in contract with Kumar et al. (2017a) with respect to wheat. As a result, the osmo-adaptive reaction includes the accretion of proline, which emphasize an undefined function in the forbearance to abiotic stress (including drought and salinity) is a substance of debate. There are many possible explanations for this discrepancy. The utmost conspicuous among them are stress intensity, stress duration, genotype or species, and biological stage alterations amid research (Ebrahim et al. 2020).

The salvation of plasmid membrane integrity in plant cells is a serious adaptive approach in contrast to free radicals (Isayenkov and Maathuis 2019; Kaya et al. 2019). It has been found that greater electrolyte escape was established in the wheat cultivars as compared to the agitated-salt forbearing *Aegilops cylindrica* and amphidiploid genotypes during stress environments. These outcomes are helpful and upkeep the indication that plasma membrane may possibly epitomize a capable approach for refining the effectiveness in adaptable metabolite fluxes and transmembrane ions throughout the period of environmental stress. Radi et al. (2013) witnessed a rise in EL in the genotypes of wheat because of salt stress and also establish that the salt-sensitive genotype had higher EL values as compared to the "salt-forbearing plants. There are numerous biochemical methods that defend plants alongside the destructive effects of salt stress." Phenolic complexes are the utmost copious "secondary metabolites in the plant kingdom as well as the most essential antioxidants against scavenging the too much free radicals that is produced by the bulk of stressors." Flavonoids are also recognized to have antioxidant properties (Hichem and Mounir 2009; Tohidi et al. 2017).

"During the course of earlier decades, investigators have constantly institute that the resilient connotation among polyphenols and abiotic stress forbearance is an exceptional prognostic of the degree of patience, and therefore can be utilized as a sign of upkeep of the redox state inside the cells (Hodaei et al. 2018). Though there are massive organizations of writings that in detail discourse phenolic compounds of the appetizing parts of the plant (e.g., seeds in cereals), chiefly due to the curiosity in well-being remunerations of polyphenol feeding, scarcity leftovers on examination that examines the incentives in arrears the improving influence of polyphenols on the phyto-noxiousness of photosynthetic tissues bring about by salt stress. Martinez et al. (2016) described a rise in the accretion of flavonoids in tomato plants in answer to abiotic stress corresponds with double defensive consequence as antioxidant in contrast to oxidative impairment prompted by the stress, and consequently as the health-endorsing complexes of edible plants."

The consequences of the investigation evidently indicate that Aegilops and wheat genotypes vary in case of the polyphenol's accumulation in their foliage. These complexes remained suggestively amplified against "salt stress." It has been described that salt stress-prompted a substantial rise in TPC (total phenolic content) in the "salt-forbearing genotype of wheat" (Kumar et al. 2017a). A substantial genotypic variance was detected in the TPC (total phenolic content) in durum wheat grains (Boukid et al. 2019). The outcome of the study commonly showed that "*Aegilops cylindrica* (male parent) had greater antioxidant property than female parents (wheat cultivars) in both control and salt stress situations. Additionally, the outcomes also spectacle that in association with female parent, amphidiploid plants had sophisticated antioxidant activities expressed by DPPH (2,2-diphenyl-1-picryl-hydrazyl-hydrate) (IC50)." In detail, the examination accessible "here is not only encouraged but also sustained our preliminary mechanism conferring genotypic alterations for antioxidant enzymes, malondialdehyde (MDA), and H_2O_2 in the same set of genotypes" (Kiani et al. 2021).

In the mechanism of oxidative stress, it has the ability to donate electrons and maintain electrons' redox reaction. The inactivation of antioxidants by reducing agents in redox reactions reduces reactive oxygen species at the expenditure of oxidative ions known as nonenzymatic antioxidants. The estimation of reducing power ions explores the homeostasis of redox reactions in the natural polyphenolic extract. Synthetic samples were compared with "ferric reducing antioxidant power" with IC50 equal to 0.3 mg/ml. These samples were capable of donating electrons to the process of "oxidative stress and produces reactive oxygen species." It has strongly reduced power which donates an electron to the reactive oxygen species. "The most plentiful polyphenols are ellagic acid, gallic acid, vanillic acid, chlorogenic acid, caffeic acid, etc." Accumulated phenolic acids increases the salt stress in the leaf tissues. The previous study reported that mostly abundant flavonoids are found in the leaf tissues (Sarker and Oba 2018a, b). Instead of this, these detected polyphenols deteriorate yield loss "under salt stress conditions." Therefore, the accumulation of total polyphenolic content plays a fundamental, biochemical, and physiological role in plant cell tissues. It helps to ameliorate Abiotic stress conditions (Sharma et al. 2019a). Besides, ferulic acids account for total phenolic content (87.10–90.60%) which ranges from 21.8 to 37.3 μg/g in the wheat grain." The yield of grains is an association between biochemical and physiological response to the plants, anthropogenically obligatory stressor conditions. In addition to this, these factor influences the genetic variety of plants. It depends upon yield grain variation and genetic diversity of wheat genotypes, and the degree of difference to ubiquitous in the environmental conditions. It affects negatively on yielding of grains both biochemical and physiological alterations. Salt stress effects on yield of grains and salinity of irrigated water reduces sodium chloride which decreases the yield of grains (Chamekh et al. 2016; Araus et al. 2008).

"Besides this, adverse and sturdy correlation coefficient of TPC (total phenolic content) and TFC (total flavonoid content) with IC50 (Half Maximal Inhibitory concentration) of DPPH (2,2-diphenyl-1-picryl-hydrazyl-hydrate) radicals revealed that there is contribution of phenolic compound to antioxidant potential in the known genotypes." Dykes and Rooney (2006) reported a similar correlation among RSA and TPC in cereals. It was also studied "that the hyper salt-tolerant genotype" has the considerable inhibition on the "DPPH (2,2-diphenyl-1-picryl-hydrazyl-hydrate) radicals between the known genotype. Also, it has been found that the genotypic variation and substantial increment in foraging of DPPH (2,2-diphenyl-1-picryl-hydrazyl-hydrate) (%) in the flowering plant of two among four wheat varieties in response to salinity stress and antioxidant activity of TPC (total phenolic content)" has also been confirmed by Kumar et al. (2017b). Additionally, a significant correlation was found between FAC (ferulic acid content) and TPC. Hura et al. (2007) revealed that a significant relationship occurs between "FAC (ferulic acid content) and TPC (total phenolic content) in triticale genotypes under drought stress circumstances. The present study revealed the CAC was correlated considerably through DPPH (2,2-diphenyl-1-picryl-hydrazyl-hydrate) scavenging rate. According to Yan et al. (2016) there is an increase in CA (chronological acid) associated with DPPH scavenging response induced by water stress in case of *Origanum vulgare*."

Ferulic acid or hydroxycinnamic acid is the originator of biogenesis of "lignin and vanillic acid" having antioxidant and age-defying roles. It serves as a restrictor of the enzyme that speed up the construction of unrestricted radical species and intensify the activity of scavenging enzyme as well as free radical scavengers. Hence, the activation of lignification inhibitors might be performed by salt stress which results in the accretion of ferulic acid (Boz 2015). No evidence is available till now, that explain the role of these phenolic acids to facilitate the stress in wild plant species. The biosynthetic pathways may explain the affirmative relation between chlorogenic acid and luteolin, ferulic acid and apigenin, and apigenin and luteolin as well. There is a significant contribution of multivariate regression analysis, "RAS (reticular activating system), TFC (total flavonoid content), and DPPH (2,2-diphenyl-1-picryl-hydrazyl-hydrate)." It has been reported that "phenolic and flavonoid compounds are basic nonenzymatic antioxidants that contain scavenging of reactive oxidation species" (Tohidi et al. 2017; Sharma et al. 2019c). Additionally, particularly these compounds are induced through oxidative stress throughout stress (Chen et al. 2019a, b, c).

7.7 Plant Phenolics

“Plants are exposed to different types of abiotic stresses during their life cycle and different genes are turned switched on and off, leading to the risen the level of different “metabolites and proteins, some of which might be responsible for discussing certain degree of defense against these stresses” (Ahmad et al. 2008; Jaleel et al. 2009). “Abiotic stress promotes the formation of active oxygen species within the cells” (Dar et al. 2017). “Phenolics comprises diverse secondary metabolites, viz., flavonoids, tannins, hydroxycinnamate esters, and lignin presently in large quantities in plant tissues and are actively associated in defense mechanisms combat the biotic and abiotic stress.” In comparison to nonstressed conditions, the plant sometimes produces phenolic in large quantities “under certain stress conditions” (Selmar 2008). “Phenolic compounds act as an antioxidant, stops the production of free radicals, and chelate the redox-active metal ions that are having the potential to catalyze lipid peroxidation” (Schroeter et al. 2002). “Phytophenolics, specifically polyphenols, act as antioxidants and support the primary ascorbate dependent detoxification system as an alternate defense mechanism of vascular plants in comparison to monophenols” (Yamasaki et al. 1995, 1999). “Polyphenols are most effective antioxidants in vitro than ascorbate and tocopherols and have an ideal chemical structure to neutralize the free radicals.” This antioxidant activity of polyphenols might be because they resonate the unpaired electrons (chain-breaking function) and “(termination of the Fenton reaction)” (Rice-Evans et al. 1997). Kagan and Tyurina (1998) “evidenced that phenolics are univalently oxidized to their individual phenoxyl radicals when they act as antioxidants either by enzymatic or direct radical scavenging mechanisms.”

Plants manufacture polyphenolics to adapt themselves under various “stress environments” such as UV radiation, drought, salt, metal, and low-temperature stress. Most plants commonly produce “phenylpropanoids” such as flavonoids and HCAs. Nevertheless, deposition of phenolics in plants can be induced by exposing them to abiotic and biotic stresses such as “UV radiation, high light illumination, low temperatures, wounding, low nutrients, and pathogen attack” (Dixon and Paiva 1995; Yamasaki et al. 1995). However, synthesis of some bioactive components becomes modulated under abiotic stress situations “drought where these act as antioxidants” (do Nascimento and Fett-Neto 2010). Phenols are the most common metabolites produced in plants, which are further divided into five subgroups “coumarins, flavonoids, lignins, phenolic acids, and tannins” (Gumul et al. 2007), produced in plants through “shikimic acid and chorismic acid pathways” (Solecka 1997). Along with the beneficial role of phenolic in plants they are also beneficial for animals (França et al. 2001; Amarowicz and Weidner 2009). During a stressful environment, some genes of the biosynthetic pathways are upregulated and some pathways are downregulated (Wróbel et al. 2005; Weidner et al. 2007, 2009; Dixon and Paiva 1995). In *Rehmannia glutinosa* under water scarcity and chilling condition the biosynthetic pathway of phenolic becomes upregulated Chung et al. (2006). Posmyk et al. (2005) reported that soybean exposure to cold stress increases the activities of enzymes, “PAL, CHS, and other enzymes involved in their biosynthesis and also phosphoenolpyruvate (PEP)-carboxylase activity also increases." Therefore, after analyzing all these findings it may be concluded that phenolic helps the plants to adopt them under different environmental stressful conditions like "hydration, dehydration, and methylation of cinnamic acid" (Lattanzio et al. 2009; Dixon and Paiva 1995).

7.8 Role of Plant Phenolic Against the Abiotic Stresses Induced ROS Production and Their Toxic Effects

Many changes in physio biochemical machinery of plants can lead reduction in the growth and yield of plant. These stress result in the quick alteration in the redox balance of cells along with the increased "production of oxygen species (ROS)" which causes damage to cellular organelles and affects the ROS-promoted signaling pathways. The excessive generation of ROS interferes with the normal physiological redox and hampers normal cellular functions as well as adversely suppresses the immune system, which indicates that plant requires the threshold quantity of ROS to carry out fundamental metabolic functions. "Unnecessary ROS formation during abiotic stresses increases itself leads to the production of ROS in exponential manner, which leads to the "peroxidation and destabilization of biological membranes." Rehman et al. studies that "heat stress and Zn deficiency leads to the decrement in growth (shoot and root biomass, and root length), subsequently decreases uptake of nutrients, increases peroxidation of lipids, and impairs the photosynthetic ability." "In plants, ROS generated from 1% to 2% of entire O_2 consumed in highly active cellular organellar such as chloroplast, mitochondria, and peroxisomes." Common ROS includes "singlet oxygen ($^1O_2$), superoxide radical (O_2^-), hydrogen peroxide (H_2O_2), and hydroxyl radical (^-OH)." Abiotic stresses disrupt the balance between the production and neutralization of ROS and favors the accelerated production of ROS which in turn damages fundamental macromolecules (nucleic acids, proteins, carbohydrates, and lipids) and sometimes causes the death of the cells. ROS induces damages to proteins due to the "oxidation of amino acid residues (e.g., cysteine) for the formation of disulfide bond of arginine, lysine, and threonine residues and finally results in the irreversible breakage in side chains and oxidation of methionine residues to sulfoxide." Generation of ROS also restricts the CO_2 fixation in chloroplast which are the major site for generation of ROS in green plants. "These ROS reacts with chlorophyll during photosynthesis and forms the chlorophyll triplet state which can rapidly produce $^1O_2$, and hence causes damage to photosynthetic complexes (principally PSII) and also interferes the photosynthetic molecular reaction cascade." Moreover, under abiotic stress, ROS production also increases in mitochondria which affect the cellular process in plants (24). It has been reported during Fenton reaction in mitochondria about 1–5% of O_2 consumed leads to the production of H_2O_2 which in turn gets converted into ^-OH. In addition to this, higher respiratory/photorespiratory metabolism requires higher electron transfer which leads to the excessive production of ROS and results in peroxidative damage to proteins (61). Peroxisomes are the principal sites for the generation of ROS, especially H_2O_2, having 2–50-fold higher load of H_2O_2 load than chloroplast and mitochondria, respectively. "H_2O_2 is involved in stress-induced oxidative damage and can pass easily across the lipid membranes." Under the physiological limit, various antioxidant defense mechanism neutralize these ROS. Whereas, excessive generation of ROS can downregulate the defense system, resulting in the generation of oxidative stress, cellular damage, and cell death (Fig. 7.1).

7.9 Protective Role of Phenolics Against Abiotic Stress Produced Reactive Oxygen Species in Plants

Under abiotic stress synthesis of secondary bioactive components such as polyphenols increases in plants. Phenolic compounds provide protection against the different types of abiotic stress because these compounds possess the antioxidative potential and free radical scavenging activity and ultimately result in the reduction in peroxidative damage in biomembrane systems thus protecting the cells against the ill effect of oxidative stress. The synthesis of phenolic compounds during environmental stress is controlled by the modified activities of different key enzymes of phenolic biosynthetic pathways including PAL and CHS (chalcone synthase). Increased activities of enzymes along with the upregulation of the gene transcription which encodes major enzymes of biosynthetic pathways, viz., "PAL, C4H (cinnamate 4-hydroxylase), 4CL (4-coumarate: CoA ligase), CHS, CHI (chalcone isomerase), F3H (flavanone 3-hydroxylase), F30H (flavonoid 3 0-hydroxylase), F305 0H (flavonoid 305 0-hydroxylase), DFR (dihydroflavonol 4-reductase), FLS (flavonol synthase), IFS (isoflavone synthase), IFR (isoflavone reductase), and UFGT (UDP flavonoid glycosyltransferase)."

Metals also induce oxidative stress in plants by accelerating the production of deleterious ROSs and finally lead to toxic manifestations and retardation of growth (1,18,788). Nonetheless, increased synthesis of plant phenolics under metal-induced stress protects the plants against "oxidative stress." "Flavonoids can increase the chelation process in metals and helps in reduction of deleterious hydroxyl radicals in plants," and this provided strong evidence that biosynthesis of flavonoids increases during the metal toxicity-induced oxidative stress. Metal stress-induced toxicity leads to the accumulation of particular flavonoids which are associated with the defense of plants is increased including anthocyanins and flavonoids. "Accumulation of phenolics occurs due to the upregulation of genes involved in the synthesis of phenylpropanoid enzymes such as phenylalanine ammonia lyase, chalcone synthase, shikimate dehydrogenase, cinnamyl alcohol dehydrogenase, and polyphenol oxidase," which depend on the modulation of the level of transcript genes coding the enzymatic biosynthesis due to metal stress. Flavonoids are having predominant free radical scavenging ability such as H_2O_2 and play a significant role in the phenolic/ascorbate-peroxidase cycle (98.99). "Two major enzymes, Viz., Shikimate dehydrogenase (SKDH) and glucose-6-phosphate dehydrogenase (G6PDH) contribute in catalyzing the biochemical reactions required for the generation of essential precursors of phenylpropanoid pathways." "Cinnamyl alcohol dehydrogenase

(CADH) catalyzes biochemical reactions required for the biosynthesis of lignin." Metal-induced oxidative stress leads to the production of free radicals, in response to this plant stimulates the phenylpropanoid biosynthetic pathway and upregulation of various enzymatic activities such as "PAL, SKDH, G6PDH, and CADH." Additionally, polyphenol oxidase (PPO) neutralizes the ROS species and increases the tolerance in plant against metal-induced abiotic stress.

Accumulation of phenolics is important to compensate for the adverse effect of stressors like drought. Transcriptomic and metabolomic investigations revealed that synthesis and accumulation of flavonoids increase under drought stress to increase the survivability of the plant. Drought stress initiates the biosynthesis and accumulation of flavonols to protect the plant against the toxic effect of free radicals. These flavonoids work as antioxidants and prevent the negative effect of ROS species and these flavonoids are also indicators of water deficit example tomato. Accumulation of flavonoids in the cytosol can effectively detoxify the H_2O_2 molecules produced due to the "drought stress and at the end oxidation of flavonoids along with ascorbic acid-mediated reconversion of flavonoids into primary metabolites. The major cause for the drought-induced deposition of polyphenols is due to the activation of phenylpropanoid biosynthetic pathway."

"Reactive oxygen species (ROS) such as superoxide anions, hydrogen peroxide, and hydroxyl" ions during salt stress needs the stimulation of a well-orchestrated and well-tuned antioxidant system in a plant to downregulate the production of ROS. Phenolic compounds being strong antioxidants helps in the neutralization of harmful ROS in plants under salt stress. Furthermore, during salt stress in plants, phenylpropanoid biosynthetic pathway becomes activated and leads to the generation of different phenolic compounds which acts as powerful antioxidative capability. "Various genes including VabHLH1 are associated in the increased generation of flavonoids by controlling the genes of the biosynthetic pathways and confers the salt stress to plants." NtCHS1 contributes to the biosynthesis of flavonoids under salt stress as reported in tobacco plants; however, accumulation of these flavonoids directly increases the free radicals. Under the saline conditions biosynthesis of flavone increases by upregulation of the flavone synthase gene expression in glycine max GmFNSII-1 and GmFNSII-2 and in some plants under the saline stress various phenolic acids becomes accumulated such as "caffeic acid, caftaric acid, cinnamylmalic acid, gallic acid, ferulic acid, and vanillic acid." It has been reported that the synthesis of anthocyanins increases in growing plants under saline environment.

7.10 Conclusion and Future Perspectives

The plant phenolic are considered as communal and extensive tributary metabolites. They contain significant pool of biological organic variety with an enormous number of enzymes and compounds and an extensive range of procedures for the regulation of genes as well as transportation of enzymes and metabolites. Phenolic compounds are gathered in the plant tissue and provide a robust reaction towards hostile ecological stresses such as pathogen attack, wounding, deficiency of minerals, and temperature stress. Development of plant is enhanced by polyphenols that interact with ethylene which is a plant growth hormone. Also, these compounds act as indicators for lignin and suberin that are polymerized into the cell wall. Recent studies have shown that cell wall thickening helps the plant in preventing freezing stress. An elevation in the thickening of the cell wall reduces the risk of cell collision for the period of cold prompted mechanical strength and dehydration therefore preventing cold stress in plants. Polyphenols impact the source and movement of organic and inorganic nutrients present in soil accessible to plant or microbes. They also respond to nutrient deficiency therefore offering means for detecting nutrients disorder before the onset of symptoms. In spite of few works done on phenolic compounds biosynthesis and their deposition as adaptive feedback in contrast to abiotic stresses, a thorough study dealing with the mechanism behind their deposition and their connections between other cell metabolites should be done in order to have a better indulgent of their elevated expression and carrying forbearance under such conditions.

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Phenolics Biosynthesis, Targets, and Signaling Pathways in Ameliorating Oxidative Stress in Plants

8

Manpreet Kaur, Yamini Tak, Surekha Bhatia, and Harjeet Kaur

Abstract

In plant cells, acquaintance to drought, salinity, temperature excesses, air pollutants, heavy metals, ultraviolet radiations, and pathogens outcomes in the reactive oxygen species (ROS) formation due to which intracellular redox milieu modifies ultimately effecting signaling pathways and cell fate. In the context of their response, plants exhibit increased phenolic compounds biosynthesis to cope up with the environmental constraints. Since phenolics are specialized metabolites concerned with essential cell functions like development, cell division, photosynthetic activity, hormonal regulation, and scavenging of damaging ROS and molecular active oxygen species. The signaling pathways influenced involve various targets namely NADPH oxidases, phosphotidyl inositol-3-kinases (PI3K), protein kinase targets of rapamycin (TOR) auxin transport, and phenylpropanoid pathway. On the other hand, phenolics as antioxidant act in phenolic/ascorbate/peroxidase system that eliminates harmful peroxides. Here, we explore the functions/biosynthesis, targets, and signaling pathways of phenolics not only relative to unfavorable conditions or stress, but also in the wider perspectives of environmental responses and plant development.

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Phenolics · Signaling molecules · Amelioration · Oxidative stress · Antioxidant

8.1 Introduction

Plants productivity is severely affected by constantly changing environments due to several biotic and abiotic stresses which include drought, salinity, temperature extremes, i.e., chilling and heat, flood, heavy metals, ultraviolet radiations, and pathogens (Choudhary 2012; Ramegowda et al. 2020). Owing to these, an imbalance between amid antioxidants and pro-oxidants occurs, in due course causing oxidative stress in plants. Biochemically in favor of the former, plant cell is considered by an improved metabolism favoring reactive oxygen species (ROS) formation (Van Breusegem and Dat 2006). Environmental stresses inhibit Calvin or C3 cycle which alters ATP and NADPH consumption and carbon dioxide (CO_2) fixation eventually exacerbating the situation in mitochondria and chloroplast where imbalance between reductant consumption and electron acceptor regeneration leads to electron transfer to alternative acceptors, mainly molecular oxygen (Walker et al. 2016) such as, chilling, drought stress, and chemical agents limit CO_2 fixation despite the fact that light-driven transport of electrons proceeds at higher rates. The surplus excitation energy transfer to O_2 or its univalent reduction led to ROS formation which is an inescapable feature of life and plants evolved an antioxidative defense system to keep its level under control (Bhattacharjee 2019). Plants being sessile need to acclimatize with the varying environments caused by several stress conditions and accumulation of phenolics is reflected as an adaptive response to it (Hasanuzzaman et al. 2013).

Polyphenols or plant phenolic compounds are the furthermost occurring and predominated secondary metabolites in plant kingdom having considerable morphological, biochemical, and physiological (Aviles-Gaxiola et al. 2020; Marchiosi et al. 2020). These are described by a minimum one aromatic ring (C6) having one or more OH groups and monomeric and polymeric phenols are produced from cinnamic acid; emerge from shikimate or malonate pathway. Plant phenolics act as a key defense compound against unfavorable conditions, moreover they also exhibit vital activities like antioxidant, anti-inflammatory, and antimicrobial activity (Moura et al. 2010). Many phenolic compounds produced in plants are known, identified, and their characterization is ongoing and increasing continuously (Rohela et al. 2020). Plant phenolics constitute flavonoids and their derivatives, hydroxycinnamic acids (HCAs), their glycosides and amides, suberin, lignin, sporopollenin, etc. (Bärlocher and Graça 2020). Polyphenols such as flavonoids and HCAs act as electron donors for guaiacol peroxidases and scavenge hydrogen peroxide (H_2O_2) proficiently (Tsao 2010). In chloroplast under several stress conditions, ascorbate pools get oxidized might exceed their scavenging capacity. Polyphenols as antioxidant play a vital *via* supporting the chief ascorbate-dependent detoxification mechanism by means of standby defense pathway and help to deal with the severe stress environments (Naikoo et al. 2019). Therefore, this chapter emphasizes targets, signaling, and the roles of phenolics in plant metabolism of ameliorating oxidative stress and tolerance.

8.2 Molecular Structure, Classification, and Biosynthesis of Phenolics

Phenolics are very large group of chemical compounds having great structural diversity extending from simple molecules to polymers known as polyphenols and can also exist as esters and methyl esters functional derivatives (Vuolo et al. 2019). They contain a minimum one aromatic benzene ring (C6) with one or more OH groups attached. Phenolics are classified in various means such as carbon atoms number present in the molecule, i.e., simple phenolics, benzoquinones containing 6 carbon atoms, acetophenones, and phenylacetic acids containing 8 carbon atoms, phenylpropanoids (coumarins, isocoumarins, chromones, chromenes) containing 9 carbons, rare hydroxycinnamic acids, rare to common naphthoquinones containing 10 carbons, xanthones containing 13 carbons, rare stilbenes and anthraquinones containing 14 carbons, rare flavonoids and isoflavonoids containing 15 carbons, common betacyanins containing 18 carbons, rare lignans and neolignans containing 18 carbons $(C6–C3)_2$, biflavonoids, exceptional lignin $(C6–C3)_n$, melanins containing N carbons $(C6)_n$, condensed tannins (proanthocyanidins flavolans) $(C6–C3–C6)_n$ (Naikoo et al. 2019). The distinctive biological, physical, and biochemical activities of each compound depend in the number of carbon atoms present and their characteristics. In plants, glycolysis and hexose monophosphate pathway (HMP) intermediate, i.e., phosphoenolpyruvate and erythrose-4-phosphate act as precursors for phenolics biosynthesis through phenylpropanoid or shikimic acid pathway or specific flavonoid pathway (Lavhale et al. 2018). Firstly, ribulose-5-phosphate is formed from glucose-6-phosphate with the help of glucose-6-phosphate dehydrogenase enzyme through which HMP converts into erythrose-4-phosphate which reacts with phosphoenolpyruvate generated through glycolysis, to form phenylalanine through shikimic acid pathway. Then phenylalanine converts into trans-cinnamic acid with the help of phenylalanine ammonia lyase (PAL) enzyme. Some other phenolic compounds for example flavonoids, lignins, tannins, coumarins, lignans, and monolignols are synthesized by phenylpropanoid pathway (Lavhale et al. 2018).

8.3 ROS Generation, Oxidative Stress, and Phenolics

Plants being sessile are vulnerable to formation of ROS because of their exposure to various unfavorable environmental conditions (Dvorak et al. 2020). Normally under the nonstressed conditions, these toxic reduced oxygen species are produced in fewer amounts through redox reactions occurring in some specialized organelles such as mitochondria, chloroplast, nucleus, and cytoplasm as well (Zechmann 2014). But when plant is under the stress conditions either abiotic such as temperature extremes, drought, salinity, UV-light exposure, heavy metals or biotic stress such as pathogen or herbivore attack, their production enhanced to a large extent which has the devastating impact on plants; survival as these reduced oxygen species are exceptionally reactive and can oxidize a large number of biological molecules (Vinod 2012).

The ROS formation results from reduction of oxygen molecule by adding one, two, or three e^{-}(s) to form oxygen free radical ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2), or hydroxyl radical ($^{\bullet}OH$) (Mehler reaction), respectively or by transfer of excess excitation energy to O_2 resulting in singlet oxygen formation ($^1O_2$). Firstly during O_2 reduction, oxygen-free radical ($O_2^{\bullet-}$) is produced by Mehler reaction, secondly reduction of O_2 produces H_2O_2, which is a relatively long-lived molecule and can oxidize SH groups (Singh et al. 2019) and thirdly formation of hydroxyl radical ($^{\bullet}OH$) which is utmost reactive amongst ROS thereby causing oxidative stress. It has been reported that H_2O_2 in the presence of $^{\bullet}O_2^{-}$ can generate highly reactive hydroxyl radicals ($^{\bullet}OH$) by Haber Wiess reaction which is a metal-catalyzed process; therefore H_2O_2 scavenging is vital to circumvent oxidative impairment in plant cells (Kehrer 2000). In the occurrence of heavy metals like Cu^{+} and Fe^{2+}, H_2O_2 converts into $^{\bullet}OH$ via metal-catalyzed Fenton reaction. In chloroplast, ROS restricts CO_2 fixation as it rejoins with chlorophyll and forms triplet state which produces $^1O_2$ rapidly which damages photosynthetic complex particularly PSII, as a result of disturbing photosynthetic reactions (Foyer 2018). Approximately 1–5% of oxygen utilized in mitochondria leads to the formation of H_2O_2, successively producing $^{\bullet}OH$ which results in protein oxidation. Apart from this, peroxisomes are likewise leading sites for generation of ROS, chiefly H_2O_2 which is in comparatively much higher concentration.

The presence of excess ROS in the cellular environment is threatened to structure of various sub-cellular organelles, biochemical processes, micromolecules, macromolecules, and eventually it devastates the plants' defense system, producing oxidative stress, cellular damage, and cell disease (Kohli et al. 2019). Contrary to excess generation of ROS, redox state obstructs cellular processes and disturbs plant growth and development, signifying that an optimum ROS level is required for usual plant functioning. The excess ROS production in rejoinder to various unfavorable stresses has been anticipated to coordinate various defense mechanisms in plants cells to defend them from oxidative impairment and has been a chief reason for the advent of some specified natural products (Lattanzio 2013). In response to the former, biosynthesis and accumulation of secondary metabolites comprising phenolics get boosted in plant tissues reflecting as an adaptive phenomenon. Various studies showed the augmentation of phenolics in various plant tissues in stress or unfavorable conditions (Naikoo et al. 2019). Plant phenolics perform several physiological functions which are necessary for plants' adaptation and existence in response to different disturbances and act as antioxidants thereby scavenge excess ROS eventually defending the plant from harsh impacts of oxidative stress (Lattanzio et al. 2012).

8.4 Phenolics Targets and Modulation of Various Signaling Pathways

In this, we focus on the targets of plant-derived phenolics and signaling pathways of various biochemical processes which are essential for survival and adaption in response to environmental disturbances. The association between targets and signaling pathways may play an imperative role in providing the information regarding the importance of phenolics in ameliorating oxidative stress and acting as a defense molecule as elucidated in Fig. 8.1.

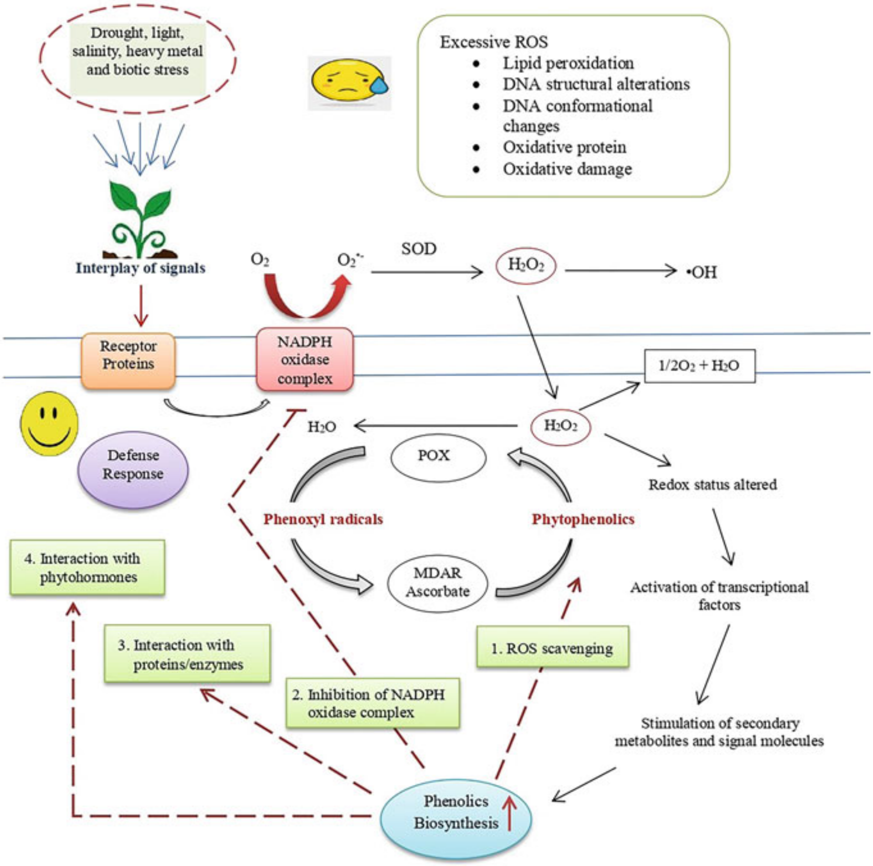

Fig. 8.1 Role of phenolics and signaling pathways involved in ameliorating the oxidative stress in plants. *Abbreviations*: *MDAR* monodehydroascorbate reductase, *POX* peroxidase, *ROS* reactive oxygen species, *SOD* superoxide dismutase

8.4.1 Antioxidant Defense System: Phenolics as Antioxidants

ROS in plants is primarily formed by the photosynthetic ETC (electron transport chain) under the unfavorable conditions (Dumanović et al. 2020). Amongst all, H_2O_2 is of great stability and is permeable across the plasma membrane and can generate OH^- which is highly reactive (Sharma et al. 2012); therefore, to avoid its deleterious effect in plants, it is very crucial to scavenge H_2O_2. Usually, ascorbate-glutathione pathway is the most vital mechanism to detoxify H_2O_2 into water. But later on, it has been demonstrated that polyphenols are also efficient in H_2O_2 scavenging by serving as e^- donor for guaiacol peroxidases. During extreme stress conditions when chloroplast ascorbate pools turn out to be oxidized, polyphenolics serve as the standby antioxidant defense system thereby supporting chief ascorbate-dependent scavenging system (Świętek et al. 2019). Additionally, in vitro studies revealed that phenolics can directly scavenge ROS ($^{\bullet}O_2^-$, H_2O_2, $^{\bullet}OH$, and $^1O_2$) because of their antioxidant action to give e^-(s) or hydrogen atoms (Moukette et al. 2015). On the other hand, there is one other mechanism elucidating antioxidant role of phenolics that they inhibit peroxidation of lipids through deceptive alkoxyl radical which cringe free radical chain oxidation under oxidative stress (Félix et al. 2020). However, this activity varies depending upon phenolic structure, presence, and position of hydroxyl groups. Later on, it has been revealed that phenolics alter lipid peroxidation kinetics by changing their packaging in such a way that they can bind phospholipids polar head resulting in stabilization of membranes and integrity maintenance by this means limits diffusion of free radicals, access of damaging molecules toward phospholipids bilayer hydrophobic part and peroxidative reactions.

8.4.2 NADPH Oxidase, a Key Source of ROS: Phenolics as Inhibitors

NADPH oxidase, a multisubunit complex enzyme, is the utmost significant source of ROS generation. Excessive increase in ROS under stress conditions is very deleterious as it leads to the damage to lipid membranes, cellular organelles, and disruption of cellular homeostasis. It has been reported that expression of NADPH oxidase is augmented under the excessive ROS condition (Huang et al. 2019). Both in vitro and in vivo conditions, phenolics especially flavonoids inhibit NADPH oxidase activity ultimately devastating excess ROS generation. This activity of phenolics is due to their high antioxidant strength and ability to disrupt the assembly of NADPH subunits (Yousefian et al. 2019). In this way, phenolics can decline oxidative stress through inhibiting ROS producing enzymes, i.e., NADPH oxidase, direct free radicals scavenging or metal interaction. As phenolics are classified to several groups according to their structure, this activity varies amongst different classes of phenolics and highest being possessed by flavonoids due to the occurrence of two OH groups in the ortho position of ring B of their base skeleton which generates a steady radical with ROS indirectly scavenges excess ROS (Baskar et al. 2018). Moreover, occurrence of other OH groups in the ring B increases their activity due to formation of stable half quinone radical (Treml and Šmejkal 2016). Likewise, 2,3-double bond and 4-keto in ring C basic structure of flavonoids enhances this activity. Thus, quercetin possesses developed bioactivity than catechin due to better delocalization of the formed radical electron (Salehi et al. 2020). However, the model structure for NADPH oxidase inhibition is the presence of benzene ring with OH group and a methoxy group at the ortho position and a saturated bond and a keto group at position 2–3 and 4 respectively, in ring C. Hence, phenolics possessing such type of structure are further influential in contrast to those which have two OH groups in benzene ring.

8.4.3 Targets of Rapamycin (TOR) and Phosphotidyl Inositol-3-Kinases (PI3K): Potential Targets of Phenolics

TOR kinase recognized as a chief regulator of development in plants and incorporates nutrient and environmental signals in eukaryotes (McCready et al. 2020). This is predominantly imperative in plants, as due to their sessile nature, they requisite to sense and retort to outward signals to appropriately synchronize multicellular progression. However, TOR activity must be in control as its over expression can lead to the cellular over-proliferation ultimately leading to tumor formation in plants. Thus, TOR is crucial for proper development of plants in milieu of available resources for their growth.

Unregulated and uncontrolled cellular proliferation is the core hallmark of developmental deformities. Cells proliferation is under the control of sequences of various cyclin-dependent kinases which are basically serine tyrosine kinases and act as a checkpoint to decide whether the cell has to go through division or arrest at that point (Atkins and Cross 2018). Various phenolic compounds act as cell cycle regulatory agents. Epigallocatechin-3-gallate as an enriched polyphenol extracted from green tea has shown various antiproliferative properties via targeting PI3K and Akt ultimately decreasing its phosphorylation level (Mirza-Aghazadeh-Attari et al. 2020). Pomegranate being enriched with polyphenols showed antitumor properties on various types of cancerous. Likewise, Banerjee et al. reported in Sprague-Dawley rats that decline in cellular proliferation was found when it was supplied with pomegranate juice (Banerjee et al. 2013). A flavonoid called myricetin present in grapes and berries possesses antiproliferative properties on glioblastoma multiform cells because of its binding to PI3K and JNK ultimately declining PI3K/Akt and JNK signaling pathway expressions (Vidak et al. 2015). Both in vivo and in vitro studies demonstrated that a flavonoid called fisetin showed satisfactory decline in proliferation of cancer-causing cells by inhibiting PI3K/Akt/mTOR signaling pathways.

8.4.4 Auxin Transport and Phenylpropanoid Pathway: Role in Photoprotection

Plant's shape is controlled by the irradiance of sunlight, such as shady plants or sciophytes with large and thin leaves and extended internodes and sunstroke plants or heliophytes with small internodes and short, thick leaves. Phenolics are optimally located either in vacuoles, trichomes, epidermal cell walls, and chloroplast or in nucleus reduce oxidative damage induced by sunlight irradiance or UV-B stress in the sites of ROS production eventually protects DNA damage (Agati et al. 2020). The interactions between the phenolics and auxins which are synthesized through shikimate pathway from different precursors have biochemical, morphological, and physiological alteration in the metabolism of plants likewise phenolics affect the auxin transport and act as defense signaling molecules (Ahmed et al. 2020). Phenolic compounds especially flavonoids modify auxin movement and actively inhibiting basipetal transportation for being capable of binding to the ATP sites of auxin efflux facilitator proteins called PIN proteins, hence capable of regulating plant development under varying sunlight irradiance intensity (Peer and Murphy 2007). This property is dependent on structure of flavonoids, B-ring orthodihydroxy substitution, and degree of C2–C3 bonds unsaturation. As morphological traits in sunlight irradiance like plant's shape, internodes length, leaf size, and thickness are under control of hormones especially auxins and flavonoids-controlled auxin movement plays a role in regulating architecture of individual-organ and whole-plant and increases self-shading (Buer and Djordjevic 2009). Some phenolics such as flavonoids with substituted orthodihydroxy B-ring inhibit free radicals' formation either via metal ions chelation or decreasing xanthine oxidase activity (Eghbaliferiz and Iranshahi 2016). This property may provide a good explanation of sudden rise in dihydroxy to monohydroxy B-ring substituted flavonoids ratio under UV radiation or high sunlight stress. Hence, modifications in phenylpropanoid metabolism in stress conditions primarily reduced the oxidative damage.

8.5 Role of Phenolics in Stress Tolerance

Phenolics in plants are mostly deliberated as key defense compounds contrary to oxidative stress produced by the ROS accumulated under environmental stresses, such as salinity, temperature extremes, UV light, heavy metals, nutrient deficiency, and heavy metals (Kumar et al. 2020b; Naikoo et al. 2019). Then increased phenolics content deliberates an array of physiological roles which help the plants to acclimatize and endure in such environmental disturbances (Table 8.1).

8.5.1 Light Stress

Oxidative stress induced by high sunlight exposure or UV-B radiation in plants modifies metabolism and badly affects membranes, DNA, and proteins. In response

Table 8.1 Role of phenolics in ameliorating diverse stresses (UV light, salinity, drought, heavy metal, and temperature stress)

S. no.	Stress	Plant species	Status of phenolic compound	Reference
1.	UV light	*Ribes nigrum*	Escalation in phenolics content especially anthocyanins, hydroxycinnamic acids, flavonols, and hydroxybenzoic acids	Huyskens-Keil et al. (2012)
		Kalanchoe pinnata	Rise in total flavonoids and quercitrin content	Nascimento et al. (2015)
		Arbutus unedo	Increase in phenolics such as theogallin, avicularin, and juglanin	Nenadis et al. (2015)
		Vitis vinifera	Proliferation in phenolics such as astilbin, quercetin, malvidin, myricetin, gallic acid, vanillic acid, protocatechuic acid, and kaempferol	Berli et al. (2011), Alonso et al. (2016)
		Brassica oleracea	Increase gallic acid and sinapic acid content	Moreira-Rodriguez et al. (2017)
		Solanum lycopersicum	Rise in total phenolics	Mariz-Ponte et al. (2018)
		Lactuca sativa	Rise in total phenolics contents, flavonoids and anthocyanins, phenolic acids	Sytar et al. (2018)
		Caryopteris mongolica	Upregulation of phenylpropanoid pathway enzymes resulting in increased phenolics content	Liu et al. (2012)
		Vigna radiate		Goyal et al. (2014)
		Fragaria × *ananassa*		Xu et al. (2017)
		Triticum aestivum		Chen et al. (2019a, b)
		Cuminum cyminum		Ghasemi et al. (2019)
		Daucus carota	Increase in phenolics biosynthesis	Surjadinata et al. (2021)
		Cichorium intybus	Phenolics content enhanced	Sytar et al. (2020)
2.	Salinity	*Cynara cardunculus*	Rise in phenolics including luteolin-*O*-glucoside, gallocatechin, leucocyanidin, and quercitin	Lucini et al. (2016)
		Olea europaea	Enhanced expression of phenylpropanoid pathways resulted in the increased amount of total phenolics, kaemperol, and quercetin	Rossi et al. (2016)
		Solanum lycopersicon	Rise in total caffeoylquinic acid	Martinez et al. (2016)
		Thymus spp.	Rise in phenolics including caffeic acid, luteolin, gallic acid, cinnamic acid, trans-2-hydroxycinnamic acid,	Bistgani et al. (2019)

(continued)

Table 8.1 (continued)

S. no.	Stress	Plant species	Status of phenolic compound	Reference
			syringic acid, rosmarinic acid, rutin, naringenin, quercitrin, vanillic acid, and apigenin	
		Ocimum basilicum	Enhanced content of phenolics especially caffeic acid, rosmarinic acid, caftaric acid, quercetin-rutinoside, and cinnamyl malic acid	Scagel et al. (2019)
		Lonicera japonica Thunb.	Elicited phenolics biosynthesis	Yan et al. (2020)
3.	Drought	*Vitis vinifera*	Rise in the phenolics like caffeic acid, ferulic acid, trans-resveratrol-3-*O*-glucoside, cis-resveratrol-3-*O*-glucoside, kaempferol-3-*O*-glucoside, cyanidin-3-*O*-glucoside, quercetin-3-*O*-glucoside, and catechin, epicatechin, caftaric acid, epicatechin gallate, and enhanced expression of phenylpropanoid pathway	Castellarin et al. (2007), Griesser et al. (2015)
		Olea europaea	Phenolics accumulation increased	Mechri et al. (2020)
		Salix daphnoides and *Salix purpurea*	Increase in phenolics biosynthesis	Köhler et al. (2020)
		Olea europaea	Rise in content of phenolics such as kaempferol derivatives, oleuropein, and lucidumoside C	Dias et al. (2021)
4.	Heavy metal	*Erica andevalensis*	Phenolics biosynthesis enhanced under Cd stress	Márquez-García et al. (2012)
		Fagopyrum esculentum	Rise in total phenolics, flavonoids, anthocyanin content, and phenylpropanoid pathway enzymes	Smirnov et al. (2015)
		Ocimum basilicum	Phenolics biosynthesis enhanced under Al and Cd stress	Đogić et al. (2017)
		Vaccinium corymbosum L.	Increase in content of phenolic compounds under Al and Cd stress	Manquián-Cerda et al. (2018)
		Solanum lycopersicum	Increase in phenolics biosynthesis under heavy metal stress	Dursun et al. (2019)
		Cicer arietinum	Phenolics enhanced under heavy metal stress	Bhagyawant et al. (2019)
		Kandelia obovata	Increased biosynthesis of phenolics under Cd and Zn stress	Chen et al. (2020)
		Hordeum vulagare	Phenolics accumulation increased under combined Cd and Cu stress	Lwalaba et al. (2020)

(continued)

Table 8.1 (continued)

S. no.	Stress	Plant species	Status of phenolic compound	Reference
		Malva parviflora	Enhanced phenolics accumulation under Cd stress	Zoufan et al. (2020)
5.	Heat and cold	*Juglans regia* L.	Increased expression of phenylpropanoid pathway enzymes leading to accumulation of phenolics under cold stress	Christopoulos and Tsantili (2015)
		Nicotiana langsdorffii	Total phenolics content including *p*-coumaric acid, chlorogenic acid, cryptochlorogenic acid, and ferulic acid increased under heat stress	Ancillotti et al. (2015)
		Lens culinaris	Rise in total phenolics and flavonoids including gallic acid, chlorogenic acid, ferulic acid, salicylic acid, and naringenin under heat stress	Swieca (2015)
		Nicotiana tabacum	Modifications in the several metabolites of phenylalanine metabolic pathway resulting in increased accumulation of phenolics under heat stress	Zhou et al. (2018)
		Festuca trachyphylla	Rise in phenolic compounds content such as salicylic acid and vanillic acid under heat stress	Wang et al. (2019a)
		Prunus persica	Enhanced phenolic compounds content such as catechin, cholorogenic acid, neo-cholorogenic acid, rutinoside under cold stress	Wang et al. (2019b)
		Solanum lycopersicum L.	Increase in phenolics biosynthesis under heat stress	Alsamir et al. (2021)

to it, phenolics synthesized in plants protect them from these harmful radiations by acting as UV direct shields and amending antioxidant defense system at cellular and molecular levels. It has been demonstrated in literature in various plant species that synthesis of phenolics especially flavonoids, isoflavonoids, psoralens, and phenolic acid esters enhanced under light stress (Michalak 2006; Falcone Ferreyra et al. 2012; Winkel-Shirley 2002; Liang et al. 2006) and prevent from deleterious effects of harmful radiations. With light manipulation using different colors and intensities, many phenols, flavones, and flavonols elicited and reported to have many health beneficial bioactivities like antioxidant, cardioprotective, and anti-inflammatory (Gutiérrez-Grijalva et al. 2020). A study on the mutants of *Arabidopsis* that has the blocked biosynthesis of flavonoids showed the functions of phenolics in stress tolerance which coincides with the increase content of ROS. This higher ROS accumulation preceded the rise in membrane injury, lipid peroxidation, and decrease in chlorophyll content, CO_2 assimilation, and biochemical pathways alterations (Wani et al. 2018). Applying UV radiations in whole cucumber and barley seedlings enhanced the phenolics biosynthesis. Various reports in literature showed that exogenous supply of phenolics augments plant growth and productivity under light stress conditions. Likewise, phenolic compounds especially flavonoids production increased in the roots of pea plants, *Picea abies* and *Catharanthus roseus* during exposure to UV (300–400 nm) light. Moreover, Perez-Lopez et al. (2018) phenolics content augmented in lettuce when developed in high light and elevated CO_2. It has been verified in numerous plant species that the chalcone synthase expression is enhanced transcriptionally under UV light, providing a good explanation of increase in flavonoids under such type of stress (Kreuzaler et al. 1983; Jenkins et al. 2001; Qian et al. 2019; Park et al. 2020). In general, effects of phenolics in mitigating the adverse effects of light stress have been ascribed to some enzymatic reactions' activation, stabilization, and protection of membranes and the photosynthetic apparatus from oxidative damage

8.5.2 Salinity

Salinity outcomes excessive ROS production in plants and necessitates the stimulation of well-organized antioxidant defense system to counteract its propagation. Being influential antioxidative agents, phenolics scavenge detrimental ROS under salinity in various plants such as *Salvia mirzayanii* (Valifard et al. 2014), *Triticum aestivum* (Kaur and Zhawar 2015), *Chenopodium quinoa* (Aloisi et al. 2016), *Mentha piperita* (Çoban and Baydar 2016), *Amaranthus tricolor* (Sarker and Oba 2018), *Thymus vulgaris* L. (Bistgani et al. 2019), and *Hordeum vulgare* (Ma et al. 2019). Likewise, increase in total phenols and flavonoids has been showed by Wang et al. 2016 in *Carthamus tinctorius*. Additionally, increase in various phenolic compounds content such as caffeic acid, caftaric acid, cinnamyl malic acid, feruloyl tartaric acid, quercetin-rutinoside, and rosmarinic acid has been reported in *Ocimum basilicum* (Scagel et al. 2019). Al-Ghamdi and Elansary (2018) demonstrated that phenolics such as caffeic acid, robinin, chlorogenic acid, rutin, and apigenin enhanced in *Asparagus aethiopicus* under salinity stress. It has been studied that phenolic content augmentation induced by salinity stress is primarily by the outcome of phenylpropanoid pathway activation which leads to the accretion of several phenolic compounds possessing sturdy antioxidative property. Ben-Abdallah et al. 2019 reported that increase in quercetin 3-β-D-glucoside, caffeic acid, and total phenolic levels in *Solanum villosum* due to enhanced phenylalanine ammonia lyase and flavonol synthase expression. Similarly, in *Fragaria ananassa*, *Salvia mirzayanii*, and *Salvia acrosiphon*, increased transcript levels of phenylalanine ammonia lyase and flavonol synthase were demonstrated in salt stress (Perin et al. 2019; Valifard et al. 2015).

8.5.3 Drought

Drought stress has an adverse impact on agricultural productivity owing to its damaging effects on plant survival and development. Various studies showed that phenolics level heightened in drought conditions in several plants such as *Triticum aestivum* (Ma et al. 2014), *Lactuca sativa* (Galieni et al. 2015), *Larrea* spp. (Varela et al. 2016), and *Ocimum* spp. (Pirbalouti et al. 2017). It has been revealed by metabolomic and transcriptomic approaches that accumulation of phenolics is imperative to develop drought resistance in wild-type *Arabidopsis thaliana* mutants by Nakabayashi et al. (2014). Drought stress delimited the biosynthetic pathways resulting in enhanced-to-enhanced accumulation of phenolics and flavonoids in plants which efficiently detoxify ROS induced by water scarcity conditions ultimately protecting it from adverse effect and abnormalities caused by stressful conditions (Kumar et al. 2020a) such as quercetin contents improved considerably in white clover (Ballizany et al. 2012), flavonols in *Crataegus laevigata*, *Crataegus monogyna* (Kirakosyan et al. 2003), and *Cistus clusii* (Hernández et al. 2004), flavonoids like kaempferol and quercetin in tomato (Sanchez-Rodriguez et al. 2011), flavonoids in wheat leaves (Ma et al. 2014), total phenolics in *Brassica napus* (Rezayian et al. 2018), phenolic metabolites like vanillic acid and 4-hydroxycinnamic acid in *Cucumis sativus* (Li et al. 2018), and total flavonoids and polyphenols in *Thymus vulgaris* (Khalil et al. 2018) under drought stress. Phenolic compounds accumulation induced by drought stress is basically the outcome of phenylpropanoid biosynthetic pathway alteration as it controls several chief genes encoding main enzymes of this pathway ultimately stimulating phenolics biosynthesis. Similarly, content of phenolics such as luteolin-7-*O*-glycoside, rutin, chlorogenic acid, kaempferol, caffeic acid, apigenin, 1,3-dicaffeoylquinic acid, and luteolin increased under drought stress of 21 days due to enhanced transcript levels of phenylalanine ammonia lyase, chalcone synthase, chalcone isomerase, and flavonol synthase in *Achillea* spp. (Gharibi et al. 2019). Under water scarcity conditions, enhanced expression of various enzymes of phenylpropanoid pathway is reported in *Lotus japonicas* (Garcia-Calderon et al. 2015), *Chrysanthemum morifolium* (Hodaei et al. 2018), *Nicotiana tabacum* (Silva et al. 2018), and *Fragaria ananassa* (Perin et al. 2019).

8.5.4 Heavy Metals

Amongst abiotic stresses, toxicity caused by heavy metals is very prevalent harmfully affecting the plants by modifying various metabolic and physiological mechanisms. It has been reported in literature that phenolics content enhanced under high ions concentration and protects the plant by chelating transition metal ions ultimately inhibiting ROS production (Mira et al. 2002; Williams et al. 2004; Kaur et al. 2017a; Kohli et al. 2018; Handa et al. 2019). These metal ions chelation under their high concentration is an active form of defense in plants as reported by Kidd et al. (2001). Betalains production was enhanced in hairy roots under high metal stress to improve their tolerance (Thimmaraju and Ravishankar 2004). Increase in phenolics like anthocyanin, kaempferol, caffeic acid, catechin, and coumaric acid under heavy metal Cu stress (Poonam et al. 2015), flavonoids, polyphenols, and anthocyanin under Cd stress (Kaur et al. 2017b, 2018) and Pb stress (Kohli et al. 2018) were reported. Likewise increase in total phenolics and polyphenols such as chlorogenic and vanillic acid in *Zea mays* under Cu, Pb, and Cd stress (Kisa et al. 2016) and increase in total flavonoids and phenolics content were studied in *Withania somnifera* in cadmium stress (Mishra and Sangwan 2019). Level of phenolics like kaempferol, diosmin, ferulic acid, daidzein, luteolin, cinnamic acid, resveratrol, caffeic acid, naringenin, vitexin, quercetin, and myricetin got enhanced under Pb stress in *Prosopis farcta* (Zafari et al. 2016) and significant rise in total phenolics, flavonoid, and anthocyanin content were reported in *Fagopyrum esculentum* under Al stress (Smirnov et al. 2015). Augmentation of phenolics in the presence of heavy metals is primarily due to the transcriptional activation of various enzymes of phenylpropanoid pathway and its precursors (Michalak 2006; Kovacik et al. 2009; Keilig and Ludwig-Mueller 2009; Mishra et al. 2014; Leng et al. 2015; Handa et al. 2019; Chen et al. 2019a; Mishra and Sangwan 2019). Enhanced expression of phenylpropanoid pathway enzymes was reported in *Brassica juncea* under Cr (Handa et al. 2018, 2019), Cd (Kaur et al. 2017b), and Pb (Kohli et al. 2017) stresses; in *Kandelia obovata* in Cd and Zn stress (Chen et al. 2019b); in *Vitis vinifera* under Cu stress (Leng et al. 2015); and in *Prosopis farcta* under Pb stress (Zafari et al. 2016).

8.5.5 Heat and Cold Stress

The temperature stress enhances the biosynthesis of phenolics in plants (Isah 2019; Naikoo et al. 2019). *Brassica oleracea* when exposed to extreme temperatures (heat and cold) leads to the high phenolic compounds' accumulation due to enhancement of antioxidative defenses in response to high concentration of ROS produced under these conditions (Soengas et al. 2018). Higher phenolic content helps the plant to combat the unfavorable circumstances. Likewise, Rivero et al. (2001) demonstrated that high amount of phenolics in tomato and watermelon provide resistance to heat and cold stress. Short-term temperature stress when applied to kale enhanced the phenolic antioxidants level (Lee and Oh 2015). Król et al. (2015) studied that when two varieties of grapevine were exposed to constant low temperature stress, more resistant variety is considered by high phenolics accumulation. The temperature stress outcomes the stimulation of enzymes convoluted in the biosynthetic processes of phenolics ultimately enhancing its production (Lattanzio et al. 2001; Sharma et al. 2019). It has been revealed that temperature treatments resulted in elicitation of phenylpropanoid pathway and phenolic accumulations in *Phaseolus vulgaris* (Ampofo et al. 2020). The transcriptome analysis of *Saccharum spontaneum roots* envisaged that phenylpropanoid pathway responds to the cold stress and arouse the phenolics biosynthesis (Dharshini et al. 2020).

8.6 Conclusion and Future Prospects

Phenolic compounds are the utmost vital and widespread secondary metabolites, consisting of a wide array of natural diverse compounds. In response to the hostile environmental stress conditions like salinity, heavy metal, drought, temperature stress, and pathogen attack, phenolic compounds' biosynthesis enhanced in order to combat with such conditions. Phenolics alter antioxidant defense system, biochemical pathways, and the emerging status of the plant self-reliantly by acting as antioxidant or intermingling with other signaling molecules subsequently upregulating the phenylpropanoid pathway transcriptionally. Upsurged plant's resistance is interrelated by way of the manifold roles of phenolics essentially comprising their ROS scavenging capability and the ability to defend the plant from extreme stress conditions such as light, temperature, drought, etc. By understanding the targets and signaling pathways of phenolics under stress conditions, the corresponding mechanism responsible for their resistance can be easily elucidated which can be further besieged to enhance their resistance through novel approaches by modifying the signaling pathways and associated targets. Apart from the vast matter available on this context, advance research is looked-for on the way to excavate, for instance, the title role of focused and specific phenolic compound as an adaptive comeback to explicit intensive stress mechanism involved in response to the particular unfavorable condition to define the resistance providing contrivances including the up-regulation of phenylpropanoid and other biochemical pathways involved, which is one of the chief targets to combat with numerous stressors.

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Crosstalk of Ethylene and Salicylic Acid in the Amelioration of Toxic Effects of Heavy Metal Stress in Mustard

9

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Abstract

Mustard is considered as a central crop all over the globe since it is a inexpensively important product. Plant toxicity caused by heavy metals (HMs) in agricultural fields results in a drop in yield. Using multiple ways targeting either ethylene production or the ethylene signaling system to manipulate ethylene in plants to cope with HM stress has yielded promising results. Recent advancements in ethylene study have revealed that ethylene is playing its role in a variety of vital physiological activities and metal stress tolerance in plants. The efficiency of endogenic ethylene level in plants beneath HM stress, based on our present understanding of ethylene and its regulatory actions, is thought to open the way for the growth and development of transgenic crops with enhanced HM tolerance in brassica. This research paper investigates ethylene synthesis and signal transduction in plant response to HM stress, as well as crosstalk between ethylene and other signaling molecules under extreme HM stress, and ways for modulating ethylene activity to advance HM resistance in brassica.

Keywords

Ethylene · Salicylic acid · Heavy metals · Stress · Signal transduction · Crosstalk

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9.1 Introduction

As predicted the population of world may reach nine billion in 2050, optimizing plant development and ensuring food and feed supply is more critical than ever. Because of industrial applications, noxious metals and metalloids mount up in the atmosphere. Stress variables such as drought, nutrient inadequacy, salt, metal contamination, etc., on the other hand, have a significant impact on plant yield (Mittler 2006; Dolferus 2014). Furthermore, metal-contaminated fertilizers, insecticides, and sewage sludge all contribute to cause pollution of metals, which must not be overlooked (Alloway 2012). Plants do not require metals like cadmium (Cd), mercury, or lead. As a result, even low quantities disrupt plant growth and development, resulting in severe output losses around the world. Excess amounts of metals like copper, iron, nickel, and zinc on the other hand can be phototoxic (Cuypers et al. 2009; Hansch and Mendel 2009).

Plants being the lone manufactures on this plant, hence serve as a vital link connecting the soil's basic makeup and the food series. As a result, improving our existing accepted metal-created pressures in flora and providing technical hints to improve plant extraction tactics are critical. In metal-exposed plants, improved production of reactive oxygen species (ROS) such as superoxide ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2), and the hydroxyl radical ($OH^{\bullet}$) is a common cellular response, regardless of species or exposure period (Schutzendubel and Polle 2002; Sharma and Dietz 2009). The same transport channels that deliver essential nutrients also transfer supplementary less important elements like Arseic and Cadmium into tissues of plant (Verbruggen et al. 2009; Seth et al. 2012a). Too much lethal metal deposition in foodstuff and supply to plants is a harsh healthiness risk (Jarup 2003), highlighting necessitate to clean up the soil contaminated with metals. Metal phytotoxicity has hampered recent efforts to use plants to fresh up soils using phytoextraction (Vangronsveld et al. 2009). The antioxidative defence network of plant cells, on the other hand, strictly controls and maintains their ethylene and metal stress production at a low level. Superoxide dismutase (SOD), catalase (CAT), peroxidises (POD), and peroxiredoxins (Prx) are enzymes that neutralise $O_2^{\bullet-}$ and H_2O_2, and they are supported by metabolites like ascorbate (AsA) and glutathione (GSH). ROS are constantly formed in cell compartments like chloroplasts, mitochondria, and peroxisomes as end-products of aerobic metabolism under ideal physiological conditions. Therefore, the goal of this study is to sketch awareness to the role of ethylene and salicylic acid (SA) involvement in plants to overcome the effects of heavy metals (HMs). Various studies support a relation among ethylene and metal resistance, and practical data for the link connecting ethylene and exposure of metals are examined at both the ethylene production and signaling levels.

9.2 General Description About Elicitors

The name elicitor was originally applied to molecules capable of causing the development of phytoalexins, but is now routinely applied to chemicals that stimulate any type of plant defence (Ebel and Cosio 1994; Hahn 1996; Nurnberger 1999). Exogenous elicitors (pathogen-derived chemicals) and endogenous elicitors (pathogen-derived compounds) are both included in the definition of elicitors (Ebel and Cosio 1994; Boller 1995). Elicitors are classified as physical, chemical, biotic, abiotic, complicated, or defined depending on their origin and molecular structure. Elicitors are divided into two categories: general and race specific. Common elicitors can trigger defence in host and non-host plants, while race-specific elicitors can only trigger defence in some host cultivars, resulting in disease confrontation. A complimentary pair of genes in a pathogen race and a host cultivar determines cultivar-specific (gene-for-gene) resistance. As an outcome, a race-specific elicitor generated by or transcribed by a virulence gene in attendance in a pathogen race will only elicit resistance in a host plant variety carrying the resultant confrontation gene. The absence of either gene product is typically the cause of disease (Nurnberger 1999; Tyler 2002). General elicitors, on the other hand, detect probable infections in both the host and non-host plants (Nurnberger 1999). However, the non-specific nature of generic elicitors is relative, and some are only recognized by a small number of plants (Shibuya and Minami 2001). Recent research has found striking parallels connecting the resistance mechanisms induced by elicitors and animal inherent immunity, leading to the enticing hypothesis that plant innate immunity is triggered by identification of general elicitors (Nurnberger and Brunner 2002). At low doses, elicitors work as chemical signals providing data to plants instigate resistance as contrasting to toxins, which show effects at superior doses and damage the crop with no activation of its biochemical processes (Boller 1995).

9.3 Phytoremediation Potential and HM Uptake

Heavy metal contamination has spread throughout the world's arable soil (Nagajyoti et al. 2010; Neilson and Rajakaruna 2015). Increased crop production pressure might guide to the usage of spoiled soils, posing a risk of contamination of food (He et al. 2005). Some edible plant species in genus brassica studied in this review have revealed to accumulate high quantities of hazardous metals.

As a result, researchers are looking for plant species that can be used for phytoremediation which have the following properties (Marchiol et al. 2004b): (1) ability to collect HMs above the surface of soil; (2) resistance to elevated metal doses in soils; (3) quick development and elevated collection of biomass; and (4) simple to cultivate and harvest as a farming crop.

Most studies have focused on *B. juncea*, because it is extensively considered as a high-quality crop for phytoremediation. The difficulty in constructing realistic experimental setups is one of the issues with the usability of plants for phytoremediation objectives. Some investigations are carried out in a hydroponic solution, while others are carried out in HM-spiked soils, and yet others are carried out in naturally polluted soils. The majority of the research published was conducted under controlled settings, mainly in pots, with only a handful conducted in the field. The results acquired from all of these distinct experimental circumstances are extremely varied, and extrapolating results from one investigational state to an additional one can be challenging at times (Grispen et al. 2006; Armas et al. 2015). Several studies are available that compare the performance of some brassica plants to harmful HM doses. Hernandez-Allica et al. (2008) conducted a thorough investigation of tolerance of HMs of various species (including *B. campestris*, *B. rapa*, *B. napus*, *B. oleracea*, and *B. carinata*) and concluded that these species have high tolerance to Zn, but not to Pb or Cd. Purakayastha et al. (2008) investigated the phytoextractive potential of five species (*B. juncea*, *B. campestris*, *B. carinata*, *B. napus*, and *B. juncea*). Zn, Cu, Ni, and Pb are four HMs that *B. nigra* is exposed to. They came to the conclusion that *B. carinata* outperformed the others in terms of Zn, Ni, and Pb, and hence considered an essential contender for phytoremediation among previous ones, particularly *B. juncea* are generally thought to be very tolerant. In terms of Cu, *B. juncea* metal has had the most uptakes. In 1997, Ebbs and Kochian (1997) promulgated a research work evaluating the hazards effects and collection of Zn and Cu in three Brassica species (*B. juncea*, *B. napus*, and *B. rapa*) and concluded that Zn removal was more successful than Cu removal. Gisbert et al. (2006) evaluated the resistance of three brassica varieties to a multi-contaminated soil and determined that the resistance sequence was *B. juncea* > *B. carinata* > *B. oleracea* based on a calculated resistance index. Marchiol et al. (2004a) concluded that the phytoextraction behaviour of *B. juncea*, *B. napus*, and *B. carinata* was similar, and that all three species had equivalent Cd and Zn potential. Brunetti et al. (2011) found that the collection of several metals (Cd, Cr, Cu, Ni, etc.) was extra prominent in aerial parts of plant than roots in their investigation using *B. napus* plants in polluted soil. Feigl et al. (2013) found that when *B. napus* and *B. juncea* were exposed to Cu stress for 7 and 14 days in hydroponic solution, the roots acquired more Cu than the shoots.

Within the same species, different varieties and even distinct accessions have varied absorption capacities (Grispen et al. 2006). Qadir et al. (2004) investigated the Cd extraction capacity of ten *B. juncea* cultivars. Although all cultivars responded similarly to the tested settings, some had higher Cd tolerance than the others. Although exceptionally high quantities of Cd (up to 2000 μM) were utilized, the highest period of toxicity was 3 days. Gill et al. (2015) compared the resistance of four *B. napus* cultivars to Cr stress and discovered substantial variances in their resistance abilities. Nouairi et al. (2006) investigated Cd uptake in *B. juncea* and *B. napus* shoots and found that the former was able to significantly collect more Cd in the aerial parts, owing to greater Cd concentrations in hydroponic solution. *B. juncea* was also deemed suitable for phytoremediation by Seth et al. (2012b), not only for Cd pollution, but also for Cr, Cu, and Pb. Podar et al. (2004) conducted an intriguing investigation with *B. juncea* that used an assorted metal allocation, which the authors believe is more representative of what happens in true contaminated areas. These findings show that phytoremediation tests in harmonized environments may underrate the amount of toxins that plants may absorb.

As several mustard members are essential in making oil, for both human being utilization and for biodiesel generation, some research have looked into the possibility of blemish of seed and oil from these plants, as taint of the food web and the environment could result. The suitability of *B. napus* for phytoremediation and the utilization of oil extracted from plants cultivated in contaminated areas were explored by Park et al. (2012). They stated that because the HM content was low, the plants could thrive and endure relatively high amounts of a variety of HMs while also generating oil that was safe to use as an energy source (they claimed that most of the left-over HMs were reserved in the oil extraction process residues). Sankaran and Ebbs (2008) performed an intriguing experiment in which they tested the toxicity of Cd in *B. juncea* and its gathering in seeds when it was sprayed at various phases of growth. They came to the conclusion that, while Cd levels in seeds varied depending on the developmental stages of plant, they could rapidly collect in doses above tolerable confines for crops, posing a risk to their utilization.

The growing water demand for cultivation has prompted researchers to look into unique methods, such as the use of waste water treatments, which have high percentage of plant nutrients but also include a variety of pollutants, including HMs. Some recent research on the use of waste water treatment in plants including a few from the genus brassica have demonstrated the hazards of utilizing polluted waters in the irrigation of foliage that can be consumed by humans (Parveen et al. 2014, 2015). Other serious metals have received less attention since their presence in dangerous concentrations is less of a worry. For example, Hale et al. (2001) presented an intriguing work on molybdenum toxicity in *B. juncea* and *B. rapa* species. Molybdenum is an important element that plants require in extremely little quantities but having a high resistance for reasons that are yet unknown. Increased absorption and amelioration of *B. napus* related to Pb (Hale et al. 2001) and Cd contamination (Shakoor et al. 2014) were observed when citric acid was added to the contaminated medium. The authors of the first study attributed this to the mobilization of vital nutrients, which improved various metabolic processes; however, the exact mechanism is yet unknown. Quartacci et al. (2006) and Irtelli and Navari-Izzo (2006) published two papers related to *B. juncea* plants developing in Cd pressure, in which the effect of addition of citric acid and sodium nitrilotriacetate to polluted soil was studied. The same group reported in a follow-up investigation (Quartacci et al. 2007) that (*S*,*S*)-ethylene diamine-*N*,*N*-disuccinic acid (EDDS) was even more successful than NTA at promoting plant extraction of various infected soil, this period with *B. carinata* varieties. In another study, EDTA has been shown to promote HM uptake by brassica species from contaminated soils (Zaier et al. 2010; Turan and Esringu 2007; Lim et al. 2004), there are concerns about the chelating agent's environmental persistence and chelating capability (Meers et al. 2009). Clemente et al. (2005) investigated the useful application of *B. juncea* for plant extraction in various tainted soils (mostly spoiled with Zn, Cu, and Pb), both with and without additional amendments (cow dung and fertilizer). Plant development and metal uptake were found to be significantly dependent on pH of soil, despite the fact that supplementary amendments boosted plant development. Brunetti et al. (2011) stated that adding municipal solid waste compost to *B. napus* plants enhanced the removal of HMs by these species, but they predicted that cleaning up a contaminated site would take more than 1000 years, making this plant inappropriate for phytoextraction. It is possible that the collective toxicity of all of these metals overwhelms the plant's defence and resistance mechanism. Herrero et al. (2003) validated the comparatively high tolerance of *B. napus* var. oleifera to another multi-contaminated soil in their study with this plant (Zn, Cu, Cd, and Pb).

Houben et al. (2013) investigated the consequence of biochar on *B. napus* species cultivated in Zn-, Cd-, and Pb-contaminated soils. Biochar is said to minimize HM accessibility to plants and enhance the quality of soil, allowing for better plant development. The authors confirmed that adding 5% and 10% biochar to the soil decreased metal uptake and increased rapeseed growth considerably when compared to the control. These findings suggest that, while the addition of biochar makes rapeseed unsuitable for plant extraction due to decreased metal consumption, it might be a useful technique for plants to become more stable. Adediran et al. (2015) also found that phytoremediation of Zn with *B. juncea* is a promising method.

9.4 Ethylene and Metal Stress Relationship

The outcome of many investigations is reviewed in the following sections, and they all indicate that ethylene is playing a role in plant metal stress responses (Table 9.1). However, it is critical to consider numerous characteristics of the experimental design when interpreting these findings. First and foremost, metal-specific features must be taken into account. Both essential and non-essential metals, as previously stated, elicit phytotoxic effects, but at differing amounts of exposure. Experiments can also be carried out with enormous or realistic metal concentrations in the environment. Tissue injury and necrosis may simply enhance ethylene production under extreme stress situations (Lynch and Brown 1997). Nonetheless, the magnitude and effects of increased ethylene production must be understood in light of the functional exposure dosage (Thao et al. 2015). The commencement of particular indicator transduction pathways, such as those associated to ethylene, will be affected by the intensity of stress (Kacperska 2004). Even though Kacperska (2004) suggested that enhanced ethylene production is a defining aspect of the alert scenario through extreme stress, it has also been seen when exposure to modest and practical Cd doses (Schellingen et al. 2014). The distinction among main and inferior metal stress-induced processes in plants is critical. Metal poisoning, for example, frequently causes nutritional deficiencies (Lynch and Brown 1997), which is linked to changes in ethylene biosynthesis and signaling (Iqbal et al. 2013).

Finally, various experimental procedures are employed in order to determine the practical function of ethylene under metal stress. On the one hand, pharmaceutical inhibition of ethylene production or signaling is possible. When investigating mutants that are deficient in one or both processes, however, alternative results can be produced. Furthermore, due to functional redundancy, not all mutations will

Table 9.1 Impacts of metal exposure on ethylene production and signaling in plants

Metal	Concentration	Exposure time	Tissue type	Species	Observations	References
Al	10 or 50 μM	24 h	Root apices	*L. japonicus*	↑ ACO activity ↑ Ethylene (max after 30 min) Al and cobalt/AVG ↓ Ethylene ↓ Inhibition of root elongation	Sun et al. (2007)
	10 μM $AlCl_3$	2 and 24 h	Root apices	*M. truncatula*	↑ ACS and ACO expression	Sun et al. (2007)
	50 μM $AlCl_3$	24 h	Roots, root apices	*A. thaliana*	↑ Ethylene (max after 30 min)	Sun et al. (2007)
Cd	0.5 μM $CdCl_2$	14 h	Leaf discs	*T. aestivum*	↑ Ethylene	Groppa et al. (2003)
	5 or 50 μM $CdSO_4$	2, 6 and 30 h	Shoots and roots	*A. thaliana*	↑ ACS expression ↑ ERF expression (all conditions)	Herbette et al. (2006)
	10 or 50 μM Cd	2 h	Roots	*A. thaliana*	↑ ACS and ERF expression	Weber et al. (2006)
	400 μM $CdSO_4$	24 h	Different plant parts	*A. thaliana*	↑ Ethylene	Arteca and Arteca (2007)
	0.1 μM $CdSO_4$	75 h	Suspension cells	*L. esculentum*	↑ Ethylene ↓ Cell death	Iakimova et al. (2008)
	50 μM $CdCl_2$	14 days	Leaves	*P. sativum*	↑ Ethylene	Rodríguez-Serrano et al. (2009)
	200 mg^{-1} $CdCl_2$	30 days	Leaves	*B. juncea*	↑ ACS activity ↑ Ethylene	Masood et al. (2012)
	10–25 mg^{-1} $CdCl_2$	3, 6 and 24 h	Root tips	*G. max*	↑ ACS expression ↑ Ethylene	Chmielowska-Bak et al. (2013)
	50 μM $CdCl_2$	30 days	Leaves	*B. juncea*	↑ ACS activity ↑ Ethylene	Asgher et al. (2014)

(continued)

Table 9.1 (continued)

Metal	Concentration	Exposure time	Tissue type	Species	Observations	References
	5 μM $CdCl_2$	15 days	Leaves	*H. vulgare*	↑ Ethylene Cd tolerant genotype ↑ ACO expression Cd sensitive genotype ↓ Ethylene responsive genes	Cao et al. (2014)
	200 mg/kg $CdCl_2$	30 days	Leaves	*T. aestivum*	↑ ACS activity ↑ Ethylene	Khan et al. (2015)
As	100 and 200 μM As(V)	1.5 – 3 h	Roots	*A. thaliana*	↑ Expression of ethylene related genes in tolerant Col-0 ecotype ERF = As tolerance associated	Fu et al. (2014)
Cu	10 μM $CuSO_4$	48 h	Leaves	*N. glutinosa*	↑ ACO expression	Kim et al. (1998)
	25, 100 or 500 μM $CuSO_4$	7 h	Whole plant	*A. thaliana*	↑ Expression Cu and AVG ↓ Ethylene	Mertens et al. (1999)
	0.5 μM $CuCl_2$	14 h	Leaf discs	*H. annuus* *T. aestivum*	↑ Ethylene	Groppa et al. (2003)
Cr	200 μM K_2CrO_4	1–3 h	Roots	*O. sativa*	↑ ACS, ACO and EIN3;4 expression	Trinh et al. (2014)
	500 or 1000 μM $HgCl_2$	15 days	Roots	*H. vulgare*	↑ Expression of ethylene responsive gene	Lopes et al. (2013)
	10 μM $HgCl_2$	6, 12, 24 and 48 h	Whole plant	*M. truncatula*	Altered expression of ethylene responsive genes	Zhou et al. (2013)
Hg	25 μM Hg	1–3 h	Root apices	*O. sativa*	↑ Expression of ACS, ACO and ethylene responsive gene	Chen et al. (2014)
	3 μM $HgCl_2$	3, 6 and 24 h	Roots	*M. sativa*	↑ Expression of ACS, ACO and ethylene responsive gene Hg^+ 1-MCP ↓ Induction of ethylene related genes	Montero-Palmero et al. (2014)
Ni	50, 100, 200, 400 and 800 μM $NiSO_4$	24 h	Inflorescence, stalk and leaves	*A. thaliana*	= Ethylene	Arteca and Arteca (2007)
	200 mg/kg $NiSO_4$	30 days	Leaves	*B. juncea*	↑ ACS activity ↑ Ethylene	Khan and Khan (2014)

	500 mg/L $(PbNO_3)_2$	12 days	Shoots and roots	*S. drummondii*	↑ Expression of a pyruvate ACS/ACO gene shoots	Srivastava et al. (2007)
	0.5 μM $(PbNO_3)_2$	14 days	Whole plant	*A. thaliana*	↑ EIN2 expression	Cao et al. (2009)
Fe	200 mg/L $FeSO_4$	24 h	Leaves	*O. sativa*	↑ Ethylene	Yamauchi and Peng (1995)
	300 mg/L $FeSO_4$	10 days	Shoots and roots	*O. sativa*	= Ethylene	Yamauchi and Peng (1995)
	300 mg/L $FeSO_4$	24 h	Leaves of de-rooted plants	*O. sativa*	↑ Ethylene	Yamauchi and Peng (1995)
Zn	50, 100, 200, 400 and 800 μM $ZnSO_4$	30 days	Inflorescence, stalk and leaves	*B. juncea*	↑ Ethylene	Arteca and Arteca (2007)
	25, 100 and 500 μM $ZnSO_4$	7 h	Whole plant	*A. thaliana*	↑ Ethylene	Mertens et al. (1999)
	200 mg/kg $ZnSO_4$	30 days	Leaves	*B. juncea*	↑ Ethylene	Khan and Khan (2014)

result in total suppression of ethylene biosynthesis or signaling (e.g., different ethylene receptors). To investigate the practical function of ethylene in metal resistance, several research use transformants that over express ethylene-related genes, which are commonly taken from other plants or even species. As a result, correct data understanding is only achievable when the configuration is considered (Thao et al. 2015). The research documented in this study evidently shows that ethylene and metal stress in plant life have a close association.

However, considerable work is still to be done in order to establish the molecular processes that underpin this relationship and utilize this information in real-world situations, such as during phytoremediation.

9.5 Modifications and Responses of Plants to HM Stress and Ethylene Signaling

A number of chemical chelating agents have been planned to augment plant metal uptake and translocation from roots to shoots without troubling plant development in order to allow the successful application of phytoextraction techniques (Gupta et al. 2013). Several investigations with various chelating agents have been conducted in Brassica species (Neilson and Rajakaruna 2015). Increased absorption and amelioration of *B. napus* in relation to Pb (Shakoor et al. 2014) and Cd contamination (Ehsan et al. 2014) were observed when citric acid was added to the contaminated medium. In Arabidopsis, ethylene is recognized by the ETR1 and ETR2, Ethylene Response Sensor1 (ERS1) and ERS2, and EIN4 genes, which are part of a five-member ethylene receptor family (Clark et al. 1998; Yoo et al. 2009). As a result, EIN2's movement to the nucleus is aided, resulting in the stability of EIN3 protein, which starts the signaling cascade (Ju et al. 2012; Qiao et al. 2012; Wen et al. 2012). The use of natural alterations to minimize the extent use of HMs to foliage or promote plant development is another technique for improving soils infected with HMs. Plant development and metal uptake were found to be significantly dependent on pH of soil, despite the fact that supplementary amendments boosted plant growth.

Ethylene production has been discovered to be stimulated by HM stress, such as Cd stress mostly through the build-up of ACS2 and ACS6 transcripts (Schellingen et al. 2014). The Arabidopsis acs2-1 acs6-1 double knockout transformed exposed to Cd had a lower level of ethylene, which resulted in a beneficial outcome on biomass of leaf (Schellingen et al. 2014), implying that HM stress-inserted ethylene is negatively regulated in plant growth. The MAPK cascade has been shown to be involved in ethylene signaling and/or ethylene production pathways by targeting at least ACS2 and ACS6 (Liu and Zhang 2004; Hahn and Harter 2009; Yoo et al. 2009; Opdenakker et al. 2012). Ethylene receptor blockers are extremely efficient in agriculture because they protect tissues from both endogenous and external ethylene (Sisler and Serek 1997; Feng et al. 2000). They are more selective than ethylene biosynthesis inhibitors because they connect to a specific receptor (Sisler and Serek 1997; Hua and Meyerowitz 1998; Klee 2004). The use of 1-MCP, an ethylene blocker in plants, has been extensively researched (Sisler and Serek 1997;

Blankenship and Dole 2003), and numerous applications of 1-MCP for the relief of plant stress responses have been documented (Grimmig et al. 2003; Huang and Lin 2003; Yokotani et al. 2004).

9.6 Salicylic Acid Role in Mustard Plants Under HM Stress

SA is recognized to have a key function in changeable plant morphology like shape, growth, blossoming and stomatal closure (Miura and Tada 2014; Mohsenzadeh et al. 2011). In response to SA, Khan et al. (2013) found that corn and soybean produced more leaf margin and dry weight. Furthermore, when wheat plants were sprayed with SA, Hussein et al. (2007) found enhanced expansion, leaf number, dry biomass, and stem width. Rate of transpiration and stomatal index rose after being supplemented with SA (Khan et al. 2013). When wheat seeds were exposed to a low absorption (10^{-5} M) of SA, the pigment content in the seeds increased considerably. Under abiotic stress, such as high temperature, salt, and HM, SA a phenolic plant hormone modulates photosynthesis, respiration, and antioxidant resistance mechanisms in plants (Miura and Tada 2014; Wang et al. 2012; Zengin 2015). SA pre-treatment protects plants from several metals such as Pb, Hg, and Cd (Ghani et al. 2015; Gondor et al. 2016; Zhou et al. 2009). Exogenous treatment of SA was found to reduce Cd toxicity in mustard plants (Ahmad et al. 2011). The elevated amounts of SA in mustard plants caused by Cd could have acted as a direct antioxidant to counteract the ROS. Many studies have shown that salicylic acid can reduce the HM effects (harmful) on plant life (Mishra and Choudhuri 1999; Zhou et al. 2009). Because there is so much support of the negative effects of Cd on growth of plant, it was anticipated that salicylic could help to minimize the negative effects of Cd on *B. juncea*. The main goal of this study was to document if SA might reduce stress in brassica by modulating the antioxidant resistance system and a number of critical stress-related physiological processes (Fig. 9.1).

9.7 Crosstalk of Ethylene with Other Growth Regulators and Signaling Molecules in the Regulation Tolerance of Plant to HM Stress

Excessive HM has discovered to influence not just ethylene synthesis but also the production of other phytohormones. Plants' levels of jasmonic acid (JA), SA, abscisic acid, and ethylene rise in response to stress, while GA_3 and auxin levels fall (Metwally et al. 2003; Maksymiec et al. 2005). The molecular mechanism by which brassica cope with various HM challenges differs from other plants. Generally, ethylene and its relations with other growth regulators are critical for plant adjustment to HM-caused oxidative stress (Thapa et al. 2012; Montero-Palmero et al. 2014). It was revealed that treating Arabidopsis with aluminum (Al) enhanced the expression of ethylene biosynthesis-related genes including AtACS (AtACS2, At ACS6, and AtACS8) and AtACO (AtACO1 and AtACO2) genes (Sun et al.

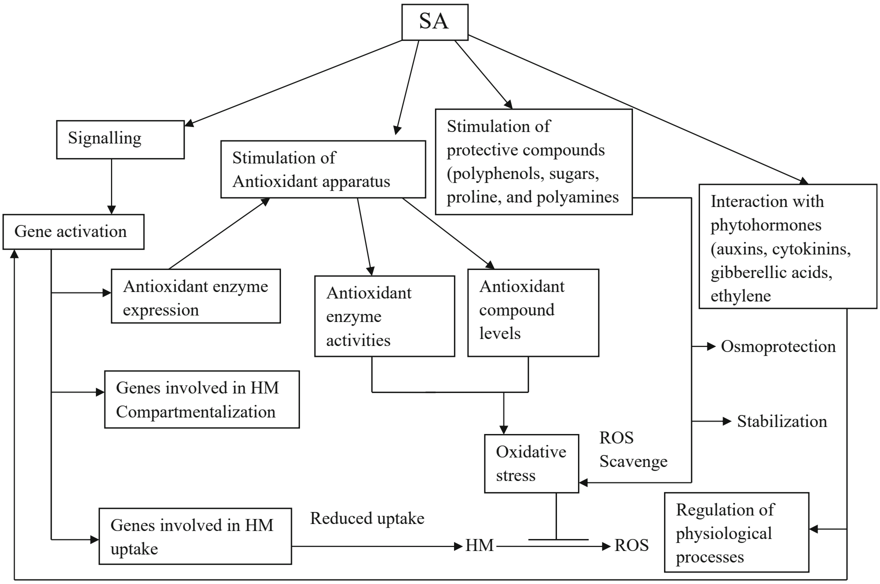

Fig. 9.1 Diagrammatic representation of defensive function exerted by SA in HM-stressed plants. *HM* heavy metal, *ROS* reactive oxygen species, *SA* salicylic acid

2010). The auxin-insensitive single mutant's aux 1–7 and pin2 have a smaller Al-induced loss in root development than the wild type. These findings demonstrated that Al-induced ethylene synthesis influences auxin polar transport systems via AUX1 and PIN2 (Sun et al. 2010), demonstrating that ethylene and auxin may interact in plant responses to HMs. Furthermore, the ethylene synthesis inhibits Co and AVG, as well as the ethylene perception inhibitor silver, all suppressed the Al-induced expression of AtAUX1 and AtPIN2 in wild-type plants, whereas the ethylene perception inhibitor silver suppressed the Al-induced expression of AtAUX1 and AtPIN2. In mustard and Arabidopsis, the ethylene and JA signaling pathways have recently been shown to converge at two ethylene-stabilized transcription factors, EIN3 and EIL1, and to influence gene expression in a synergistic manner (Zhu et al. 2011). Other research has discovered that ethylene and JA regulate ERFs post-translational without the involvement of EIN3/EIL1 (Bethke et al. 2009; Van der Does et al. 2013). These two hormone signaling pathways were engaged when mustard plants were exposed to excessive Cd, resulting in the up-regulation of Nitrate Transporter1.8 (NRT1.8) and the down-regulation of NRT1.5, which facilitated the stress-initiated nitrate distribution to roots.

An efficient GA_3 signaling corridor was revealed to be vital for enhanced ethylene production in mustard by examining the gibberellin insensible ethylene overproducing 2-1 dual mutant, revealing a probable relationship amid ethylene and GA_3 (De Grauwe et al. 2008). Masood and Khan (2013) recently proposed that action with GA_3 and sulphur (S) at appropriate level abridged undesired pressure ethylene initiation, hence alleviating photosynthetic inhibition induced by Cd stress.

Application of S to Cd-treated plants, on the other hand, has been shown to optimize stress-induced ethylene content, resulting in a maximum GSH content, thereby offering superior defense against oxidative stress and minimizing adverse Cd-induced symptoms in plants (Asgher et al. 2014). Under normal conditions, S assimilation results in Cys biosynthesis, which is vital equally for ethylene and GSH production (De Grauwe et al. 2008). Furthermore, Cd stress altered both the ethylene and S assimilation pathways, which were found to govern GSH production under Cd stress. Many physiological, pharmacological, and inherent studies have demonstrated that GSH is the substrate for phytochelatin production, which could explain GSH's role in HM detoxification (Cobbett 2000).

In plant reactions to HM stress, ROS has also been observed to interact with ethylene. The inoculation of ethephon or NBD to mustard plants treated with Ni and Zn was discovered to affect the stress-induced ethylene, reducing photosynthetic reserve and declining oxidative stress, presumably through the improvement of SOD, APX, and GR metabolism (Khan and Khan 2014). In tomato, ethylene and hydrogen peroxide are thought to work together, and hydrogen peroxide plays a key part in ethylene-related Cd-induced cell death (Liu et al. 2008). HM stress such as Cd, Cu, Fe, Zn, Hg, Mn, and Al have been shown in several studies to stimulate ROS manufacture and modify the actions of antioxidant enzymes in mustard plants, with catalase, peroxidase, ascorbate peroxidase (APX), and glutathione reductase (GR) (Sun et al. 2010; Yuan et al. 2013; Montero-Palmero et al. 2014; Khan et al. 2015; Mostofa et al. 2015).

Plants including *Brassica napus* were cultivated under Cd, Cu, or Pb stress; not only ethylene, but also brassinosteroids, auxin, SA, GA_3, and cytokinin were demonstrated to promote antioxidant responses in order to scavenge various ROS in response to HMs (Hayat et al. 2007; Noriega et al. 2012). JA also caused ROS to develop in Arabidopsis and Brassica napus plants that had been treated with Cu or Cd (Maksymiec and Krupa 2006). Nevertheless, it has been discovered that the oxidative state of GSH mediates JA-induced ROS, and that JA boosted the manifestation of GSH metabolic genes (Xiang and Oliver 1998; Mhamdi et al. 2010). SA treatment increased GSH levels and induced antioxidant and metal detoxification systems in wheat and pea, resulting in Cd stress tolerance and alleviation of the harmful effects of Cu stress in *Brassica napus* (Srivastava and Dwivedi 1998; Khademi et al. 2014; Kovács et al. 2014). As a result, more research is needed to determine how JA is implicated in HM-induced oxidative stress and plant tolerance. To learn more about the crosstalk between ethylene and other hormones in plant responses to HM stress, researchers should look at changes in the levels of all other hormones, ROS, and antioxidant systems in ethylene-deficient or -overproducing plants under normal and HM stress circumstances. Nitric oxide (NO), another signaling molecule, is recognized to regulate ethylene emission (Leshem and Haramaty 1996), biotic and abiotic responses (Leshem and Haramaty 1996; Delledonne et al. 2001; Mostofa et al. 2015), cell abundance, and plant improvement (Leshem and Haramaty 1996; Ribeiro et al. 1999). However, NO, like ethylene, has a contentious role in HM tolerance. Exogenous NO has revealed to improve plant tolerance to extreme Cd, Ni, and Al (Laspina et al. 2005), whereas endogenous NO has been implicated in Cd toxicity in plants (Laspina et al. 2005; Kazemi et al. 2010). These data point to the possibility of NO playing a role in the HM-induced ethylene pathway. Under Ni stress, however, both NO and SA greatly abridged Pro build-up, lipid peroxidation, and ROS levels in *B. napus* foliage, as well as enhanced total chlorophyll, lowering Ni′s harmful effects on *B. napus* (Kazemi et al. 2010). These findings point to a complicated system involving phytohormones, such as ethylene, and signaling molecules in response to HM stress.

9.8 Role of Ethylene as a Regulator of Plant Responses to Metal Stress

Several studies have looked into the role of ethylene in plant adjustment to harmful metals, and plant genotypes that emit extra ethylene have been hypothesized to be more challenging than those that discharge fewer metals (Lu and Kirkham 1991). Furthermore, when the Pb-hyper accumulator *Sesbania drummondii* was exposed to Pb, the mRNA levels of a putative ACS/ACO gene increased (Srivastava et al. 2007). Fu et al. (2014) undertook transcriptome profiling of genes and pathways associated with As tolerance and toxicity in *A. thaliana* ecotypes. After short-term As treatment, genes encoding components of the ethylene signaling pathway were significantly enriched in the Columbia ecotype compared to the sensitive Wassilewskija ecotype (Fu et al. 2014). Similarly, Cao et al. (2014) claimed that ethylene signaling activity is associated with Cd tolerance in *H. vulgare*. Transgenic *N. tabacum* plants over expressing a *Lycium chinense* ERF gene were more resistant to Cd than non-transformed plants (Guan et al. 2015). The ethylene-insensitive *A. thaliana* mutant's etr1-1 and ein3-3, on the other hand, have been demonstrated to be less responsive to Li than WT plants (Bueso et al. 2007).

9.9 Conclusion

Ethylene is engaged in a variety of actions in plants throughout their lives, including responses to environmental cues like metal exposure. Our understanding of ethylene's significance in metal-induced stress responses, as well as its incorporation into a larger network of signaling chemicals, is slowly growing. Recent research suggests that ethylene, the cellular redox balance, which includes GSH as an essential antioxidant, and other phytohormones including JA and SA, all play a role in plant metal sensitivity vs. tolerance. However, there is still a lot of work to be done before this knowledge can be used in practice.

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Stressed Plants: An Improved Source for Bioactive Phenolics

10

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Abstract

The generation of environmental changes, as well as the implementation of agricultural and cultural practices, induces a large number of problems related to abiotic or biotic stress in plants, which produce not only negative, also positive effects, since the plant uses its engineering mechanical, biochemical and molecular to defend its integrity. In this sense, various primary and secondary metabolites are produced under these conditions of stress, and among the secondary ones, phenolic compounds are the most synthesized. These compounds are considered one of the most important and diverse groups in plants, mainly due to their structural characteristics that provide important antioxidant activity. Antioxidants have the ability to neutralize reactive oxygen species; likewise, this defense mechanism can be used to consider plants as biofactories of phenolic compounds with a possible potential in health. In addition, the increase in the content of phenolic compounds could be manipulated depending on the plant, through its exposure to stress conditions.

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Stress · Bioactive compounds · Metabolites · Phenolic compounds · Oxygen species

10.1 Introduction

Phenolic compounds are obtained mainly from plants, which are characterized by presenting in their structure the phenyl ring and a C3 side chain; they mainly derive from the phenylalanine. Within those compounds, there is a large number of phenolic derivates such as flavonoids, phenolics acids coumarins, lignins, and proanthocyanidins; they all represent the main antioxidant system of defense in plants. Also, they are considered as antibiotics, natural pesticides, attractants for pollinators, protectors against abiotic conditions, and structural material in plants (Heldt and Piechulla 2011). Climate changes like extreme temperature, drought, light, deforestation, and rain contribute to stress in plants as well as that produced by infestations that can also be derived from the same environmental change (Karuppanapandian et al. 2011). Plants use different mechanisms to counteract stress, and one considered important is the production of phenolic compounds (Koyro and Huchzermeyer 2018). The production of these compounds is from a stimulus that generates the activation of different transcription factors (TF), which regulate various signals for the activation of genes that intervene in the metabolic pathways where phenolic compounds are synthesized (Lamers et al. 2020).

Therefore, due to these changes constant in natural conditions as well as in the management of some plants, the synthesis of different metabolites that are generated in the plant is promoted to establish a balance between antioxidant systems and reactive oxygen species (ROS), by the increase of phenolic compounds, this not only generates a positive effect on the plant but could also be exploited as a biofactory of phenolic compounds as they can be isolated or used in synergy for the development of products of agronomic interest and possible drugs with potential benefits on health.

Currently, the interest in the use of products of natural origin has come to revolutionize science and technology, and plants being a source of a large number of metabolites can be considered as a biofactory, since different exogenous and endogenous factors promote the generation of various compounds. Mainly, phenolic compounds are synthesized, due to their property of donating an electron to free radicals to stabilize them and, in turn, create species less damaging to the integrity of the cell (Madrigal-Santillán et al. 2013). Phenolics can be overproduced under stress and are of pharmaceutical interest, which makes them an excellent natural resource for the treatment of diseases (Koyro and Huchzermeyer 2018).

10.2 Stress in Plants

Due to their inability to mobilize, plants have developed defensive strategies to protect themselves to the continuous attacks from abiotic (environmental conditions) and biotic (bacteria, viruses, oomycetes, fungi, among others) factors that may affect their growth, development, or productivity (Hammond-Kosack and Jones 2015; Shinozaki et al. 2015). Under conditions of abiotics stress, the plants may trigger a defense called pathogen- and effector-triggered immunity, which are activated as a result of pathogen-associated molecular patterns. Moreover, under abiotic stress, plant signaling is activated by complex cellular and subcellular receptors (Meraj et al. 2020). The molecular signaling pathway triggered in response to these stresses involves diverse and intricate mechanisms such as ROS, mitogen-activated protein kinase, ethylene, salicylic acid, and jasmonic acid (Meraj et al. 2020; Camejo et al. 2016; Creelman and Mullet 1995; Fujita et al. 2006; Pitzschke et al. 2009; Yang et al. 2004).

As a defense mechanism, plants synthesize a set of a rich diversity of secondary metabolites as alkaloids, terpenoids, flavonoids, and phenolic acids. These molecules are normally produced at a low and steady rate to protect plants; however, during stress conditions, the biosynthesis of these molecules can be modulated positively or negatively (Meraj et al. 2020; Croteau et al. 2015). However, abiotic plant stresses have been the focus of many studies because of cultivation levels. Phenolic accumulation is a trait that has been exploited in agricultural research. Nonetheless, abiotic stresses might cause plants to accumulate bioactive compounds like phenolic compounds. However, this might also have a detrimental effect on the yield and organoleptic quality of fruits and vegetables (Toscano et al. 2019).

10.2.1 Abiotic Stress

Some authors define abiotic stress as any factor that might affect the ideal functions of an organism. Some of the most common abiotic factors are salinity, drought, nutrient depletion, temperature, and altitude; these can cause alterations in plants such as their growth and even might even cause death (Ali et al. 2020). Abiotic stresses elicit a response in plants, some of them are non-favorable; for instance, abiotic stress can overproduce ROS like superoxide (O_2^-), singlet oxygen ($^1O_2$), hydroxyl radical (OH^-), and hydrogen peroxide (H_2O_2 a precursor of ROS), among others (Broad et al. 2020). As a result, abiotic stress triggers a signaling cascade to activate a plant response mechanism to try to recover homeostasis and protect damaged membranes or proteins (Ali et al. 2020; Ahmad et al. 2010). Within the action mechanisms of the plant in response to abiotic stress, is the activation of the enzymatic antioxidant machinery. Short-term exposure to abiotic stresses might enhance the phenolic content of plants (Zhou et al. 2017). However, long-term exposure to these conditions might cause damage to plant tissues and slow down the secondary plant metabolism, thus, decreasing the phenolic content (Król et al. 2015).

10.2.1.1 UV Light Stress

Within solar radiation, there is the ultraviolet wave (UV), visible, and infrared light, which have an impact on the development and growth of plants, because they are implicated in different physiological processes such as photosynthesis where they can also activate photoreceptors causing modifications in macromolecules (Verdaguer et al. 2017). UV radiation is divided into three regions UV-A (315–400 nm), UV-B (280–320 nm), and UV-C (200–280 nm). UV-C radiation being short wavelength is all but complete absorbed by the ozone layer, likewise also most solar UV-B is absorbed, and just a few passes thought the atmosphere while UV-A radiation passes almost unaltered to the earth’s surface (Morales et al. 2010; Solovchenko and Merzlyak 2008). UV-B light has the highest energy in daylight and could cause cell damage in plants, causing DNA mutations and raising levels of ROS. In this case, the plant cell responds by accumulating phenolic compounds in the epidermal cells (Sharma et al. 2019; León-Chan et al. 2017; Isah 2019). Light is an important factor that can affect plant production of phytochemicals (Naikoo et al. 2019). Phenolic compounds like anthocyanins and other flavonoids can absorb visible and UV radiations, granting protection against free radical damage and oxidative stress (Lattanzio 2013; Landi et al. 2015; Sharma et al. 2019).

10.2.1.2 Temperature Stress

High or low temperatures are the most common environmental abiotic factors that affect plant growth, as well as the production of primary and secondary metabolites (Hounsome et al. 2008; Son et al. 2020). Temperature strongly influences metabolic activity, and species have to adjust their metabolism to survive variations in both climate change and different seasons of the year (Akula and Ravishankar 2011). The plant response will depend on the plant species, and sometimes its effect on the phenolic accumulation can be detrimental and, in other instances, it favors their accumulation. It might often be used in combination with other types of abiotic stress to enhance the content of these molecules to improve its potentially beneficial effect on human health (Son et al. 2020; León-Chan et al. 2020; Sharma et al. 2019; Sakamoto and Suzuki 2015).

10.2.1.3 Water Stress

One of the most common water stresses plants suffer drought, which causes an impact in plant development and growth, because under this condition there is a lack or insufficient water in the soil, to carry out the different physiological processes of the plant as photosynthesis and homeostasis general of the plant (Impa et al. 2012). High temperatures and solar radiation generally accompany this drought. It has been become a problem in different regions all the world, mainly in the arid and semi-arid areas (Xu et al. 2010). However, this stressful condition can enhance the increase of phenolic compounds in response to the generation of ROS. Some studies report that drought causes overexpression of MYB12/PFG1 or MYB75/PAP1 TFs, increasing the biosynthesis of flavonols and anthocyanins (Nakabayashi et al. 2014; Kirakosyan et al. 2003).

10.2.1.4 Salinity

Salinity in soil or water causes of abiotic stress in plants, especially those growing or cultivated in semi-arid and arid climates. Salinity has been related to harmful effects produced in the plant such as nutritional imbalance, reduction in osmotic potential, as well as an effect on specific ions, and/or a combination of the aforementioned factors (Acosta-Motos et al. 2017; Ashraf and Harris 2004). The severity of the effects of soil or water salinity on plants also be determined by factors as environmental conditions and the capacity of plants to survive to saline conditions. In this sense, plants can be classified as glycophytes or euhalophythes. Most crop plants belong to the classification of glycophytes and are highly sensitive to increased salinity levels. On the other hand, euhalophythes are plants that have adaptative saline systems (Ashraf and Harris 2004). Also, this type of stress could increase the phytochemical content of plants due to the ionic and osmotic stress caused by salinity (Akula and Ravishankar 2011).

10.2.2 Biotic Stress

Plants can suffer from biotic stress from the attack of viruses, bacteria, fungi, insects, and herbivores, affecting plant germination, growth, and plant production (ul Haq et al. 2019). Biotic stress triggers the production of ROS and increases the risk of oxidative stress and cell death. In addition, biotic stress causes losses before and after harvest. Fortunately, plants have an adaptive complex defense system, as a reaction to the different types of biotic stresses (ul Haq et al. 2019; Dodds and Rathjen 2010). Plants have two main mechanisms to respond to pathogens, one is known as the pathogen-associated molecular patterns, which are elicitors that trigger a reaction recognized by pattern recognition receptors (Dodds and Rathjen 2010; Koeck et al. 2011). The intricate signaling molecular network is complex, and there are currently ongoing studies trying to understand the precise mechanisms of action of biotic stress plant response. However, biotic stress is less explored than abiotic stress. For instance, our literature research using the keywords "biotic stress" and "phenolic compounds" from 2010 to 2020 showed only 112 studies, of which 103 were original research papers and 9 reviews. On the other hand, abiotic stress studies on the Web of Science database showed 416 original research papers and 42 reviews. The high number may be explained because abiotic stress has been extensively studied to take advantage of the plant response in the phytochemical enhancement (Jacobo-Velazquez et al. 2011, 2015; Villarreal-Garcia et al. 2016; Heredia and Cisneros-Zevallos 2009).

10.3 Plant Response Mechanism to Stresses

Plants have many reactions to different stresses, basically depending on the type of abiotic or biotic stress. For example, it could reduce their growth and photosynthesis, close stomata, generate ROS, and increase their production of secondary metabolites

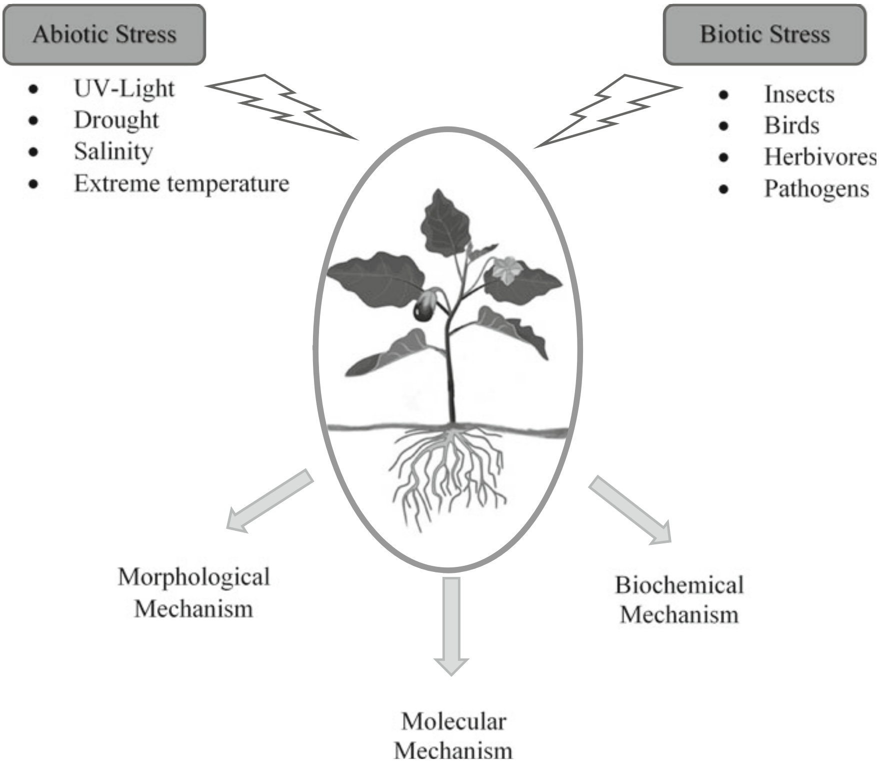

Fig. 10.1 Main mechanisms of defense of plants against abiotic and biotic stress

under abiotic stress. (Mahajan et al. 2020). Plants can change or modify their morphological structure or produce toxic chemicals as alkaloids, terpenoids, anthocyanins, phenolic compounds, and quinones; also, when herbivores attack them, insects, pathogens or to protect themselves of environmental factors negatives (drought, extremes temperatures, salinity, and radiation) (War et al. 2012). In stress situations, the plant activates a cascade of signals, which activate ion channels, kinases, TFs, phytohormones (salicylic acid, SA; abscisic acid, ABA; ethylene, ET; and jasmonic acid, JA) all of these signals lead to activate defense mechanisms. However, the response to the stress may be subject to the type of plant and stress conditions (Fraire-Velázquez et al. 2011; Cass et al. 2015).

Under biotic and abiotic stress situations, the plant uses defense mechanisms different, alone, or combined (Fig. 10.1). The first response is about morphological or structural changes, which includes the reduction of the cycle of life or the growing season, transpiration control by the stomatal closure, the change of the roots architecture system, and the shedding of leaves to reduce the surface area (Farooq et al. 2009; Das and Bhattacharya 2017). In this mechanism, there are structural deterrents of various types such as spines, hairs (trichomes), sclerophylly, leaf surface wax, cell wall thickness, lignification, and deposit of granular minerals; this mechanism is considered as "direct defense" of the plant (Hanley et al. 2007; War et al. 2012).

Likewise, under stress conditions, other mechanisms can be initiated, the molecular where some genes are expressed, and can affect the synthesis of some proteins to their protection and depend on the stress type duration and severity (Das and Bhattacharya 2017; Dos Reis et al. 2012; Moreno 2009). The different types of stresses (biotic and abiotic) generate a response in the activation of genes for the expression of enzymes that allow the biosynthesis of secondary metabolites (Suárez-Medina and Coy-Barrera 2016). In this sense, under a stress condition, specific TFs (essential proteins in the signaling network) are activated and regulate the stress-induced gene expression, through the binding to specific DNA sequence in the promoters of respective target genes (Verma et al. 2013; Woodrow et al. 2012). WRKY (tryptophan, W; arginine, R; lysine, K; tyrosine, Y) is an important TFs, which perform regulatory functions in defense of the plant against different types of stresses as mechanical damage, salinity, drought, cold, pest, and diseases (Vinod 2012). Other TFs such as MYB and bHLH (basic helix-loop-helix) are important for the regulation of phenylpropanoid biosynthesis pathway (Zhao et al. 2005).

On the other hand, in each stress type, different classes of TFs participate. For example, TFs that are involved in drought are called dehydration element-binding proteins (DREB), which induce genes to promote the adapting to the stress (Woodrow et al. 2012). Likewise, several TFs are mediators in phytohormone signaling pathways, which are widely recognized for their role in signaling abiotic and biotic stress. The hormones involved in biotic stress are JA, ET (necrotrophic pathogens and herbivorous insects), and SA (biotrophic and hemibiotrophic pathogens), while in abiotic is ABA (Fraire-Velázquez et al. 2011; Moreno 2009; Gómez and Rodríguez 2012; Verma et al. 2013).

Interestingly, the response of plants can vary activating different TFs depending on stress, as expressed in *Arabidopsis thaliana*, where they were subjected to different temperatures and nitrogen depletion, finding that TFs *PAP1* and *PAP2* increase strongly at low temperatures (5–10 °C) and depletion of nitrogen, as well as TFs *GL3* and *MYB12*, which coincides with an increase in flavonols but not in kaempferols and quercetin (Olsen et al. 2009).

Another mechanism is biochemical, which involves an osmotic adjustment, an antioxidant defense system, and a purifier. For which the plant uses enzymatic and non-enzymatic compounds (Das and Bhattacharya 2017). In the osmotic adjustment, some compounds like amino acids, carbohydrates, and organics acids have an osmolytic function and can provide plant protection against some abiotic stresses mainly (Mantri et al. 2012; Farooq et al. 2009).

The enzymatic system refers to the reaction of the cell to control the ROS excess, which is produced by stress. This reaction involves the oxidative enzymes catalase (CAT), superoxide dismutase (SOD), glutathione peroxidase (GPX), ascorbate peroxidase (APX), and glutathione reductase (GR). These enzymes are contained in chloroplast, mitochondria, and peroxisome (Impa et al. 2012). Each enzyme has a significant role in the reduction of ROS (hydrogen peroxide, superoxide anion, singlet oxygen, hydroxyl radical, nitric oxide, and peroxynitrite). The SOD enzyme, act in the superoxide decomposition, is the first line of defense and converts $^{\bullet}OH$ to H_2O_2; then H_2O_2 (a new ROS formed) is dealt with CAT and APX obtaining water and dioxygen as byproducts (Huang et al. 2019; Cruz de Carvalho 2008; Smirnoff 2008). The isozyme GPX reduces both H_2O_2 and organic peroxides. Finally, GR regulates the levels of reduced glutathione because an excessive accumulation of oxidized glutathione is harmful to the plant (Huang et al. 2019; Ahmad et al. 2010).

The non-enzymatic compounds are indispensable to protect plants against environmental stresses as well as pathogens, insects, and herbivores (Akula and Ravishankar 2011). The non-enzymatic compounds with antioxidant activity are glutathione, α-tocopherol, ascorbic acid, and phenolic compounds, which eliminate hydroxyl radicals and singlet oxygen mainly (Choudhury et al. 2013; Huang et al. 2019). The compounds derived of secondary metabolism are considered non-essential. However, they participate in the survival of the plant, based on their attributed effects against ROS, which are produced during a systematic response to stress conditions. They are located in a majority of the plant cells and can act in different ways against stress, such as ascorbic acid, which it is used as a substrate for the reduction of H_2O_2 by the activity of the enzyme ascorbate oxidase; this antioxidant compound plays a role minimizing damage caused by the oxidative process and can react with superoxide, hydrogen peroxide, and singlet oxygen (Suárez-Medina and Coy-Barrera 2016; Choudhury et al. 2013).

The α-tocopherol is a lipophilic antioxidant and an efficient singlet oxygen radical scavenger. Due to its nature, it has the ability to interact with polyunsaturated acyl groups and it eliminates and quenches ROS. Glutathione is a tripeptide with functions as an antioxidant, scavenges H_2O_2, and also reacts with the radicals singlet oxygen, superoxides, and hydroxyls (Shao et al. 2007; Choudhury et al. 2013). Carotenoids are lipophilic compounds with a positive effect against the stress through the stabilization of the lipid phase of the thylakoid membrane, besides participating in the biosynthesis of ABA (Arbona et al. 2013). The phenolic compounds are a diverse group of secondary metabolites in plants that act as a mechanism of defense against stress biotic and abiotic. Under adverse conditions, those compounds are synthesized by the phenylpropanoid or shikimate pathway (Arbona et al. 2013; Smirnoff 2008).

10.4 Biosynthesis of Phenolic Compounds Under Stress Conditions

Phenolic compounds constitute a wide group of metabolites derivate of the secondary metabolism of the plants (Das and Bhattacharya 2017); they are synthesized from phenylpropanoids/shikimate pathway, starting with the amino acids L-phenylalanine or L-tyrosine as their primary precursors. The molecular structure of the phenolic compounds contains at least one aromatic ring joined with one or more hydroxyl groups (Lattanzio 2013; Del Rio et al. 2013; Peñarrieta et al. 2014). This group comprises simple to very complex molecules, which exist more than 10,000 compounds, and is classified in phenolic acids, stilbenes, flavonoids, and lignans (Cheynier 2012; Li et al. 2014).

The phenolic compound production is one of the mechanism defense developed by the plant immune system (Isah 2019). Under stress conditions, there is an increase of phenylalanine ammonia-lyase (PAL) activity and other enzymes implicated in the phenylpropanoid pathway (Arbona et al. 2013).

The mechanism cellular for the biosynthesis of phenolic compounds begins when the plant receptors receive an extracellular or intracellular signal in the plasma membrane or endomembrane, which triggers a signal transduction network; this allows de novo activation or biosynthesis of TFs that promote the expression of genes implicated in the synthesis of secondary metabolites (Isah 2019; Zhao et al. 2005).

The genes encoding PAL proteins differ depending on the plant species, and a single species can present from two to ten or more copies. Likewise, the isoenzymes of this family of genes are expressed in different tissues. That is to say, in the same species, we can find different isoenzymes expressed in different parts (stem, leaves, roots, and flowers) of the plant (Kong 2015). PAL is an important enzyme in the phenylpropanoid pathway; however, other enzymes are also relevant in this pathway, such as the isoforms of the ligase coumarate-4-hydroxylase and 4-coumaroyl CoA, which are also activated under stress conditions (Bartwal et al. 2013).

The biosynthesis of phenolic compounds in plants is increased under stress conditions, which starts from the formation of aromatic amino acids and of the shikimic acid in the pathway of the shikimic acid. Subsequently, the aromatic amino acid L-phenylalanine derived from the before-mentioned pathway is catalyzed by PAL (which is increased under stress conditions) and loses an ammonium molecule to form *trans*-cinnamic acid, which is hydroxylated by the *trans*-cinnamate-4-hydroxylase and forms *p*-coumaric acid (Heldt and Piechulla 2011; Singh et al. 2010).

On the one hand, this *p*-coumaric acid can be oxidized to caffeic acid, then methylated in the meta position producing ferulic acid. Then it is oxidized and methylated again, resulting in synaptic acid. Likewise, *p*-cumaric acid is also transformed by the enzyme 4-coumarate/CoA ligase into an activated CoA-ester, the coumaroyl-CoA. The later compound plus three molecules of malonyl CoA catalyzed by the enzyme chalcone synthase produces chalcone from which all flavonoids are generated and also condensed tannins (flavonoid polymers). While, the hydrolyzable tannins (from gallic acid linked to hexoses molecules) are formed from products of the shikimate pathway (Fig. 10.2) (Sakihama et al. 2002; Barros and Dixon 2020; Martin 2018; Heldt and Piechulla 2011; Grace 2008; Deng and Lu 2017).

Diverse studies have been shown the increase in the content of phenolic compounds in different plants when they are in stress conditions. In this sense, Nag and Kumaria (2018) found in the plant *Vande coerulea* Griff. Ex Lindl. from the family Orchidaceae that the enzyme VcPAL (*Vande coerulea* Phenylalanine Ammonia Lyase) maintained a proportional relationship with the expression of the PAL gene, in function to the stress condition to which the seedling was subjected.

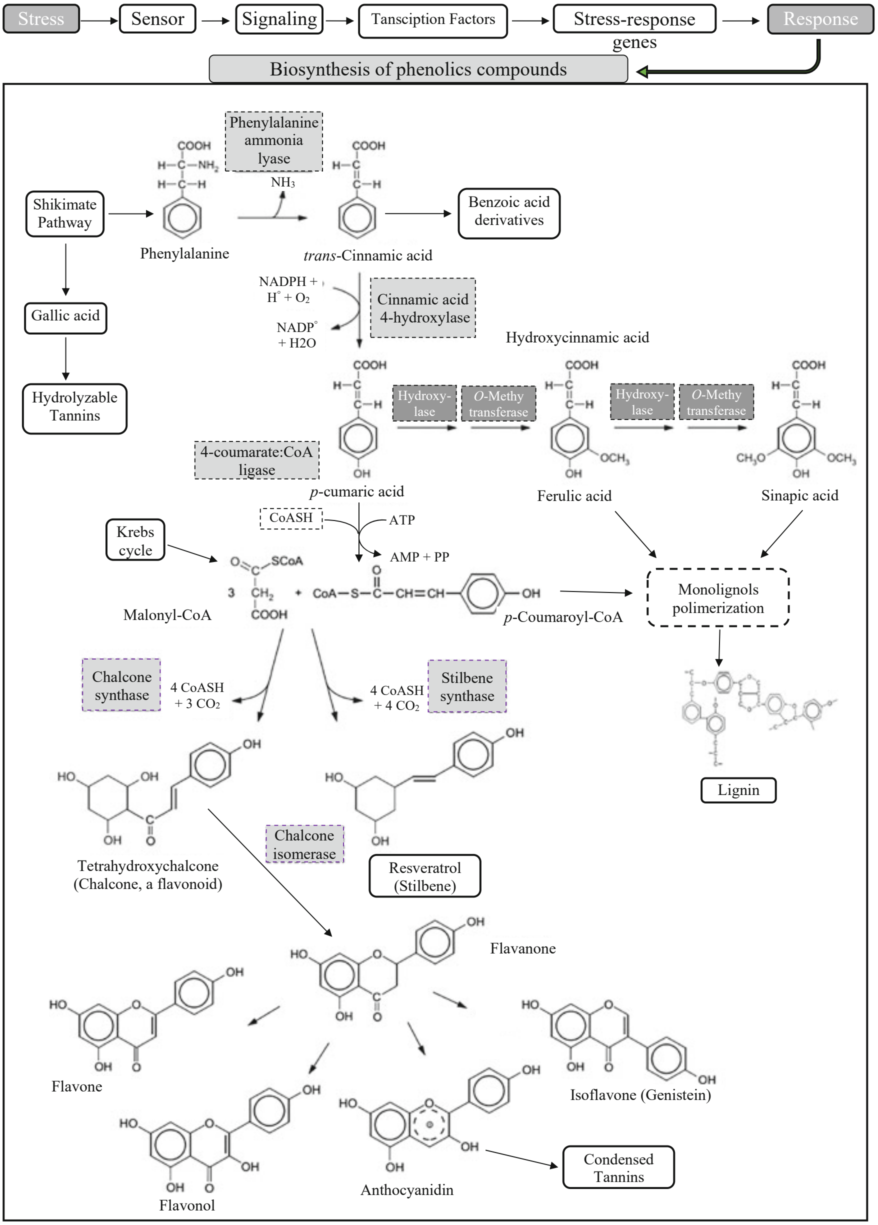

Fig. 10.2 Biosynthesis of phenolic compounds under abiotic and biotic stress

Treatments were salinity (5–200 μM NaCl), UV-B (1500 μJ/m^2), cold (4 °C), dark, and wounding (cutting leaves in pieces of 1 cm), all the treatments were collected after 0, 24, 48, 72, 96, and 120 h. Likewise, the content of phenolic compounds and flavonoids was evaluated concerning the different stresses. Results showed that there is an increase in the content in these phytochemicals of up to 3.54-fold more in flavonoids and 2.76-fold more in phenolic compounds, compared to the groups control. In the end, a relationship with the enzymatic activity as observed, indicating that the exposure to abiotic stress allows an increase in phytochemicals by stimulating the activity of the PAL enzyme.

For their part, Koyama et al. (2012) studied the effect of exposure to visible light and UV light of grapes (*Vitis vinifera*) cv. Cabernet Sauvignon, where they found that proanthocyanidin biosynthesis is induced under visible light and flavonols by UV light effect. In this sense, Agati et al. (2011) exposed *Ligustrum vulgare* plant outdoors under 100% sunlight irradiance without UV waveband, also to UV light and salinity (125 mM NaCl in the root zone); they found a dramatic increase in flavonoids (quercetin 3-*O*-glycoside, luteolin 7-*O*-glycoside, and cyanidin 3-*O*-glycoside) in leaves, concluding that flavonoids have an antioxidant function in photoprotection. Similarly, Takshak and Agrawal (2015) exposed the *Coleus forskhlii* plant to stress by UV-B radiation and found that the content of the different phenolic compounds in the leaves and roots increased. In this sense, the anthocyanin content increased in the roots, more than in the leaves under stress. However, flavonoids, phenols, lignin, and tannins were higher in the leaves than in the roots. Likewise, the enzymatic activity related to the biosynthesis of those metabolites presented an increase.

Fini et al. (2012) experimented with *Flaxanis ornus* plants which were subjected to solar radiation and different humidity conditions (100%, 40%, and 20% irrigated daily); they found that quercetin 3-*O*-glycoside content increased as the sun exposure time elapsed as well as at each humidity level, presenting a high content of this flavonoid in severe drought. The phytochemical esculetin showed the same behavior. The compounds acted as filters by accumulating in the vacuoles of the mesophyll cells, Likewise, the authors mention that these compounds exert a reducing power on H_2O_2 produced during stress due to exposure to excessive leaf light.

Leaves of *Mikania glomerata* Spreng. and *Mikania leavigata* Sch. Bip. Ex Baker were treated with full light, 25% shade, and 50% shade, also were exposed at 10, 17, and 22 °C of temperatures and water availability (excess and deficiency). The results showed that *M. leavigata* and *M. glomerata* have different responses in the biosynthesis of metabolites as phenolic compounds depending of the type of stress. However, in both species under sunlight and low temperatures, there was an increase of chlorogenic and dicaffeoylquinic acid.

On the other hand, in water availability, *M. glomerata* presented lower chlorogenic and dicaffeolyquinic acid content under drought, likewise *M. leavigata* had more coumarins content, with more shade (50% shade) (de Lazzari Almeida et al. 2017). In this sense, Caser et al. (2019) reported the drought stress (irrigation at 100% as control, 50% as moderate and 0% as severe) during 34 days in *Salvia dolomitica* Codd. leaves, and they evaluated phenolic compounds and flavonoids; it was found a decrease in those metabolites, contrary to what it was reported in other plants, which corroborates that the response in the synthesis of phenolic compounds is based on the species. The response may be through the activation of another biosynthetic pathway since, in this study, genes that enabled terpenoid biosynthesis were activated. For their part, Cheng et al. (2018) found in *Scutellaria baicalensis* Georgi roots that the mild drought stress increases the baicalin (flavone) and decrease in severe drought and was associated with the enzymes (PAL, phenylalanine ammonia-lyase; C4H, cinnamate 4-hydroxylase; 4CL, 4-coumarate-CoA ligase; CHS, chalcone synthase) involved in the biosynthesis of flavonoids.

Two species *Larrea divaricata* and *Lycium chilense* (leaves and roots) under drought stress due to seasonal changes (autumn, winter, spring, and summer) showed drought effects in the biosynthesis of phenolic compounds. The specie *L. divaricate* presented a higher accumulation of flavonols in leaves in autumn and spring seasons than that of *L. chilense*. Also, a higher concentration of proanthocyanidins in leaves and roots of both species was observed, which could be related to the structural role of these compounds. The phenolic acids were higher in *L. divaricata* leaves than in *L. chilense* leaves in autumn. The most evident effect was in the autumn because, at that time, the water is limited by the scarce rain and the low humidity of the soil (Varela et al. 2016).

Salinity is an important stress condition, especially in crops. In a studio developed by Elsheery et al. (2020), cucumber plants grafted in four rootstocks of pumpkin (*Cucurbita moschata* L.), bottle gourd (*Lagenaria siceraria* L.), Nubian watermelon (*Citrullus lanatus* L. var. *colocynthoide*), and winter squash (*Cucurbita maxima* L., commercial cultivar Flexil). The phenolic compounds showed an increase in all rootstocks when different doses of NaCl (0 control, 50, and 100 mM) were applied. Likewise, the authors associated the increase in the polyphenol oxidase activity with the phenolic content and suggested that those are positive factors against salinity stress.

Similarly, Arman et al. (2019) germinated hulled barley to 60 mM NaCl to induce saline stress; they found an increase in the content of free and bound phenolic compounds (including gallic acid, *p*-hydroxybenzoic acid, protocatechuic acid, sinapic acid, vanillic acid, *p*-coumaric acid, ferulic acid, and syringic acid) during the 6 days of evaluation. The ferulic acid increased 1.21 times more than the control treatment. *Mentha pulegium*, an important medicinal plant, was exposed to salt treatments (25, 50, 75, and 100 mM NaCl) for 2 weeks. The results showed a diminished growth at 75 mM NaCl in all organs; however, the accumulation of salt as higher in leaves compared with roots, which allowed the leaf to present a greater synthesis of phenolic compounds in response to saline stress (Oueslati et al. 2010).

The extreme temperature is another abiotic stress factor, by which plants can synthesize different phenolic compounds, as reported by Schmidt et al. (2010). They studied the effect of temperature and radiation conditions on kale of different genotypes. Results showed variations in flavonoid content depending on the genotype, also as temperatures decrease and radiation intensifies, quercetin and isorhamnetin increase its content, while kaempferol decreases. In this sense, two varieties (pink and violet) of *Lantana camara* were found an increase of lignin under extreme heat more than cold stress. Likewise, the content of phenolic compounds and tannins is increased in exposition moderate stress conditions in both the varieties (Nischal and Sharma 2020).

Another study carried out by Oh et al. (2009) on lettuce subjected to conditions of heat (40 °C for 10 min), cold (4 °C for 1 day), and high-intensity light (800 μmol/m^2/s for 1 day) showed similar total phenolic content both in the cold as in heat at day 3 of exposure, while exposure to light from day 1 showed an increase. Within the analyzed phenolic compounds profile, they obtained an increase in chicoric acid (ester of caffeic acid) and chlorogenic acid, mainly due to the effect of light and cold. The same behavior was found in luteolin-7-*O*-glucoside and quercetin-3-*O*-glucoside; these increases were four to six times higher than the control plants.

During the biotic stress, the phenolic compounds also are synthesized. They can act as feeding deterrents, where plants respond with an increase in lignin, a compound that can be a non-degradable barrier for most microorganisms (Moura et al. 2010). In this matter, phytoalexins are not detected before the attack of pathogens in plants; this phytochemical is synthesized from signaling molecules called elicitors such as fungal carbohydrates, fragments of the cell wall of the plant, and microbial enzymes that can also be activated by abiotic stress (Lattanzio et al. 2006). Phytoalexins act limiting the sporulation, spore germination, and hyphal growth in fungi, and has bacteriostatic properties (Kubalt 2016). Likewise, tannins contribute resistance to infestation, which can act in different ways: provide an astringent flavor affecting palatability, reduce feed consumption and digestibility, and act as enzyme inactivator (Lattanzio et al. 2006).

Some investigations have shown the synthesis of phenolic compounds in the presence of an infestation, such as that reported by Ballester et al. (2013). They found the presence of ten phenylpropanoid genes in flavedo of *Citrus sinensis* inoculated with *Penicillium digitatum*. This response is reflected in the presence of chlorogenic acid, acid caffeic, eriocitrin, narirutun, hesperidin, didymin, isohoifolin, diosmin, isosinensetin, hexamethyl-*O*-gossypetin, sinensetin, hexamethyl-*O*-quercetagetin, nobelin, tetramethyl-*O*-scutellarein, heptamethoxyflavone, and tangeretin, mostly in flavedo than albedo. Likewise, Chinese cabbage (*Brassica rapa* L.), under *Erwinia carotovora* subsp. *carotovora* infection, produces a mechanism of defense mognolignins (coniferyl and sinapyl) (Zhang et al. 2007).

Trichoderma spp. are fungi used as a biocontrol to protect plants, which suppress pathogens by different mechanisms but also induce the synthesis of phenolic compounds. In this sense, Pascale et al. (2017) evaluated two *Trichoderma* strains on *Vitis vinifera*, to induce polyphenols and resistance to *Uncinula necator*; they found that the fungi suppressed the disease caused by *U. necator* and increased the total phenolics. Due to these, fungi established a relation with host plants and induced several changes like the regulation of PAL and the expression of proteins to regulate pathogenesis.

De Ascensao and Dubery (2003) reported a similar effect in *Musa acuminate* roots exposed to cell wall elicitor from *Fusarium oxisporum*, showing an increase in the synthesis of phenolic compounds (conjugated and not-conjugated). The total phenolics presented an increase of 4.5-folds in 36 h compared with an initial time of exposition. In contrast, bound-phenolics, ester-bound phenolics, glycoside-bound phenolics, and free phenolics increased 6.3-, 4.2-, 3.0-, and 2.3-fold, respectively. The increase of bound phenolics was related to deposition of lignin, since it increased its content by elicitor effect, compared with the control treatment.

Likewise, Rani and Jyothsna (2010) found that rice plant increases the phenolic acids content as vanillic acid, syringic acid, cinnamic acid, and p-coumaric under infestation with *Scirpophaga incertulas* (Lepidoptera: Pyralidae), *Cnaphalocrosis medinalis* (Guenée), and *Nilaparvata lugens* (Homoptera: Delphacidae). On the other hand, the enzymatic activity of β-1,3-glucanase, SOD, and PAL decreased while peroxidase, CAT, and chitinase have been enhanced. The biochemical changes were in response to the pest attack and depended on the type of insect feeding.

10.5 Conclusions

The ability of plants to produce their metabolites as a defense mechanism or as the first line of defense against different types of stress, both biotic and abiotic, gives them the characteristic of being considered as biofactories of a wide variety of compounds derived from primary and secondary metabolism. Within these metabolites, phenolic compounds represent a large part of the secondary metabolites produced by the plant itself, which have a wide spectrum of activity against different types of stress. The presence of metabolites represents a great benefit in plants and an opportunity for the food, cosmetics, and mainly pharmaceutical industry, by producing a natural source of beneficial compounds in human health.

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Plant Phenolics: As Antioxidants and Potent Compounds Under Multiple Stresses

11

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Abstract

Reactive species are categorized into two broad sub-categories, reactive oxygen species (ROS) and reactive nitrogen species (RNS), possessing either a free radical with an unpaired electron in the valence shell or a neutral molecule. Free radicals are classified as one of the crucial steps in stress signaling which often cause unavoidable impairment to the essential biomolecules as a result of which the cell experiences various regulatory impairments. Redox homeostasis between the oxidants and antioxidants is the key to ensure normal cell functioning. As far as the current scientific evidence is concerned, almost all the plants possess natural antioxidants distributed throughout different parts of the plants. Different antioxidant assays show the potentiality of plant phenolics as an effective radical scavenger. Multiple hydroxyl and carbonyl groups of polyphenols help in the establishment of stable metal- and protein–polyphenol

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complex thereby restricting the development of free radicals. Phenols are known to work harmonious with other antioxidants thereby escalating the overall radical scavenging activity. A plentiful of research is evident on the propensity of plant phenolics as antioxidants but two things limit their current usability as food antioxidants. First, plant phenols are secondary metabolites and their continuous biotransformation inside the cells and tissues is an obvious event making their bioavailability difficult. Second, there are a few pieces of evidence on the toxicity and/or carcinogenicity of plant phenolics which restricts the considerations for the acceptability of such antioxidants as food additives. By considering the before-mentioned facts, this chapter compiles the emerging roles of phenolic compounds as antioxidant and impacts of multiple stressors on plant processes and stress managements through phenolic compounds.

Keywords

Phenolics · Antioxidants · ROS · Multiple stress · Stress management

11.1 Introduction

The basic life functions of a typical plant involve production and utilization of various plant metabolites which are categorized into primary and secondary metabolites (SMs). The latter is a derivative of primary metabolite and often described as an intermediate or end product of metabolic pathway. A great proportion of organic compounds do not participate directly in growth and development. Unlike primary metabolites, the presence or absence of these metabolites does not strictly impair the organism's established functionality. However, majority of the plant SMs are naturally constitutive and exist in their biologically active forms leaving few as inactive precursors. Damages to the plants caused by several biotic and abiotic factors trigger the activation and modulation of these inactive precursors. Complex metabolic pathway often involves overlapped intermediates of primary and secondary metabolism indicating common pathway being shared by primary and secondary metabolisms (Verpoorte et al. 2000; Yeoman and Yeoman 1996). There are three distinguished groups of SMs, includes terpenes, phenolics and nitrogen, sulphur compounds (Jamwal et al. 2018).

Phenolic compounds have one aromatic ring with one (phenol) or more (polyphenol) $-OH^-$ groups. These SMs often exist in the form of different functional derivatives (esters, methyl ethers, glycosides, etc.) synthesized either through the shikimic acid pathway or through the malonate/acetate pathway. Phenolics are broadly classified into simple phenolics (such as phenolic acids), polyphenols (such as tannins, flavonoids), lignans, coumarins, lignins, resveratrol, etc. on the basis of their carbon backbone (Harborne 1964; Cheynier et al. 2013). Solubility of simple phenolics can be changed from polar organic solvent to water through esterification and glycosylation with further facilitation through the increased number of hydroxyl groups in case of polyphenols. Even though phenolic compounds are abundant in plant kingdom but their allocated amount varies from one another depending on the selectionary advantage conferred to an individual plant during the course of evolution. Plant phenolics are divided in two classes such as preformed phenolics (synthesized during the normal development of plant) (Pridham 1960) and induced phenolics (elicitor mediated synthesis by plants during stressed environment) (Nicholson and Hammerschmidt 1992).

Plants being sessile experience multitudinous stresses ceaselessly throughout their growth and development due to the ever-changing environment (Singhal et al. 2017). Plants have no/little options to adapt with the changing conditions. One of the adaptive responses of plants is synthesize SMs, especially phenolic compounds. Phenolic compounds have been shown very effective under multiple abiotic and biotic stress and unfavorable climatic conditions and provide tolerance via antioxidant activity. This chapter compiles the overview of phenolic compounds and their role under multiple stressors.

11.2 Overview of Plant Phenolics and Its Role

11.2.1 Primary Function of Plant Phenolics as Antioxidants

Research in the field of plant ecology and plant physiology to explore the potential of plant phenolics has gained the pace by virtue of antioxidant and free radical scavenging properties of plant phenolics. Presence of more than one acidic hydroxyl groups in the phenyl ring of polyphenols makes them good donors of hydrogen or electron and hence the ability to confer free radical reduction (chain-breaking function) and termination of the Fenton reaction through the phenoxy radical intermediates. These phenoxy radical intermediates can also act as pro-oxidants at a higher pH in the presence of higher concentration of phenolic compounds and redox-active metals (copper, iron). Certain phenolics like flavonoids impede the membrane lipid peroxidation through altered membrane lipid packing. This alteration causes drastic loss of membrane fluidity and thus prevents free radical diffusion (Rice-Evans et al. 1997). Stimulatory role of phenolics cause amplification of cellular antioxidant capacity through host antioxidant enzyme responses (Shetty and Wahlqvist 2004). Phenolic coupling followed by oligomerization in case of complex polymeric phenolics (viz. tannins) escalates the antioxidant ability (Bors and Michel 2002).

11.2.2 Additional Functions of Phenolics in Plants

Phyllospheric and rhizospheric exudates containing polyphenols in the form of leachates can act as signaling compounds which when enter the soil cause alteration in the rates of decomposition and nutrient cycling through direct or indirect effects caused to soil microbial (decomposer) community (soil–microbe interaction). Flower and fruit pigmentation are also aided by phenolics (viz. flavonoids). This gives the plant a blessing in disguise for its own propagation through pollinator-mediated seed dispersal. Cross-linking among cell wall polymers ordinarily imparts the long-term maintenance of structural integrity. In this regard, hydroxycinnamate, a phenolic compound, plays a significant role making it difficult for the approaching pathogens to penetrate the cell wall. Among other physiological role of plant phenolics includes integral signal during plant–fungus interaction, maintain fruit quality and aroma, primary barrier during herbivores attack, synthesis of plant growth promoting substances, bioremediation, water and mineral absorption, chlorophyll content, pigment composition, and as allelochemicals (Zaprometov 1992; Sharma et al. 2019; Kumar et al. 2020a, b, c).

11.2.3 Impacts of Plant Phenolics on Plant Physiological, Biochemical, Reproductive, and Yield Traits

Wide distribution and as a part of key product of secondary metabolism, phenolics are known to influence various growth- and development-related physiological process in plants. Be it in normal or stress condition, plants get constant amelioration in the suboptimal conditions through phenolics-mediated tolerance and adaptation. As mentioned earlier, phenolics have diverse direct or indirect roles in nutrient mobilization through signal transduction (viz. flavonoid and salicylic acid signaling), allelopathy, plant growth promotion through plant growth promoting rhizobacteria (PGPR), pigmentation, etc. apart from their active role as antioxidants. Phenolics are involved in functional pollen development (Van Der Meer et al. 1992; Taylor and Grotewold 2005) and imbibition mediated boosting of seed germination rate (Shankar et al. 2009). Photosynthetic activity and biosynthesis of assimilatory pigments (chlorophyll *a* and *b*) can be amplified in C_3 (sunflower) and C_4 (maize) plants through polyphenols (Tanase et al. 2015).

11.2.3.1 Antioxidants: Definition, Classification, General Mechanism of Action

Antioxidants are the substances which stop the oxidation of any substance and counteract the free radicals at the same time generated during oxidative stress even with relatively low concentrations. Antioxidants discontinue these sequence reactions by eliminate free radical intermediates and obstruct other reactions by being oxidized themselves.

11.2.4 Classification of Antioxidants

Antioxidants can be grouped into natural and synthetic antioxidant system. Natural antioxidants are further categorized into enzymatic and non-enzymatic antioxidants. Enzymatic antioxidants include superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPX), glutathione reductase (GR), and glucose-6-phosphate dehydrogenase. Enzymatic antioxidants are produced endogenously where as

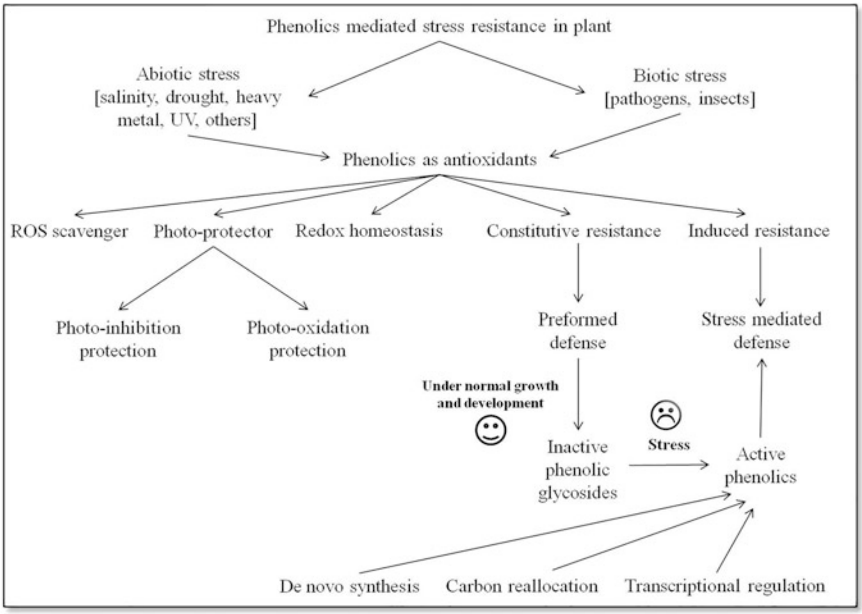

Fig. 11.1 Plant stress mitigation through phenolics-mediated resistance

non-enzymatic antioxidants are mostly from dietary origin. Non-enzymatic antioxidants include minerals (zinc, selenium), carotenoids (β-carotene, zeaxanthin, lycopene), vitamins (vit. A, C, E, K), some antioxidant cofactors (coenzyme Q_{10}), and phenolics (Bunaciu et al. 2012) of which polyphenols is the largest class (Liu 2004). On the other hand, synthetic antioxidants (given in Fig. 11.1) are man-made compounds synthesized chemically. When stressed, plants generate singlet and triplet oxygen species, peroxides, harmful enzymes. The role of antioxidant system is to scavenge these toxic radicals as singlet and triplet oxygen quenchers, synergists, enzyme inhibitors, and peroxide decomposers (Manach et al. 1998). Some of the analytical methods to measure antioxidant content and capacity of plant extracts are based on assays involving hydrogen atom, assays involving electron transfer, chemiluminescence, etc. (Huang et al. 2005).

11.2.5 Stress-Mediated ROS Generation and Redox Signaling: Good or Bad?

Exposure to various abiotic and biotic stresses leads to an imbalance in cellular redox homeostasis followed by generation of reactive oxygen species (ROS), which sooner or later leads to the oxidative stress and damage of plant cell organelles. For plant stress mitigation, optimal level of ROS acts as a priming step in the activation of antioxidant system through ROS-mediated redox signaling. On the contrary, over production of ROS leads to disruption of normal cell functions leading to the plant immune system failure (Hussain et al. 2019). Hence, generation of ROS can be considered as a necessary evil. Stress-mediated ROS generation has several impacts on plants both physiologically and biochemically through protein disruption, reduced CO_2 fixation in chloroplasts, photooxidative damage to the photosynthetic complexes (principally PSII), membrane peroxidation ultimately leading to programmed cell death (PCD) (Amist et al. 2019).

ROS-mediated redox signaling is a cascade of event where redox-sensitive signaling proteins and metabolic enzymes undergo reversible oxidation/reduction to execute cellular functions via either regulating or amplifying the downstream signaling components, such as kinases, phosphatases, and transcription factors (Suzuki et al. 2012). Physiological events in the plants are regulated by phytohormones to a large extent. ROS acts as secondary messenger in the hormone signaling pathways and can impose hormonal regulation feedback or feedforward mechanism (Noctor et al. 2018). As a consequence of this cross-linked signaling between ROS and hormone, plants undergo modified root architecture triggering lateral root emergence with enhanced root hair growth (Du and Scheres 2018).

11.3 Abiotic Stress Response Through Phenolics

Challenges from ever transforming environment coupled with increased anthropogenic activities force plants to undergo a plethora of biotic and abiotic stresses throughout their life. These create a major setback in terms of their growth, development, and yield attributes.

Plants endure this unfavorable condition through different inherent mechanisms and acclimatize in the hostile environment surrounding them. In this regard, the chapter elaborates the role of antioxidant systems with a specific reference to phenolics (plant SM) to mitigate various abiotic and biotic stresses along with the basics of the mechanism underlying.

Plant SMs are believed to be considered as by-products until the scientific evidences regarding the active involvement of plant phenolics in maintaining a harmony between plant and its surrounded environment whether for stress mitigation or growth and developmental process have popped up. The fascinating fact about plant phenolics are they not only involved in the obliteration of harmful organisms associated with the abnormal growth and metabolism of plants but also playing a crucial role in maintaining the healthy population of beneficial symbiotic microorganisms around rhizosphere. The defensive action and expression of plant phenolics against biotic stresses (pathogenic microbes, insects, etc.) are something bestowed to plants during the natural evolution process. This built-in basal level of constitutive expression plus an induced expression of phenolics through stress-mediated signaling provides two-layered protection to the plants. Counteracting mechanism of phenolics against insects or pathogens can be direct or indirect (toxicity through induced changes in phenolic profiles) (Tyagi et al. 2020; Tak and Kumar 2020; Wagay et al. 2020). Among different schemes of the phenolics-mediated plant stress tolerance, the most noticeable is the activation of antioxidant systems which is synergistic to almost all the defense mechanisms in the plants. In fact, phenolics itself can act as an antioxidant to scavenge ROS (Amarowicz et al. 2010) and hinder the activities of specific oxidizing enzymes (Elavarthi and Martin 2010). Cross negotiation among various factors such as phytohormone production, biosynthetic pathway modulation occurs by virtue of the radical scavenging ability of antioxidant system and through optimized ROS signaling.

Physiological and molecular mechanisms concerning SMs production are deeply concatenated with the interactions between signaling molecules (salicylic acid, jasmonic acid, their derivatives, etc.) and enzymes for phenolics biosynthetic (phenylpropanoid) pathway (do Nascimento and Fett-Neto 2010; Cheynier et al. 2013). There is an absolute certitude that stress mitigation through phenolics is a resultant of one or more enzymatic (phenylalanine ammonia lyase; PAL, chalcone synthase; CHS, dihydroflavonol 4-reductase; DFR, cinnamate-4-hydroxylase; C4H, flavanone 3-hydroxylase; F3H, flavonol synthase; FLS, isoflavone synthase; IFS, isoflavone reductase; IFR, UDP flavonoid glycosyltransferase; UFGT) modulation (s) involved in phenolic biosynthetic pathway (Sharma et al. 2016, 2019; Ashraf et al. 2018; Naikoo et al. 2019).

11.3.1 Phenolics-Mediated Resistance Towards Salinity Stress

Phenylpropanoid-mediated synthesis of phenolics helps in scavenging ROS effectively in osmotic and ionic mismatches during salt stress (Rossi et al. 2016; Al-Ghamdi and Elansary 2018). Up-regulation of flavonoid biosynthetic genes like VvbHLH1, NtCHS1, GmFNSII-1, GmFNSII-2, etc. helps in accumulation of flavonoid thereby aiding phenolic-mediated ROS scavenging (Tanase et al. 2014; Wang et al. 2016; Zheng et al. 2017). Similarly, enhanced transcript levels of PAL, C4H, F3H, DFR, FLS facilitate tolerance mechanism to the plants under salt stress (Perin et al. 2019). In Brassicaceae (Chinese cabbage, white cabbage, and kale), short-term adaption to salinity stress is species specific and phenolic compound hydroxycinnamic acid is higher in tolerant species. In this case, phenolic compounds provide tolerance via maintaining of higher levels of SM, osmoprotectants, and suffer less from metabolic imbalance or disorders (Linić et al. 2019)

11.3.2 Phenolics-Mediated Resistance Towards Drought Stress

Reports suggest under water deficit conditions both the accumulation and synergism of phenolics (such as flavonoids) with other antioxidant systems go hand in hand resulting in plant resistance against drought stress (Sánchez-Rodríguez et al. 2011). Water scarcity induces closure of stomata resulting in less CO_2 diffusion through stomatal pores. At this point, cell utilizes less reducing power ($NADPH + H^+$) and ATP to synthesize carbohydrate as there is lower concentration of CO_2 to be fixed.

The lack of CO_2 also leads to impaired Calvin cycle making it almost difficult for the conversion of NADPH + H^+ and ATP to $NADP^+$ and ADP + Pi. The non-utilization of vast number of free electrons possessed inside the reducing equivalent may then be able to break redox homeostasis through ROS generation inside the cell. Xanthophyll cycle play two key roles in drought stress. First, it helps in reverting the excess NADPH + H^+ and ATP into $NADP^+$ and ADP + Pi even in the absence of Calvin cycle. Second, it forms excess of SMs among which phenolics occupy the major proportion thus contributing towards the cellular redox homeostasis by scavenging ROS in the system if any (Gnanasekaran and Kalavathy 2017).

11.3.3 Phenolics-Mediated Resistance Towards Heavy Metal Stress

Transcriptional regulation of phenylpropanoid pathway enzymes (phenylalanine ammonia-lyase, chalcone synthase (CS), shikimate dehydrogenase, (SKDH) cinnamyl alcohol dehydrogenase (CAD), and polyphenol oxidase (PPO)) (Zafari et al. 2016; Chen et al. 2019) causes up-regulation in their activity under metal stress (Handa et al. 2019). This up-regulation is the main cause of phenolic (flavonoid)-mediated metal stress tolerance and their subsequent metal chelation process (Kisa et al. 2016) with an ultimatum of protecting the plants from oxidative stress and ROS.

11.3.4 Phenolics-Mediated Resistance Towards UV Stress

Light/UV stimulated flavonoid biosynthetic pathways and their corresponding gene transcript levels (Naikoo et al. 2019; Chen et al. 2019; Ghasemi et al. 2019) are the key to protect plant and its photosynthetic apparatus against high-intensity light and UV radiations by absorbing them (Lattanzio 2013; Landi et al. 2015). This modulation of the flavonoid biosynthetic pathway can either be a dependent or independent process on hormone (ABA) and/or jasmonic acid (Demkura et al. 2010; Berli et al. 2015).

Other abiotic factors like excess application of insecticides (Sharma et al. 2016), heat stress (Świeca 2015), chilling stress (Zhou et al. 2019; Wang et al. 2019), etc. invigorate cells' ability to accumulate phenolic compounds by up-regulating biosynthetic pathway enzymes for quenching the reactive radicals. Plant cell wall thickening through lignification and suberization enhances freezing stress tolerance (Griffith and Yaish 2004).

11.4 Plant Phenolics and Biotic Stress: Beyond Antioxidant Role

The generalized scheme of plant stress mitigation through phenolics is depicted in Fig. 11.1. Like abiotic stresses, plants have to undergo multiple biotic stresses caused by diverse living micro or macroscopic organisms. Even though plants contain a diverse group of protective molecules such as preformed peptides, proteins, and SMs against these biotic factors but the concentrations of these molecules are often at basal levels. However, pathogenic attack causes genetic reprogramming followed by elevation to their levels through elicitor-induced expressions as documented in case of phenolics where plant accumulate higher levels of phenolics through elicitor-mediated up-regulation in the activities of biosynthetic enzymes such as phenylalanine ammonia lyase and chalcone synthase (Campos et al. 2003; Yedidia et al. 2003).

Detection of potential assailants can activate the plant defense response which is otherwise kept under tight genetic control in normal condition to maintain equilibrium between primary and secondary metabolism. The sudden surging in the SMs expression levels is due to the plant signal perception in the form of damages caused due to the toxins produced by pathogens and is evident from an increased levels of phenolics under fungal infection (Verma and Shukla 2015). In fact, preformed phenolic compounds are stored as antibiotic phenolics in inactive bound forms and get activated rapidly upon pathogen attack. The beauty of plant system having SMs (phenolics) is that there is no requirement of additional transcriptional activation for their expression but mere breakage of compartmentalization is enough to create a protective shield against biotic stresses (Osbourn 1996).

Phenolics-mediated oxidative reactions consume excess oxygen making a toxic environment for the pathogen survival. Presence of acidic hydroxyl groups in polyphenols has made them suitable candidates to penetrate biological membranes of fungus, while multiple hydroxyl groups help in uncoupling of oxidative phosphorylation (Siqueira et al. 1991; Parvez et al. 2004). Complex natural phenolics such as tannins and lignans can reduce the in vitro growth of fugal mycelium through their inhibitory action on the extracellular fungal enzymes which are essential for host tissue penetration (MacRae and Towers 1984). Mechanical penetration and survival of fungal pathogens are restricted via elicitor-mediated lignifications of plant cell wall which impede the movement of water and other diffusible molecules for pathogen survival (Garcia-Brugger et al. 2006; Houston et al. 2016). In this regard, flavonoid can also serve as low-molecular weight phytoalexins which are antimicrobial in nature (Samanta et al. 2011).

11.5 Factors Affecting the Regulation of Phenolic Biosynthesis

11.5.1 Proline Accumulation Under Stress

A key linkage between environmental stress and adaptive responses of plants towards stress is discussed here. Both biotic stresses and abiotic stresses induce the accumulation of a large quantity of free proline through reduced oxidation of the amino acids. This temporary proline accumulation through proline-D1 pyrroline-5-carboxylate (P5C) cycle generates a pool of $NADP^+$ and regulates cellular redox potential (Kaur and Asthir 2015). Pentose phosphate pathway (PPP) is an established pathway for phenolic biosynthesis among others (Shetty and Wahlqvist 2004). Since

$NADP^+$ is the cofactor for the enzyme (glucose-6-phosphate dehydrogenase; G6PDH) catalyzing rate limiting step of PPP, proline-mediated high-$NADP^+$/NADPH flux may augment phenolic biosynthesis (Cheynier et al. 2013) along with other phenolic precursor forming pathways like glycolysis (Maeda and Dudareva 2012) and calvin cycle (Lattanzio et al. 2009).

11.5.2 Cellular Compartmentalization

Synthesis of plant phenolics in thylakoids of chloroplasts and their subsequent storage (as inactive phenolic glycosides) in cell vacuoles manifest that the compartmentalization is a necessary physiological event to pile the reduced form of phenolics (Wink 1997). Stress-triggered de-compartmentalization (Beckman 2000) can cause mixing up of glycosidase enzyme with its inactive substrate (phenolic glycosides) resulting in clip off of glucose moiety thus making active phenolics ready for stress response (Dai et al. 1996).

11.5.3 Carbon Reallocation: As a Function of Growth vs Defense

Tolerance and resistance mechanisms of plants come with a high cost of resource allocation for the synthesis of defensive metabolites. Therefore, plants do not synthesize these metabolites unless they are threatened with potential harm above their threshold level. Unlike a stressed plant, a healthy plant only relies on the preformed or constitutive defenses (Morrissey and Osbourn 1999; Wittstock and Gershenzon 2002; Koricheva et al. 2004). Plant's decision whether to grow or defend drives the quantitative (constitutive expression) and qualitative (de novo synthesis) synthesis phenolics through either carbon reallocation (production of defensive SMs instead of developmental primary metabolite like sucrose) or enzyme kinetics alteration at transcriptional level (Henkes et al. 2001; Nakane et al. 2003; Lloyd and Zakhleniuk 2004; Leser and Treutter 2005; Fritz et al. 2006; Walters and Heil 2007; Akula and Ravishankar 2011; Vos et al. 2013 represented in Fig. 11.2).

11.5.4 Theory of Photo-Protection and Co-evolution: Blessings in Disguise

Red to reddish-orange color of the deciduous tree leaves are due to the storing of anthocyanin, a class of flavonoids inside the acidic vacuole, a specialized leaf compartment. These color cues due to the presence of anthocyanin solve two major problems of the plants. First, it provides protection against photo-inhibition and photo-oxidation of photosynthetic pigments through light attenuation (green sunlight interception). Second, the red color might serve as a representation of plants poor nutrient status and hence not preferred by the insects and hence a low-insect

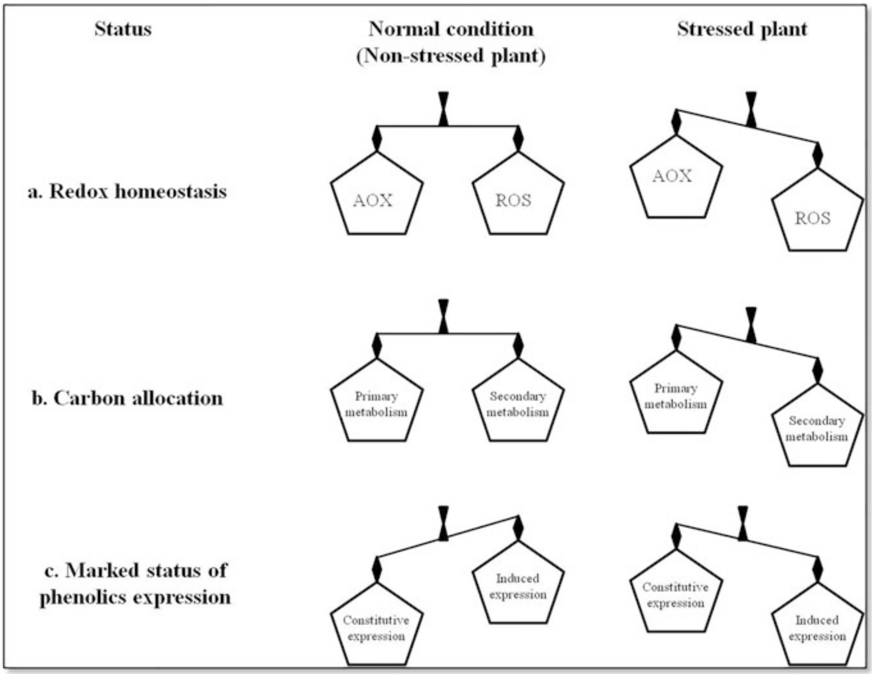

Fig. 11.2 Status of normal (non-stressed) and stressed plants. (**a**) Redox homeostasis (*AOX* antioxidant, *ROS* reactive oxygen species); (**b**) carbon allocation (primary metabolism, secondary metabolism); (**c**) marked status of phenolics expression (constitutive expression, induced expression)

load (Archetti 2009; Archetti et al. 2009; Nikiforou and Manetas 2010; Hughes 2011).

11.6 Plant Physiological, Genetical, Biochemical and Molecular Approaches to Improve Phenolic Compounds and Stress Mitigation

In terms of plant physiology, stress is defined as any abiotic or biotic factors which affect plant functioning and development. Nearly every plant has to undergo various forms of stress during their life cycle as a result of which it affects the growth and yield of the plant. Plants accumulate phenolic compounds as a defense strategy again, stress. Though it provides a defense to plants during adverse conditions but the trade-off between growth and defense has certain limitations. Since resources are limiting, the strategy of mitigating stress by improving the phenolic compound comes with certain restrictions. Three different approaches can achieve the engineering of improving phenolic content.

11.6.1 Biochemical Strategies of Phenolic Compounds to Mitigate Stress Tolerance

Growth regulators, nutrients, and fertilizers on phenolic development have crucial role in balancing of plant redox equilibrium. Treatment of grape leaf and fruit by sucrose and abscisic acid was found to be highly correlated with total phenolic content (Gambetta et al. 2010). Spayd et al. (1994) observed that nitrogen used to have an inhibitory effect on phenolic content. Under low nitrogen, the canopy was lighter and exposed for better light-enhancing phenolic accumulation. Phenolic content and metabolism have diversely been affected by growth regulators. Berhow (2000) studied that ABA had a little effect on the flavonon responsible for the bitterness of the grapefruit. Whereas GA reduced the flavonon content lowering the bitterness of grape. A plethora of literature suggests that the induction of biotic and abiotic stress response in plants is mediated by signaling molecules such as jasmonic acid, salicylic acid, and their derivatives. Such defensive phenolic compounds play a vital role when plants are infected with microbial pathogens. Lauvergeat et al. (2001) demonstrated that the application of salicylic acid in Arabidopsis resulting in accumulation of defense phenolic compounds. North et al. (2012) demonstrated that NAA and six BAP significantly increased phenolic exudation during micro-propagation. Several other studies showed that application of methyl jasmonate resulted in decreased phenolic content due to decreased gene expression of phenylalanine ammonia-lyase (PAL) important enzyme in chlorogenic acid biosynthesis. Ruiz et al. (2003) reported that calcium induces the activity of PAL. Due to the increase in total calcium content PAL activity increased, resulting in decreased phenolic content. Similarly, boron was found to have an inhibitory effect on phenols. Ruiz et al. (1998) reported that deficiency of boron leads to increase phenolic content. As provided from the information here, various biochemical factors play a significant role in increasing the accumulation in plants and hence crucial for mitigating abiotic stress.

11.6.2 Genetic/Metabolic Engineering of Phenolic Compounds to Mitigate Stress Tolerance

Flavonoids and carotenoids are one of the largest classes of plant phenolics. Both play an essential role in both abiotic and biotic stress response. Necessarily, the alteration in the biosynthetic pathway of phenolic compounds can optimize and regulate the production of flavonoids. The genetic and metabolic engineering of flavonoids and carotenoids can be achieved through following different approaches.

11.6.2.1 Blocking the Biosynthetic Pathway (RNAi Pathway)

In this technique, the RNA nucleotide, which is identical with the transcript sequence, is used. It is commonly known as the antisense RNA technique. Davuluri et al. (2005) reported that the operation of specific promoters using RNA technology increase the level of carotenoids. Casacuberta et al. (2015) reported that DET 1 gene was regulated using RNAi technology resulting in an enhanced level of flavonoids.

11.6.2.2 Endogenous Synthesis of Biochemical Compounds Using Structural and Regulatory Genes

The engineering of structural genes in the fruit peel of tomato resulted in a 70-fold elevation in flavonol (Bovy et al. 2007). CHS, CHI, F3H, and FLS are the four most essential enzymes flavonoid biosynthesis pathway. The overexpression of this for genes resulted in flavonoid production both in the peel (primary quercetin glycosides) and flesh (primary kampferol glycosides).

11.6.2.3 Inserting New Branches: The Pathway for the Production of Novel Flavonoids

Stilbene synthase is a key enzyme involved in trans-resveratrol biosynthesis. Trans-resveratrol is a phenolic compound with antioxidant properties. Bovy et al. (2007) reported that introduction of Stsy gene in lettuce enhanced the synthesis of revarstatol in transgenic lettuce. Shih et al. (2008) reported that engineering of soybean isoflavone synthase genes resulted in increased phenolic content. Through this genetic manipulation, neither the content of other phenolic compounds was altered or had any side effects.

11.6.3 Physiological Strategies of Phenolic Compounds to Mitigate Stress Tolerance

In the context of improving plant phenolics for abiotic stress tolerance, physiological strategy including screening based on mechanical wounding, chlorophyll pigment, osmolyte, nutrient stress, UV irradiation, and heat shock are essential (Godara et al. 2016). Among these various approaches, solar radiation plays a crucial role in increasing phenolic content in plants. Analysis of the metabolomics-based phenotyping of compounds, regulating physiological processes in plants, revealed that carotenoids and flavonoid content variation in different varieties could provide insight into an effective strategy for mitigating abiotic stress. For increasing the content of flavonoids and carotenoids, environmental factors play a crucial role. This happens due to the significant role of environment in modulating the physiological processes in plants. A list of environmental factors, which can be included in improving the phenolic content in the plant are enlisted below in Table 11.1.

11.7 Conclusion

In conclusion, phenolic compounds are ubiquitous in nature and have very crucial role in plant growth and developments. In the field conditions, plant faces a number of adverse situations like biotic and abiotic stresses at different growth stages and responsible for production of high ROS. These ROS are highly reactive, cause the

Table 11.1 Plant biochemical changes upon abiotic stress exposure

Sl. no.	Environmental factors	Response	Reference
1.	Sun exposure	Increase in anthocyanin content	Downey et al. (2004)
2.	Sun exposure	Increase in flavonol content	Spayd et al. (2002)
3.	UV-B exposure	Increase in flavonol and stilbene content	Booij-James et al. (2000)
4.	UV-B exposure	Increase in flavonoid content and cinnamic acid	Reuber et al. (1996), Zucker (1965)
5.	Temperature	Decrease of anthocyanin content at high temperature (30–35 °C)	Mori et al. (2005)
6.	Temperature	Decrease of cinnamic acid content under heat stress	Fletcher et al. (2005)
7.	Irrigation	Deficiency of water leads to an increase in phenolic content	Marsilio et al. (2006)
8.	Irrigation	Root zone during leads to an increase in total phenolic compounds	Santos et al. (2005)
9.	Heavy metals	Upregulation of PAL, chalcone synthase, SKDH, CAD, and PPO	Zafari et al. (2016), Chen et al. (2019)
10.	Salinity	Up-regulation of flavonoid biosynthetic genes like VvbHLH1, NtCHS1, GmFNSII-1, GmFNSII-2, etc. help in accumulation of flavonoid	Sharma et al. (2019)

membrane disruption of cell organelles, and disturb the functions of normal cell machinery. Phenolic compounds have important role in maintaining the cell functions under these situations by reducing ROS, provide structural integrity, signaling and change at biochemical and molecular levels. This chapter clearly concluded about the functions of phenolic compounds and impact of different stressors on physiological and biochemical levels of plants. Additionally, this chapter gives insight on the physiological, biochemical, and molecular mechanism of phenolic compounds under these circumstances. Therefore, a proper insight of the biochemical, physiological, and molecular understanding along with genomics, metabolomics, transcriptomics, and phenomics approach will enhance the opportunity of improving the phenolic content for mitigating multiple stress response in plants.

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Interactive Role of Phenolics and PGPR in Alleviating Heavy Metal Toxicity in Maize

12

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Abstract

Environmental pressure is one of the most significant issues restricting agrarian productivity around the world. Heavy metal stress is one of these pressures that has become a source of worry. To address expanding global food demands in a sustainable manner, reliable, ecologically friendly approaches are required. Plant-microbe interactions and phenolic compounds are two major approaches that are being widely explored among others. With the employment of plant growth-promoting rhizobacteria (PGPRs), which are now commonly used, plant-microbe interactions can reduce heavy metal stress. PGPRs are known to improve plant growth, development and tolerance to stresses, both biotic and abiotic, through a variety of ways. Phenolic compounds, on the other hand, are a developing approach for reducing heavy metal stress. Phenolic compounds are a type of secondary metabolite found in plants that perform a significant physiological role throughout their life cycle. Plants that are grown in stressed circumstances can biosynthesise more phenolic chemicals than plants that are grown in regular settings. These chemicals have antioxidative characteristics and can scavenge free radicals, reducing cell membrane peroxidation and thereby shielding plant cells from the negative results of oxidative stress. Thus, the interaction of phenolics and PGPR on *Zea mays* under heavy metal stress has been examined.

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Due to its improved adaptation to a wide range of settings, maize (*Zea mays L.*) is one of the most significant cereal crops in the world. It is primarily used as a food source and has evolved into the most effective raw material for food and feed. In addition, it can be utilised to generate bioenergy. Maize grains are high in nourishment, and their oil is used in cooking. Maize is a C4 crop that is relatively vulnerable to HM stresses. When cultivated under HM stress, however, its development and output might be severely hampered. As a result, an effort has been made to give both current and fresh knowledge on the interacting role of phenolics and PGPR in a heavy metal-stressed environment.

Keywords

Heavy metal stress · Phenolics · PGPR · Oxidative stress · Stress alleviation in maize

12.1 Introduction

Heavy metal deposition in soil as an outcome of widespread industrialisation has altered agricultural practices and reduced crop output to a great extent in recent years. Excessive heavy metal deposition in soil and vegetation results in physical damage, growth retardation and a decline in plant's physiological and biochemical processes. The impact and bioavailability of heavy metals are determined by environmental parameters such as soil texture, acidic and basic nature of soil, element species and fertilisation, as well as type of plant (Ul Hassan et al. 2017). Chlorosis, morphological abnormalities, metabolic diseases and a loss in plant development and productivity are all caused by greater concentrations of heavy metals like Cd, Cr, Ni, Co, Pb and Zn in soil (Amari et al. 2014; Mariem et al. 2014; Taamalli et al. 2014). Heavy metal accumulations in cereals have more serious repercussions since they reach the food chain (Friesl-Hanl et al. 2009).

In recent years, a serious deterioration in soil fertility and a degradation in the quality of foods and their products have been seen as a consequence of escalating use of chemical fertilisers. The mounting cost of chemical fertilisers as well as the accompanying environmental risk and health hazards linked with their use is also a matter of concern. As a result, the researchers' mind-set has turned to using biological solutions to overcome the HM toxicity challenges, such as microbial biotechnology and secondary metabolites (Jain et al. 2020; Choudhary et al. 2016; Ashraf et al. 2017).

Plant growth-promoting rhizobacteria (PGPRs) are a diverse class of bacteria found in the root zone of plants (rhizosphere) that can directly and/or indirectly enhance the quality of plant development (Ebrahim and Aly 2004; Shahzadi et al. 2012). Direct impact of PGPR in rhizosphere includes the synthesis of phytohormones such as CKs, GA and auxins (Ahmad et al. 2005; Babaloa 2010); however, indirect effects include the development of antibiotics that suppress infections (Ahmad et al. 2005; Babaloa 2010; Mahmoud et al. 2004). Drought, salt, heavy metals, water logging and high temperatures are all examples of unfavourable environmental situations when PGPRs show vital role in plant stress resistance. Abiotic stressors cause many effects in plants, including decreased water potential and leaf growth, changes in cellular metabolism and amplified ethylene synthesis (Greenberg et al. 2008). The amount of 1-aminocyclopropane-1-carboxylic acid (ACC) in plant cells is closely linked to the increase of ethylene in plants (Machackov et al. 1997). ACC deaminase containing PGPR may operate as an ACC sink, ensuring that ethylene levels do not rise to the point where root growth is compromised. As a result, PGPR in stressed plants may reduce ethylene levels, extend the life of seedlings and aid in the creation of lengthier roots (Glick et al. 1998). Moreover, PGPRs can manufacture plant hormones that encourage cell growth and cell division while also assisting plants in becoming more resistant to environmental challenges (Glick and Pasternak 2003). In metal-stressed soil, the metal-resistant PGPR can play an important part in the persistence and growth of plants (Rajkumar and Freitas 2008).

Phytoremediation is a low-cost, energy-proficient detoxifying technology that employs fundamental plant properties to accumulate metal pollution in shoot biomass and minimise heavy metal bioavailability. By secreting acids, phytoantibiotics, proteins and other chemical, soil microorganisms reduce the harmful effects of heavy metals on plants (Denton 2007), implying that PGPRs are future tools and trends for sustainable agriculture.

Plant growth-promoting rhizobacteria (PGPRs) can increase agricultural yields by encouraging plant development through a variety of processes (Singh et al. 2016). Plant growth is influenced by PGPRs, which produce phytohormones, improve phosphorus availability and expand plant's root system to absorb more H_2O and nutrients. Furthermore, PGPRs influence enzymatic activities such as ACC deaminase and the generation of rhizobiotoxine, which helps to minimise the negative effects of ethylene and improve nodulation and nitrogen fixation (Zandi and Basu 2016). PGPRs are having a major influence on soil properties and are critical in the transformation of infertile land into productive land (Gouda et al. 2018). Though the longevity of PGPRs in the soil is subject to its compatibility with the crop on which they are inoculated, its ability to interact with native microflora in the soil and environmental conditions all play an important part in their use (Singh et al. 2016). Furthermore, certain PGPRs may have extra specialised plant growth-promoting characteristics, like heavy metal detoxification, salt tolerance and biological control of phytopathogens and pests (Egamberdieva and Lugtenberg 2014). Plant growth-promoting rhizobacteria (PGPRs) are having great significance in agronomy because they promote plant growth and yield (Bharti et al. 2014; Ilangumaran and Smith 2017). A number of PGPRs have been shown to reduce HM toxicity in crop plants. In addition, because of its low prices and living nature, inoculation technique utilising PGPR is acknowledged as a valuable eco-friendly instrument for optimising sustainability in farming and related sectors (Choudhary et al. 2016). Plant colonisation by PGPR is intervened by the production of various compounds, amino acids, antibiotics and proteins that aid plants in the removal of heavy metal toxicity (Khan et al. 2013). With the help of processes like reduction, oxidation, methylation or demethylation, compartmentalisation and transforming to a less perilous form, the PGPRs have the capability to decrease the dangerous effects of heavy metals (Nazir et al. 2011).

Phenolic compounds are a type of secondary metabolites found in plants that perform a significant physiological role throughout their life cycle. Plants produce phenolics in both ideal and inadequate settings, and they play important roles in developmental processes such as cell division, reproduction, photosynthesis, hormonal control and nutrient mineralisation.

Plants produce more polyphenols such as phenolic acids and flavonoids, in response to abiotic stress, which helps the plant cope with environmental limits. Due to abiotic stress conditions like heavy metals, drought, salinity, ultraviolet radiations, high temperature and low temperature, the phenylpropanoid biosynthetic pathway is activated, following the build-up of numerous phenolic compounds that, among other things, have the potential to hunt injurious reactive oxygen species (Sharma et al. 2019). As a result, crop productivity losses can be avoided by enhancing crop performance by plant secondary metabolism stimulation (Shahzad et al. 2018a, b; Sharma et al. 2012). Stressed plants, as previously stated, have high polyphenol concentrations, which increase in response to these stresses, assisting plants in adapting to unfavourable circumstances (Pereira 2016; Lattanzio 2013). As a result, the amount of phenols in plant tissue is a good predictor of the level of abiotic stress tolerance in plants, which varies widely among plant species and is influenced by a variety of external stimuli. The growth and development of plants are influenced by phenolic compounds, which also include seed germination, biomass build-up and better plant metabolism (Raskin 1992; Yalpani et al. 1994; Senaratna et al. 2000; Nazar et al. 2011).

Maize (*Zea mays* L.) belongs to Poaceae family and is one of the world's main staple foods, alongside wheat and rice with a worldwide production of over 1×10^9 t since 2013 (Noman et al. 2015; Zampieri et al. 2019). It is farmed for a variety of reasons, including human consumption, animal feed, forage production and the creation of renewable energy (bioenergy) (Aslam et al. 2015; Ai and Jane 2016). Maize is a versatile emerging crop that can adapt to a wide range of agro-climatic situations. It is called as the "Queen of Cereals" around the world due to its highest genetic production potential of all cereals (Solaimalai et al. 2020). Maize (*Zea mays* L.) is a common cereal crop grown all over the world, and it has a lot of potential for phytoremediation of HM-contaminated soils (Rizwan et al. 2017; Vatehová et al. 2016). For many poor people around the world, maize is a vital source of nutrients like proteins, iron, vitamin B, minerals and glucose. It is also an important source of revenue for poor farmers in unindustrialised countries. Maize is in high demand since it is utilised both as silage and crop residue, and the grains are often used for food, starch and oil extraction in the industrial sector. As a result, maize development is critical in order to meet rising demand (Solaimalai et al. 2020).

Heavy metals are a class of metals and metalloids that are harmful to humans, plants and animals even in small concentrations, since they tend to accumulate in living organisms and their uptake poses a serious health risk to them. Heavy metal-contaminated soil has an undesirable influence on growth and development of plants and microorganisms, resulting in lower crop productivity (Adrees et al. 2015; Keller et al. 2015; Adriano 2001). HMs cause plant stunting, chlorosis and growth and germination inhibition (Mohamed 2011; Malar et al. 2014). Heavy metals can affect the permeability of cell membranes, hormone balance and certain sulfhydryl-containing enzymes, change mineral nutrient composition, disrupt water content and produce reactive oxygen species (ROS) once within the cell (Sharma and Dubey 2005). HMs can harm a wide range of plant species by causing oxidative stress, affecting the antioxidant defence system and overproducing reactive oxygen species (ROS). Plant stress tolerance to HMs is determined by the accumulation of osmoprotectants such as proline (Pro) and secondary metabolites such as phenolic substances, as well as the synthesis of antioxidant enzymes that help to scavenge ROS (Siddiqui et al. 2012).

Abiotic stressors affect the yield, growth and development in maize plants. Plants have evolved dynamic physiological, biochemical and molecular reactions that enable them to flee and/or survive unfavourable environmental situations (Chávez-Arias et al. 2021). As a result, in the case of maize plants, it is necessary to develop some environmentally acceptable and effective solutions to alleviate heavy metal stress.

12.2 Description About Heavy Metal Toxicity in Plants with Special Reference to Maize

The pollution caused by metals is considered as a chief environmental, plant and animal health concern. Heavy metals are naturally present in Earth's crust, but human activities including urbanisation, industrialisation and land-use change have raised their prevalence to dangerous heights. Application of fertilisers, mining activities and withering of rocks also contribute to the growth of heavy metals in Earth's crust (Gambu and Wieczorek 2012; Mohamed 2011; Shahzad et al. 2018a, b). The condition of soil is critical for growing food crops, since heavy metal accumulation reduces plant production and also its concentrations get magnified in food chains which puts human health at risk (Jaishankar et al. 2014; Mohamed 2011). Some heavy metals are needed in trace amounts and have physiological roles, whereas others are severely poisonous even at low concentrations. Zinc is a microelement that functions as a cofactor for metalloproteins such as oxidases, dehydrogenases and anhydrases (Rout and Das 2009). It is involved in photosynthesis, nitrogen metabolism and auxin production (Broadley et al. 2007). Too much amounts of Zn, on the other hand, leads to growth retardation, leaf curling, chlorosis and necrosis of the leaf tips (Broadley et al. 2007; Rout and Das 2009). Similarly, Ni acts as an activator for the enzymes involved in nitrogen fixation and is also a constituent of the urease enzyme (Shahzad et al. 2018a, b). High Ni concentrations, on the other hand, leads to chlorosis, necrosis and nitrogen metabolism impairment (Mishra and Kar 1974; Nagajyoti et al. 2010). Cu is a structural component of photosystem II's plastocyanin protein (Cook et al. 1998) and also works as a Cu/Zn superoxide dismutase (SOD) activator (Burzyski and Żurek 2007; Yruela 2005).

Excess Cu, on the other hand, can bind to proteins' sulfhydryl groups rendering them inactive (Yruela 2005). Cu poisoning leads to reduced plant development, necrosis and leaf discoloration. Cadmium is a non-essential element that serves no physiological purpose. It interferes with other important components in the soil, inhibits the establishment of helpful soil microorganisms and is highly harmful to plants (Benavides et al. 2005). It also slows plant growth by altering stomatal movement and transpiration, as well as influencing plant-water relations (Anjum et al. 2016a; Benavides et al. 2005).

To deal with heavy metal toxicity, plants rely on heavy metal uptake, transport and sequestration. Because heavy metals' physiochemical characteristics are similar to those of important microelements, their uptake is aided by plasma membrane transporters found in roots. Transport proteins present in xylem vessels are responsible for transportation of metals from the root to the shoot (DalCorso et al. 2013). These metals are supplied to proteins and cell organelles in their requirement by the help of metallochaperones. Extra metals are sequestered into vacuoles by chelators such as metallothioneins, phytochelatins, amino acids and organic acids (Callahan et al. 2007; Cobbett and Goldsbrough 2002; Sharma and Dietz 2006). Excessive heavy metal accumulation compromises the functions of the electron transport chain, mitochondria and chloroplast and disrupts redox homeostasis, ultimately leading to excessive production of reactive oxygen species (ROS) (Anjum et al. 2014; Chibuike and Obiora 2014; Cuypers et al. 2010; Schützendübel and Polle 2002). Redox-active heavy metals like Cu, Fe and Ni catalyse the creation of ROS directly through Fenton reactions, whereas redox-inactive metals like Cd, Zn and Pb cause oxidative stress by depleting antioxidants (Valko et al. 2016). Antioxidant defence systems are used by cells to deal with excessive ROS build-up. Enzymes like catalase (CAT), peroxidase (POD), superoxide dismutase (SOD), glutathione peroxidase (GPX), ascorbate peroxidase (APX), glutathione reductase (GR) and antioxidant molecules like ascorbate, glutathione and tocopherols contribute to lessen the harmful effects of ROS (Hossain et al. 2012; Mishra et al. 2013). Plants use organ-specific antioxidant arsenal components to combat oxidative stress according to the nature of stress and developmental stage (AbdElgawad et al. 2016; Mishra et al. 2013).

Roots and shoots are separate organs in terms of spatial, physiological and functional characteristics. Synchronisation between root and shoot tissues determines overall plant health. The first plant structures to come into contact with metal-contaminated soils are the roots. Heavy metals are kept out of roots by multiple alterations, including lignification and callose deposition, which act as an apoplastic and plasmodesmatal barrier, respectively (Cuypers et al. 2002). Maize is extensively produced and economically important cereal crop that has been seriously harmed by several heavy metals, resulting in global productivity losses (Gu et al. 2019; Lu et al. 2015). However, it is generally known that plants respond differently to diverse types of stresses and exposure time. Also, different plant organs and different developmental phases produce specific responses in plants (AbdElgawad et al. 2016; Kravchik and Bernstein 2013; Lazof and Berstein 1999) though an organised study equating different types of heavy metals (redox and non-redox reactive) and the responses elicited by them in the whole plant body has not been done.

Maize is grown in temperate and subtropical climates and can withstand harsh environmental conditions (Maiti et al. 2012). In addition, the corn plant is capable of extracting heavy metals from metal-polluted soils (Aliyu and Adamu 2014). Even while maize may be a good candidate for phytoextraction, it is also harmed by heavy metals when cultivated in a metal-stressed environment. Cadmium is particularly toxic to many plants, including maize (Hussain et al. 2013; Xu et al. 2014), which causes stunted growth and changes permeability of cell membranes, eventually leading to the generation of reactive oxygen species (ROS) (Ibrahim et al. 2017). The build-up of reactive oxygen species (ROS) in plant tissues induces electrolyte leakage and interrupts cell membrane integrity (Emamverdian et al. 2015). As a result, membrane protein and lipid oxidation gets disturbed, resulting in cell death (Ibrahim et al. 2015). Other cadmium toxicity symptoms on maize plants include chlorosis, necrosis, root rot and deformities in embryonic tissues (Ling et al. 2017). Chromium is another highly hazardous element that inhibits plant growth and yield, including maize (Parmar and Patel 2015; Anjum et al. 2016a, b). Chlorosis of leaves, stunted root and shoot growth and wilting are some of the toxicity symptoms related with chromium (Kumar and Chopra 2015). Chromium disturbs the lamellar system once it penetrates plant tissues. Chromium has been proven to reduce maize plant's root development and overall biomass (Maiti et al. 2012). In addition, when chromium is used alone or in combination with Al, it impedes maize plant's development, lowers photosynthetic activity and stomatal conductance and hampers seed output (Anjum et al. 2016a, b). Nickel is another hazardous metal that inhibits plant growth at greater concentrations (Amari et al. 2014), while as a trace element, it regulates plant nitrogen metabolism (Fabiano et al. 2015) and hence impacts seed germination and other essential physiological processes. Inhibition of germination, spotting and leaf discoloration, restricted growth of roots and shoots and malformation of various plant parts are the most typical effects of Ni phytotoxicity. Increased Ni content also impacts iron uptake in higher plants, resulting in crop output reductions (Nie et al. 2015) (Fig. 12.1 and Table 12.1).

12.3 Role of Phenolics in Alleviating Metal Toxicity in Maize

Plants produce a variety of chemicals that can help to combat oxidative stress. Phenolic chemicals are structurally varied metabolites that have a role in a variety of stress responses (Dixon and Paiva 1995). They have antioxidative capabilities and can directly or indirectly remove reactive oxygen species (ROS) by enzymatic processes (Sakihama et al. 2002). They also act as metal chelators (Vasconcelos et al. 1999) and are having an important function of heavy metal absorption and translocation (Kováčik et al. 2011).

The growth and development in plants have been altered by surrounding factors, and plants have developed adaption mechanisms to help them survive (Lequeux et al. 2010). Heavy metals like Cd and Pb are not needed, while Cu, Fe and Zn are important for plants to carry out its physiological processes. The high level of Cu, on the other side, has a poisonous effect and hinders plant development. They are considered as major pollutant that affects the electron transport system (ETS), carotenoids, thylakoid membrane, plastoquinone and chloroplast among other things (Sharma and Dubey 2004). The generation of reactive oxygen species (ROS) is the major reaction of plants exposed to heavy metals, and it leads to physiological alterations (Yadav 2010). As a biological stress signal, ROS can be helpful to act as stress indicator. When the antioxidant capacity is smaller than the quantity of ROS, plant damage ensues (Michalak 2006). Heavy metals can cause oxidative stress, but plants have evolved a variety of defence mechanisms, including an enzymatic and nonenzymatic systems for free radical scavenging. To eliminate oxidant molecules, plant enzymatic defence mechanisms include catalase, peroxidase, ascorbate peroxidase, superoxide dismutase and glutathione reductase. Non-enzymatic antioxidant responses in plants include ascorbate, glutathione, flavonoids, phenolic compounds, tocopherol and carotenoids (Schützendübel and Polle 2002; Gratao et al. 2005).

Phenolic molecules, which have been discovered to defend plants from stress and have a high ability to chelate metals, have antioxidant properties and are plant secondary metabolites (Tomas-Barberan and Espin 2001; Cervilla et al. 2012).

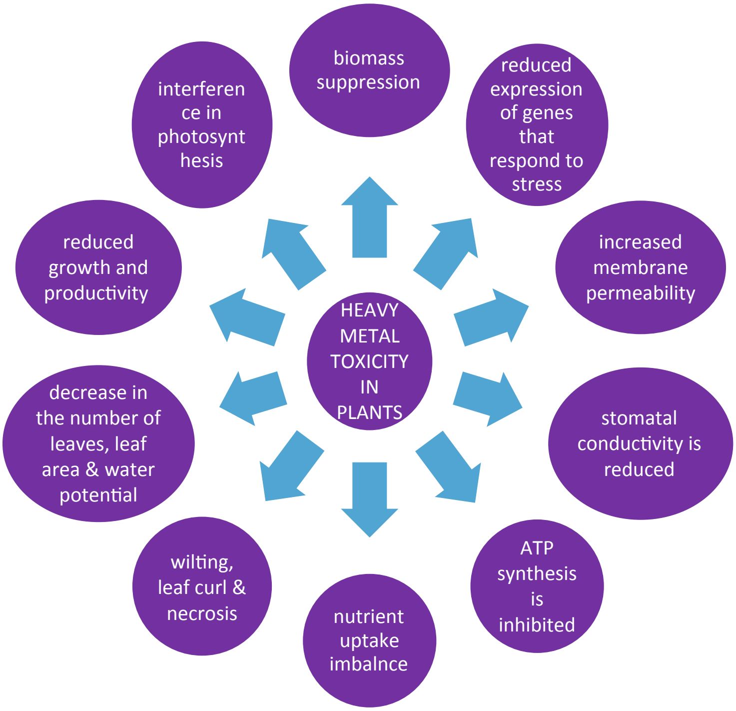

Fig. 12.1 Impact of heavy metal toxicity in plants

Some phenolic chemicals are found widely in plants, while some are found only in certain plant families or in specific plant tissues (Cheynier 2012). Plants rely on these chemicals for a variety of physiological and morphological functions. They have physiological qualities such as antioxidant and antibacterial activity, and they show a vital role in growth and reproduction (Balasundram et al. 2006). To bind heavy metals, they have hydroxyl and carboxyl groups. The high nucleophilic property of the aromatic rings may explain phenolic compounds' chelating capacity. Heavy metals produce free radicals when they break down lipid hydroperoxide, resulting in lipid alkoxyl radicals. By trapping alkoxyl radicals, phenolic substances prevent lipid peroxidation (Michalak 2006). Heavy metal exposure causes plants to produce more phenolic chemicals. They've been thought of as electron-donating agents and are key antioxidant chelating metals. The shielding action of plant phenolic

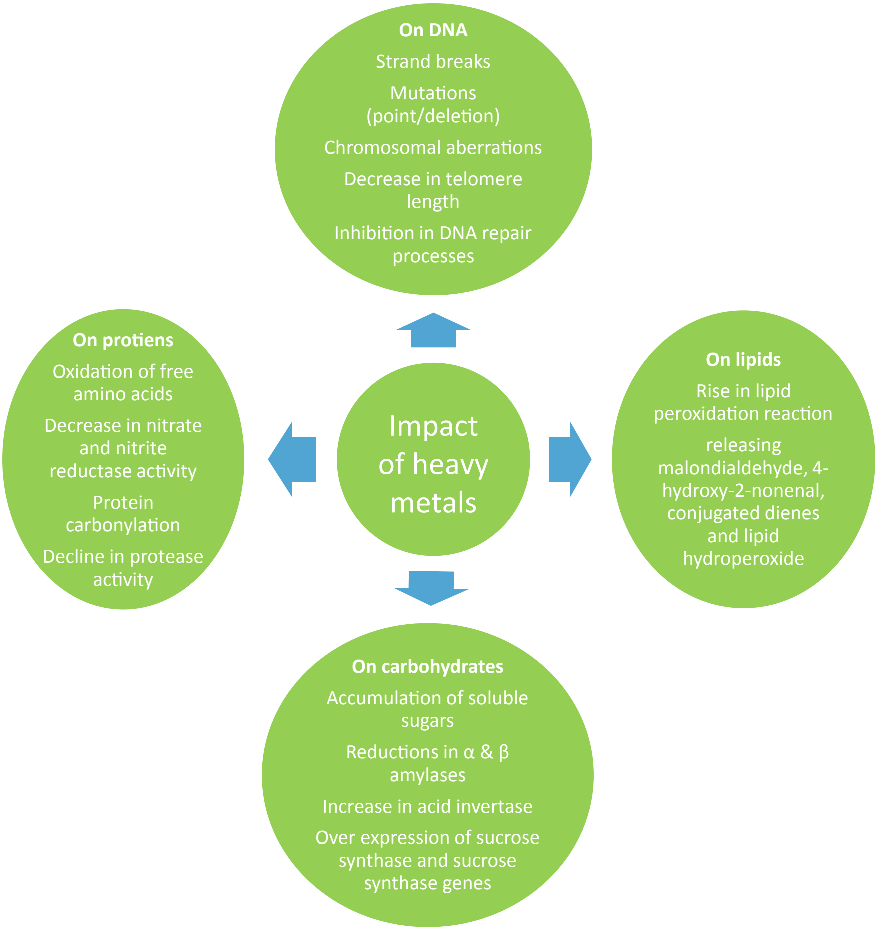

Fig. 12.1 (continued)

Table 12.1 List of heavy metals and their impacts on plants

S. no.	Heavy metal	Impact on plants	References
1.	Chromium (Cr)	• Prevents plant root cell division and elongation, therefore shortens altogether the length of roots • Strictly limits the absorption of water and nutrients • Causes reduction in shoot growth • The toxic concentration of Cr in the roots is responsible for the prolonged cell cycle as well	Shanker et al. (2005); Srivastava and Jain (2011)
2.	Aluminium (Al)	• Inhibition of root growth and root respiration • Causes disturbance in the phosphorylation of sugar by interfering with its enzymatic regulation • Causes root damage which in turn has negative impact on plant's aerial parts • Hinders uptake of nutrients by roots which causes nutrient deficiency • Leaf stunting, discoloration on leaves, leaf veins and stems which is subsequently followed by dead and yellow leaf tips • Young leaves rolling and curling and death of petioles • Small necrotic patches on the edges of new leaves, chlorosis on the borders and middle of old leaves and reduced photosynthetic activity due to reduced stomatal aperture	Ma et al. (2001); Rout et al. (2001); Steiner et al. (2012); Silva (2012); Bian et al. (2013); Wang et al. (2006); Vardar and Unal (2007)
3.	Manganese (Mn)	• Crinkled, dark leaf veins, brown patches and chlorosis on older leaves and black spots on stems	Reddy (2006); Schubert (1992); Maksimović et al. (2012); Vitosh et al. (1994)
4.	Nickel (Ni)	• By inhibiting the action of enzymes like protease and amylase, it has a negative impact on the germination and growth of seedling • Interrupts the hydroxylation of food storage in germinating seeds • Severely reduces plant height and leaf area • Leads to decrease in content of Chl, thus interrupting electron transport	Aydinalp and Marinova (2009); Sethy and Ghosh (2013); Al-Qurainy (2009); Sreekanth et al. (2013)
5.	Copper (Cu)	• Retardation of growth and root elongation • Leaf discoloration, necrosis and chlorosis • Disrupted membrane and formation of free radicals in plant organelles by inducing lipid peroxidation • Causes root cell impermeability and thylakoid membrane disruption • Decreases photosynthetic competency, lowers cell elongation and has a low quantum efficiency of photosystem II	Tsay et al. (1995); Chen et al. (2000); Doncheva and Stoyanova (2007); Mishra and Dubey (2005); Yruela (2009); Alaoui-Sossé et al. (2004)
6.	Zinc (Zn)	• Manganese or iron deficiency causes chlorosis in new leaves and deficiency of phosphorous causes purplish-red colour spots on leaves • Necrosis in the veins of adult leaves and inward rolling of leaf margins	Sivasankar et al. (2012); Yadav (2010); Fukao et al. (2011); Miyasaka et al. (2002); Sagardoy et al. (2009)

compounds could describe why their amounts fluctuate in response to stressful environmental situations (Kovacik et al. 2008; Marguez-Garcia et al. 2009).

Plant compounds with one or more hydroxyl groups bounded directly to an aromatic ring are known as phenolic compounds; their complexity ranges from basic to highly polymerised compounds (Vermerris and Nicholson 2006). The antioxidant property of phenolics is due to their capacity to chelate metals, remove free radicals and donate hydrogen atoms (Balasundram et al. 2006). Phenolic acids are hydroxylated benzoic and cinnamic acid derivatives. Caffeic acid is a phenylpropanoid pathway product found in a variety of plant species. Caffeic acid has influenced plant growth, photosynthesis and ROS production. Caffeic acid gets built up in the stressed plant's cell wall-bound portion (Bubna et al. 2011). Chlorogenic acids (CGAs) are a class of phytochemicals generated when cinnamic acid derivatives and quinic acids combine to create an ester. CGAs are synthesised via the shikimate and phenylpropanoid pathways and have been associated to biotic and abiotic stress responses (Ncube et al. 2014). Ferulic acid is the most common hydroxyl cinnamic acid in the plants, and it has antioxidant activity by transferring one hydrogen atom from its phenolic hydroxyl group in response to free radicals. Ferulic acid has a wide range of biological actions, including antioxidant, metal chelation and enzyme activity modulation. It is present as covalent side chains in plant cell wall components and is a powerful UV absorber (Kumar and Pruthi 2014). Rutin is a bioactive phenolic molecule that can be utilised as a natural colouring agent as well as an oxidation inhibitor (Musallam et al. 2012). Vanillic acid is a benzoic acid derivative that has free radical scavenging, reducing potential and lipid peroxidation inhibitory properties. Vanillic acid significantly restores enzymatic antioxidants (Fig. 12.2).

12.4 Role of Different Phenolics in Alleviating Metal Toxicity with Special Reference to Maize

Nutritional deficiencies, hormone imbalances, ion toxicity and osmotic and oxidative stress are all biotic and abiotic factors that affect growth and development of plant. The cellular synthesis of secondary metabolites, which include organic compounds that help plants cope with stress by increasing antioxidant activity, detoxifying toxic ions, regulating nutrient uptake and mediating the transport and distribution of various hormones, is the most efficient mechanism (Riaz et al. 2018). Phenolics are a class of plant-derived chemicals that have been shown to exhibit free radical removing properties due to their stable structure after trapping the free radical (Kashiwada et al. 1995). Salicylic acid (SA), a phenolic class molecule, is gaining momentum for regulating stress of plants and ameliorating an array of various processes of metabolism and physiology causing plant defence responses (local and systemic) to various stress stimuli (Liu et al. 2008). The important features of plant growth and development, viz. closure of stomata, uptake of food, synthesis of protein and ethylene biosynthesis suppression, are all controlled by SA (Jayakannan et al. 2015). Furthermore, SA works as a signalling molecule in various plant species

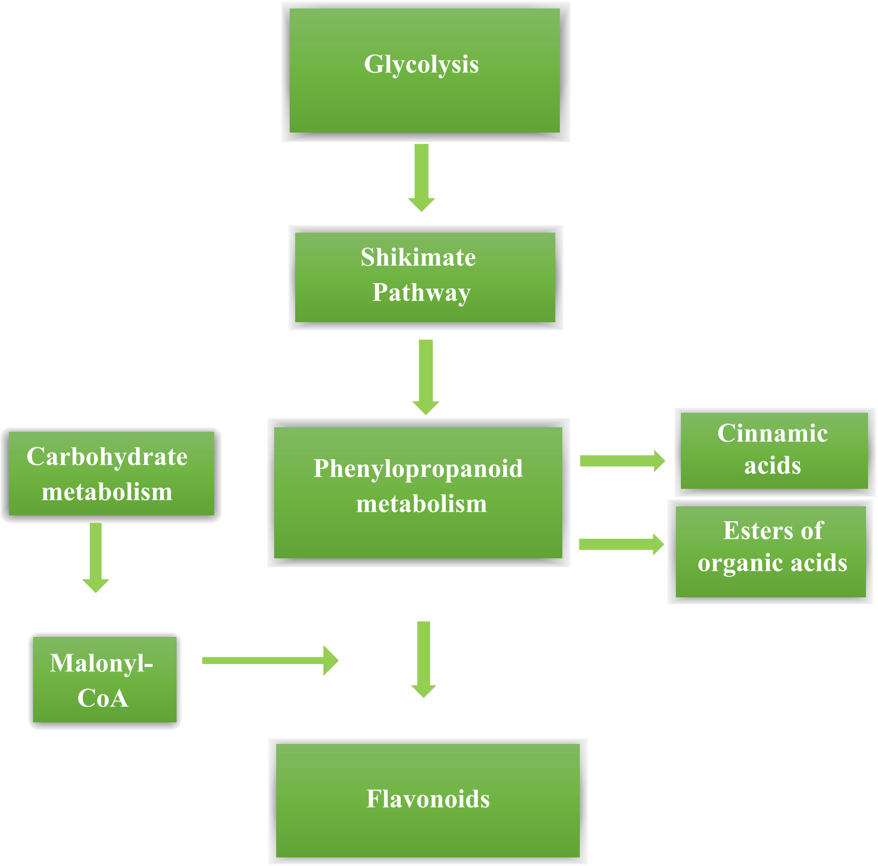

Fig. 12.2 Biosynthesis pathways leading to formation of main groups of phenolic compounds

to alleviate abiotic and biotic stress (Hayat et al. 2010; Miura and Tada 2014) including protection from toxicity of heavy metal (Hayat et al. 2010; Miura and Tada 2014; Singh et al. 2015). In rice (Mishra and Chudhuri 1999), barley (Metwally et al. 2003), maize (Pal et al. 2002) and soybean plants, exogenous SA reduced heavy metal stress (Drazic and Mihailovic 2005). Salicylic acid pretreatment reduces heavy metal uptake and transport in maize plants, improves heavy metal-induced nutrient absorption inhibition and results in a considerable increase in chlorophyll and carotenoid content. The use of salicylic acid reduces oxidative damage by lowering the levels of H_2O_2 and MDA in the plant body (Saidi et al. 2013). In corn plants that have been pretreated with SA, there is rise in both ascorbate peroxidase and superoxide dismutase activity, as well as a significant decrease in catalase activity (Krantev et al. 2008). SA's protective role primarily entails the regulation of normal metabolism, physiological function and reactive oxygen species (ROS) production (Metwally et al. 2003; Drazic and Mihailovic 2005). SA appears to affect stress acclimation and damage development in plants in a variety of ways. Caffeic acid is involved in plant physiology and stress tolerance mechanisms. It is largely used by plants to synthesise lignin, which thickens cell walls and makes plants resistant to ion toxicity and heavy metal stress. O-Methyltransferase acting as mediator in ferulic acid synthesis by caffeic acid methylation likewise reconciles high energy radiation absorption in mesophyll cells during abiotic stress. Exogenous administration of caffeic acid has been found to be the greatest alternative for dealing with salinity, ion toxicity, drought and heavy metal stress (Riaz et al. 2018).

12.5 Role of PGPR and Other Microbes in Alleviating Metal Toxicity in Maize

Plants that live in a symbiotic relationship with PGPR have increased their competitiveness for space and resources, improved their development and increased their resistance to external challenges. These microorganisms derive their nourishment from root exudates and provide plants with a variety of benefits, viz. fixation of nitrogen, stimulating growth of plant, generation of hormones for growth, production of enzymes for lysis and antipathy for pathogenicity (Subiramani et al. 2020). *Bacillus subtilis* has proved to be most essential strain of bacteria in heavy metal detoxification besides managing contaminated soils (Rizvi et al. 2019). By activating distinct defensive systems and enhancing growth, *Bacillus subtilis* and *Pseudomonas pseudoalcaligenes* improve stress tolerance of *Glycine max* (Yasmin et al. 2020). They're also effective at immobilising soil heavy metals and plummeting plant absorption. By oxidation-reduction reactions, they also reduce oxidative stress by converting heavy metal ions from a more toxic form to a less toxic one (Ke et al. 2021). Among the activities that protect roots from the damaging effects of heavy metals is the synthesis of polyphosphate, thiophosphate, glutathione and biofilm (Stress 2020). In stress situations such as salinity and HM pollution, some helpful bacteria and fungus may help plants develop faster (Sharaff et al. 2017; Yin et al. 2020). Plant growth-promoting rhizobacteria can help plants develop in heavy metal-contaminated soils by detoxifying metals (changing metal speciation) and reducing their bioavailability, resulting in reduced plant toxicity (Babaloa 2010). HM pollution is often accompanied with nutritional deficiencies and excessive amounts of ethylene in some farming methods (Rajkumar et al. 2005). PGPR's growth-promoting capabilities of plants cultivated in HM-contaminated soils have been investigated in several recent research. Under Cu toxicity conditions, inoculating mung bean (*Vigna radiata*) plants with a Cu-resistant PGPR strain (*Enterobacter* sp.) resulted in increased shoot and root biomass and length, as well as decreased Cu build-up in their roots (Sharaff et al. 2017). In alfalfa plants cultivated in Cu-contaminated soil, the use of PGPR and rhizobial strains together increased growth and N, P, potassium (K) and copper uptake (Cu) (Ju et al. 2019). Heavy metal-contaminated soil (Fe, Cu, Al, Pb, Mn, Zn) cultivated with white clover (*Trifolium repens*) was found to have improvement in biomass of plant and uptake of nutrients (N, P, K) due to *Bacillus cereus*, a heavy metal-resistant strain (Azcon et al.

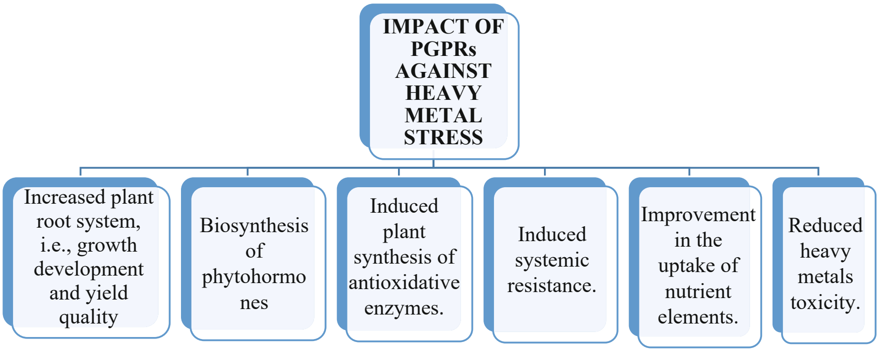

Fig. 12.3 Impact of PGPRs against heavy metal stress

2010). The PGPR *Serratia* sp. MSMC541 provided resistance to *Lupinus luteus* plants in a heavy metal-contaminated soil (Cu, As, Cd) by limiting their transit from root to shoot organs (Aafi et al. 2012). Plant growth-promoting rhizobacteria (PGPRs) inoculation might prove a viable substitute to organic improvements in reducing heavy metal-induced stress in crops (Gillani et al. 2017; Zafar-Ul-Hye et al. 2018). Heavy metal can be mobilised or immobilised in soil by PGPR (Gadd 1990). The study of the PGPR-regulated pathways that play a vital role in the alleviation of heavy metal stress in crops is still ongoing (Belimov et al. 2005). It has been established that some PGPRs are capable of producing 1-aminocyclopropane-1-carboxylate (ACC) deaminase. By converting 1-aminocyclopropane-1-carboxylic acid (ACC) into -ketobutyrate and NH3 (Hall et al. 1996; Zafar-Ul-Hye et al. 2018), this ACC deaminase enzyme can reduce metal-created ethylene stress (Hall et al. 1996; Burd et al. 1998; Grichko and Glick 2001; Glick et al. 2007; Naz et al. 2013; Glick 2014; Zafar-Ul-Hye et al. 2018; Shahzad et al. 2018a, b). ACC deaminase inoculation improves food absorption and thereby chlorophyll production. PGPR also confirmed its efficiency in the presence and absence of heavy metal-induced stress (Danish et al. 2014; Zafar-Ul-Hye et al. 2018). Higher Cr build-up beyond dangerous limits has been documented in green leafy vegetables, viz. root crops (radish, turnip, sweet potato, carrot) (Hundal and Arora 1993). Toxicity caused by Cr, on the other hand, can significantly harm maize growth and productivity (Anjum et al. 2016a, b) (Fig. 12.3).

12.6 Role of Different Microbes in Alleviating Metal Toxicity in Plants with Special Reference to Maize

It has been found that inoculating potato plants with *Bacillus* isolates increased their resistance to HM stress (Gururani et al. 2013). *Bacillus cereus*, *B. megaterium*, *Trichoderma simmonsii* and *T. longibrachiatum* all improved soybean plant's salt and drought stress tolerance (Bakhshandeh et al. 2020). Cr toxicity in plants of sunflower was found to be reduced by MT4 strain of *Staphylococcus arlettae* by limiting uptake of Cr and enhancing antioxidant defence complex of the plant (Qadir et al. 2020). *Azotobacter* and *Azospirillum* strains boosted secondary metabolite biosynthesis and drought stress tolerance in pennyroyal (Asghari et al. 2020). Furthermore, the *Bacillus* strain was discovered to reduce the stress caused by nanoparticles in mustard plants (Vishwakarma et al. 2020). Salt-tolerant PGPR improved salt stress resistance in alfalfa plants under high salinity conditions (Ansari et al. 2019). PGPR-inoculated maize seedlings have previously been found to be resistant to salt (Li and Jiang 2017; Rojas-Tapias et al. 2012), Aluminium (Al) and salt (Zerrouk et al. 2019), heavy metals (Malekzadeh et al. 2012), drought (Chukwuneme et al. 2020) and chilling conditions (Beirinckx et al. 2020). *Bacillus siamensis*, when applied to wheat plants, increased tolerance to Cd stress by limiting Cd accumulation and enhancing the antioxidant defence system (Awan et al. 2020). However, under Cu toxicity, the underlying mechanisms of inoculation of maize plants with phosphate- and potassium-solubilising bacterial strains *P. polymyxa* and *B. circulans* receive trivial attention.

Advances in fertiliser use will be required to uphold soaring up of maize production, resulting in increased costs of production and detrimental environmental impact. Rhizobacteria that promote crop development and yield have multiple documented advantages. *Paenibacillus alvei*, *B. safensis*, *B. pumilus* and *Brevundimonas vesicularis* increased yield by 24–34% (Breedt et al. 2017). Cassán et al. 2009 investigated combined effect of *A. brasilense* with *Bradyrhizobium japonicum* and found that seed germination rate and early development were increased. Kuan et al. (2016) reported that plant growth-promoting bacteria may provide a biological alternative to fix atmospheric N_2 and delay N remobilisation in maize plants to increase crop yield, promoting ear yield up to 30.9% with reduced fertiliser N input, based on the understanding that plant N remobilisation is directly correlated to plant senescence. According to Di Salvo et al. (2018), PGPRs utilised as inoculants in cereal crops such as maize can boost growth and grain yield.

Several bacteria that can create IAA have good effects on maize shoot and root weight and nutrient uptake. Furthermore, activities such as phosphorus solubilisation, as well as other PGPR features that drive plant growth, are not examined (Lobo et al. 2019). PGPR's bioprotective role in maize crops has also been investigated. *Fusarium*, a toxigenic fungus, is one of the most important genera associated with maize. When applied as seed coatings, several PGPRs, such as *Bacillus amyloliquefaciens* and *Microbacterium oleivorans*, were able to protect maize against *Fusarium verticillioides* (Pereira et al. 2011). Some PGPR species, interestingly, appear to stimulate plant growth by functioning as both biofertilisers and biocontrol agents. Strains of *B. cepacia*, for example, have been found to have biocontrol properties against *Fusarium* spp. Simultaneously, they can enhance maize growth in iron-deficient environments by producing siderophores (Bevivino et al. 1998) (Table 12.2).

Table 12.2 Bacteria species, abilities, experiment condition and results promoted by the application of many plant growth-promoting rhizobacteria in maize crop

S. no.	Rhizobacteria/consortium in maize	Condition	Abilities	Results	References
1.	*Lysinibacillus sphaericus* (T19)	Field	BNF and IAA production	Increased productivity	Breedt et al. (2017)
2.	*A. brasilense* Az39, *Bradyrhizobium japonicum* E109 (individual experiments and consortia)	Growth chamber	Phytohormone production	Increase in promoting seed germination and early seedling development (use of isolated or combined species)	Cassán et al. (2009)
3.	*B. pumilus* S1r1	Greenhouse	BNF	Higher corn cob productivity (up to 30.90%)	Kuan et al. (2016)
4.	*A. brasilense* and *P. fluorescens*	Field	IAA production and phosphate solubilisation	Higher grain yield	Di Salvo et al. (2018)
5.	*P. fluorescens* F113	Greenhouse	Nutrient acquisition	Addition of N, K, Ca, Mg and Mn = 40%, 49%, 60%, 100% and 141%, respectively, in the shoots	Rocha et al. (2019)
6.	*Enterobacter cloacae*	Greenhouse	ACC deaminase production	Increase of 60%, 73%, 43%, 69%, 76% and 42%, respectively, in grain production, photosynthetic rate, stomatal conductance, chlorophyll a, total chlorophyll and carotenoids	Danish et al. (2020)
7.	*B. subtilis* and *A. brasilense*	Field	Phosphate solubilisation	Higher grain yield	Pereira et al. (2020)
8.	*Chryseobacterium* sp. NGB-29 and *Flavobacterium* sp. O NGB-31	Greenhouse	BNF and production of large amounts of IAA	Increased growth parameters	Youseif (2018)
9.	*Ralstonia eutropha* 1C2 and *Chryseobacterium humi* ECP37	Greenhouse	Zn bioavailability in the soil	Increase biomass and Zn accumulation and availability in plants	Moreira et al. (2019)
10.	*Pseudomonas aurantiaca* SR1	Field	Production of phytohormones, antibiotics and siderophores	Increase productivity, length and root and shoot dry weight	Rosas et al. (2019)

11.	*B. subtilis* 320	Field	Phosphate solubilisation and phytohormone production	Increase in productivity and P in the shoots	Lobo et al. (2019)
12.	*Burkholderia cepacia*	Greenhouse	Biocontrol and phosphate solubilisation	Increased leaf area, length and root and shoot dry weight	Zhao et al. (2014)
13.	*Pseudomonas tolaasii* IEXb	Field	Phosphate solubilisation	Increase in seedling emergence, shoot length, grain yield, 1,000 grain weight, total dry biomass and P content in plants	Viruel et al. (2014)
14.	*Pseudomonas kilonensis* F113 and *Pseudomonas protogens* CHA0	Field	Phosphate solubilisation and biocontrol	Increase in leaf yield, height and length	Alori et al. (2019)
15.	*Enterobacter cloacae* PGLO9	Greenhouse	Phosphate solubilisation	Longer root length and shoot length and increase in shoot and root biomass	Verma et al. (2018)

12.7 Relationship Between Phenolics and Microbes in Alleviating Metal Toxicity in Plants with Special Reference to Maize

The growth and development of maize, as well as photosynthetic pigments, carbohydrate metabolism, relative membrane permeability and proline content, are all affected by HM toxicity. By reducing HM accumulation in maize, inoculation with chosen plant growth-promoting bacteria (T2Cr and CrP450) and salicylic acid treatment, either separately or in combination, eased HM toxicity or encouraged plant growth. In addition, combining dual PGPB inoculation with SA, which is a phenolic compound, treatment increases plant performance when exposed to HM toxicity (Islam et al. 2016).

Secondary metabolites act as signals for communication of plants with their surroundings. Polyphenols, for example, have a role in signalling from the root to the shoot, as well as nutrient mobilisation. Exudates from the roots contain phenolic chemicals that change the rhizosphere's physiochemical characteristics. Phenolics are converted by soil bacteria into chemicals that aid in formation of humus and nitrogen mineralisation (Halvorson et al. 2009). Additionally, phenolics boost nutrient uptake by chelating metallic ions, increasing active absorption sites and improving soil porosity, resulting in faster mobilisation of elements like Ca, Mg, K, Zn, Fe and Mn (Seneviratne and Jayasinghearachchi 2003). Rehman et al. (2018a) discovered that zinc application and treatment with plant growth-promoting rhizobacteria (PGPRs) increased the content of phenolics and organic acids like malic acid, succinic acid, oxaloacetic acid, etc. in root exudates of wheat plant, which aided in uptake and mobilisation of elements like Zn, N and Ca (Rehman et al. 2018a, b). In legumes, phenolic chemicals aid in nitrogen fixation and aid in cell division; they produce many secondary metabolites from their roots, primarily flavonoids like flavonols and isoflavonoids which have a critical part in the synthesis of Nod factors and the production of infection tubes during nodulation (Zhang et al. 2009).

12.8 Conclusion

The marine and terrestrial ecosystems are both threatened by heavy metal. The persistence of these toxic substances in ecological niches and food chains necessitates the development of long-term strategies to eradicate them from the environment. Over the years, a variety of physiochemical and biological treatments have been developed and used to remediate heavy metal-contaminated areas. PGPR and phenolics are the most promising and environmentally friendly solutions for reducing the stress induced by heavy metals. PGPRs isolated from metal-polluted environments are more resilient to heavy metals and can better endure metal toxicity than those separated from non-polluted environments. Phytohormones, siderophores, organic acids, antibiotics and enzymes are among the metabolites secreted by these ubiquitous bacteria, which minimise metal toxicity while also boosting the plant's ability to extract additional metals. Because of these unique properties of PGPRs, stunted plants grow faster. Phenolic molecules, on the other hand, have been identified as playing a role in the reactions to environmental stresses. They take part in a variety of physiological processes that help plants grow and develop. Phenolic compounds have the ability to behave as metal chelators and directly remove molecular species of active oxygen during heavy metal stress.

In conclusion, we discovered that excessive heavy metal application inhibited development, lowered chlorophyll content and reduced photosynthetic efficiency in maize plants. Overproduction of reactive oxygen species (ROS) and concomitant membrane lipid peroxidation result from higher heavy metal concentrations. The use of phenolic compounds and PGPR significantly alleviated the majority of these heavy metal toxicity symptoms. Based on these findings, it can be concluded that both phenolic chemicals and PGPR treatment can help maize plants tolerate heavy metals better.

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Impact of Phenolics on Drought Stress and Expression of Phenylpropanoid Pathway Genes

13

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Abstract

Water shortage in plant is the major environmental stress affecting plant productivity. In crops, losses in productivity induced by drought are expected to outweigh losses from all other sources, owing to both the intensity and time period of the stress. The buildup of phenolic compounds is critical for plants to resist the harmful effects of drought stress. Transcriptomic and metabolomic investigations demonstrated augmentation and stimulation in the manufacture and accumulation of flavonoids in plants, as well as improved drought tolerance. Various researchers have detected an increase in total phenolic contents and associated chemicals with drought stress; yet, it has also been confirmed that drought stress reduces plant biomass. The key factor leading to variance in total phenolic content of plants during drought stress has been identified as genotype. Drought stress can also change the biosynthetic cycles of flavonoid and phenolic acid (which protect plants with their antioxidant properties) pathway, resulting in

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greater increase of these chemicals, which cause negative impacts. Flavonoid accumulation in the cytoplasm may effectively detoxify damaging H_2O_2 molecules produced by drought stress, and flavonoids are oxidized with the help of reconversion by ascorbic acid mediation and form primary metabolites. The fundamental cause of drought-induced phenolic compound concentration is the modification and control to the expression of the gene and production of important enzymes for phenylpropanoid biosynthetic pathway, which cause the enhancement of phenolic compound production.

Keywords

Drought · Phenolic content · Metabolomics · Phenylpropanoid genes

13.1 Introduction

Members of different plant groups are subjected to a variety of abiotic stressors that are detrimental to their development and growth which are constantly changing with the environment (Zhu 2016). Drought and flooding (water stress), salinity, heavy metals, nutrient deficiency, chilling or freezing condition, excessive increase or decrease of temperatures, levels of light (low or high), ozone, sulfur dioxide, mechanical factors, and others are some of the abiotic stressors (Pereira 2016). Drought, caused by a shortage of water resources, is the single and most severe threat to the world food security. It was the spark that ignited prior great famines. Because the water supply of world is limited, future food consumption to satisfy rapidly expanding population demands is expected to intensify drought effects on entire humanity (Somerville and Briscoe 2001). Drought losses are unpredictable since they are determined by several factors including rainfall incidence and distribution, evaporative proportion of water, and moisture holding capacity of soil (Wery et al. 1994). Drought's effects on agriculture are compounded by dwindling water supplies and rising food requirement as a current demand of the world's unsustainable population growth (O'Connell 2017). The unpredictability of the drought is due to various factors, such as distribution of annual rainfall, water holding capacity of agriculture land, and evapotranspiration capacity across the rhizosphere (Passioura and Angus 2010; Devincentis 2020). Additional research into drought-tolerant plants, as well as the adoption of cost-effective and beneficial agricultural practices, will be important in fulfilling future food demand (Raza et al. 2019; Diatta et al. 2020a, b). Global climate change is expected to accelerate in the future due to the continuous rise in air temperature and atmospheric CO_2 levels, which alters rainfall patterns and distribution (Yang et al. 2019; Yin et al. 2018). Although a lack of water input from rainfall is usually the major cause of drought stress, water loss from soils owing to evaporation, which is worsened by high light intensity, high temperatures, and dry wind, can aggravate an already existing drought stress event (Cohen et al. 2021). Drought stress conditions are frequent across vast expanses of land due to the climate change all over the world.

13.2 Drought

Drought is the most significant environmental stress and has the greatest impact on plant development, growth and also on agricultural performance (Shao et al. 2009). Drought stress occurs due to restriction of water transport by roots and stress occurs at high transpiration. Available water resource for sustainable agricultural practicing is decreasing day by day. Moreover as per several climate change proposals and models, agricultural losses owing to enhanced water scarcity would increase due to climate change around many parts of the world.

Drought has a negative influence on photosynthetic activity, membrane integrity, yield, osmotic adjustment, content of pigment, plant-water relations, and growth pattern (Benjamin and Nielsen 2006; Praba et al. 2009). Climate, edaphic, and agronomic variables all have an impact on drought stress. Plant vulnerability to stress varies according to stress degree, different associated stress causes, and developmental phases (Demirevska et al. 2009). Plant acclimation to water deficiency is the outcome of several events that lead to changes in plant development and in the physio-biochemical activities like plant growth rate, osmotic potential, antioxidant defenses and plant structure (Duan et al. 2007). It has become critical to understand crop responses and adaptability to water scarcity, as well as the influence to the metabolic aspects helping to produce secondary metabolites of plant (Bohnert et al. 1995). Water availability is the key limiting resource for plants in many places of the world (Kramer 1983). When plants are deprived of water, they alter physically and chemically in a variety of ways. Indeed, it is difficult to identify plant processes that are unaffected by drought stress (Bradford and Hsiao 1982; Kramer 1983). Some changes indicate plant harm, although many others occur as the plant adapts physiologically to a situation of limited water availability. Water scarcity affects not just the plant directly but also other species that interact with it, notably its parasites (Schoeneweiss 1975; Mattson and Haack 1987; Waring and Cobb 1992; Herms and Mattson 1992).

Plants evolved suitable systems to deal with occasional water shortages to sustain their survival and reproduction as sessile creatures. Drought resistance can be split into three categories: escape, avoidance, and tolerance (Chaves et al. 2003). Escape methods may involve production of new generations before the beginning of different stress, such as a shorter life cycle, a faster rate of development, and utilization of stored for seed formation. Avoidance of dehydration, or maintaining a high (favorable) plant water condition while under stress, can be achieved by reduced loss of water (e.g., senescence of leaves, trichomes, reduced leaf area, stomatal closure, etc.) or enhanced water absorption (e.g., by enhancing growth of root). Finally, drought tolerance potential (the preservation of plant function in the presence of limited water resources and availability of plant water following stress) may include osmotic changes, and it may be due to the stiff cell walls or tiny cells.

Stress affects plants at the physiological, biochemical, cellular, and even molecular levels. The stress response is determined by the genotypes and different species (Rampino et al. 2006); the duration and severity of water loss (Araus et al. 2002; Bartels and Souer 2004); the stage of development of any plant part and age (Zhu et al. 2005); the type of cell, tissue, and organ (Verdoy et al. 2004; Cominelli et al. 2005; Zhou et al. 2007); and conditions at the subcellular compartment where chance of water loss is present (Battaglia et al. 2007).

Water stress is one among the most important abiotic stressors that has an impact on a variety of physiological and biochemical processes in plant, including phenylpropanoid metabolism. The formation of reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2), superoxide anion (O^{2-}), hydroxyl radical (OH), and singlet oxygen ($O^{\cdot}$) increases in response to water stress (Kumar et al. 2020). If the antioxidant system of plants does not protect against these, ROS cause lipid peroxidation, cell membrane damage, protein and enzyme degradation, DNA breakage, and cell death (Wagay et al. 2020). Enzymatic and nonenzymatic antioxidant systems are involved in the detoxification of reactive oxygen species in plants. Many enzymes, such as catalase (CAT), superoxide dismutase (SOD), ascorbate peroxidase (APX), and peroxidase (POD), work together to mitigate the harmful effects of reactive oxygen species (ROS). Vitamin C, carotenoids, tocopherols, glutathione, and phenol derivatives are examples of nonenzymatic antioxidants (Kumar et al. 2020a, b). The increased synthesis of phenolics (a key component of plants' nonenzymatic antioxidant system) in the presence of water stress is a clear physiological need of the plant.

13.3 Phenolics

Phenolic molecules are thought to be metabolic byproducts (Solecka 1997). Previously, several phenolic compounds were discovered in the majority of different plant species (Jwa et al. 2006). Phenolics are a varied and well-known class of substances that are classified in five subgroups: coumarins, lignins, phenolic acids, flavonoids, and tannins (Gumul et al. 2007). The chorismic acid and shikimic acid pathways are responsible for the formation of precursor molecules for phenolic compounds. Chorismic acid metabolism produces L-tyrosine and L-phenylalanine. L-Tyrosine is used to make p-coumaric acid, whereas L-phenylalanine is used to make cinnamic acid. As part of the plant's reaction to abiotic stressors, phenolic acids are formed as a consequence of the processes of hydration, methylation, and dehydration of cinnamic acid (Dixon and Paiva 1995). Phenolics are extensively dispersed and work effective roles in plant metabolism and physiological action (Boudet 2007; Kumar et al. 2019). Phenolics have an impact on a variety of physiological processes associated to seed germination, plant development, cell division, plant growth, and pigment production (Tanase et al. 2019).

Phenolic compound is used in a variety of applications, including bioremediation, allelochemicals, growth stimulation of plant, and antioxidants (food additives) (Bujor et al. 2015). Many secondary metabolites present inside the plants are having antioxidant capabilities due to phenolic compounds (Oszmanski 1995). Until now, research has indisputably shown that phenols not only play a significant part in plant defense mechanisms but also impact people and animals which ingest those phenols-enriched products (Franca et al. 2001; Amarowicz and Weidner 2009). In plants, phenolics storage in compounds is a continuous condition of plants while during stress, and it serves as a defense mechanism to deal with a variety of abiotic challenges (Cheynier et al. 2013). Plant phenolics have a vital function in a variety of physiological processes that promote plant tolerance and adaptation under adverse conditions (Andersen 2003; Lattanzio et al. 2009; Dixon and Paiva 1995). This category includes a wide variety of secondary metabolites with antioxidant capabilities (Oszmanski 1995), which can improve plant performance under stressful circumstances. Many tests have revealed that the plants subjected to drought develop larger amounts of secondary metabolites. Under drought stress, such enhancement has been reported to occur for complex and simple phenols, as well as for numerous terpenes, confirming the enhancement in the production of secondary products of plant; however, reduction in plant growth has also been reported in most plant species under drought stress conditions. In all plants, phenolic accumulation and storage is a continuous feature of plants under stress, and it serves as a defense mechanism to deal with a variety of abiotic challenges (Cheynier et al. 2013). Plant phenolics have a vital function in a variety of physiological processes that promote plant tolerance and adaptation under adverse conditions (Andersen 2003; Lattanzio et al. 2009; Dixon and Paiva 1995). As a result, a simple and clear explanation for this impact is that during drought stress, the similar quantity of produced is formed and stored under well water conditions, but their concentration is simply increased owing to the reduction in biomass.

13.4 Interrelation of Phenolics and Drought Stress

Plants, since they are rooted in the environment in which they develop, must adapt to changing conditions caused by abiotic stressors, and the storage of phenolic in plant is seen as an adaptive reply of plants to this adverse condition of environment (Pereira 2016; Lattanzio 2013). During the stress tolerance acquisition process, abiotic stimuli cause morphological, biochemical, and physiological changes in plants.

Drought stress is a significant abiotic type of stress that influences growth, nourishment, and development and results in output losses in production. The phenolic buildup is a critical effect of drought stress in plants (Naikoo et al. 2019). According to numerous findings, the concentration of phenolics rises in plants developing in dry circumstances. The bioactivity of leaf phenolic compounds has been demonstrated to activate the drought stress defense system (Malik et al. 2020).

The accumulation or storage or increase of flavonoids and phenolics during drought stress is proportional to drought resistance levels (Wagay et al. 2020). The buildup of polyphenolic compounds under drought stress has been linked to plant development stage, stress severity, and species of plant (Wang et al. 2016). Drought conditions have also been linked to an increase in the breakdown of big polyphenolic compounds into small ones (Harrison and Were 2007). The changes in phenolic compound fractions seen under varied water stress circumstances might potentially be related to the synthesis of distinct phenolic acid and flavonoid compounds when different cultivars seek to adjust to variable soil moisture levels. Many findings of increased phenolic and flavonoid component accumulation in medicinal plants under water constraints improve product quality (Yan et al. 2016). In leaf cells, the "phenolic compounds" operate as a signal trigger, triggering defensive processes against drought stress (Akula and Ravishankar 2011; Wagay et al. 2020). Stress due to drought caused significant increases in the total phenolic content in the leaf and flowers of *Tridax procumbens* (Gnanasekaran and Kalavathy 2017). Drought stress also increased the levels of phenolic compound like 4-hydroxycinnamic acid in *Cucumis sativus* (Li et al. 2018). Drought resistance levels are related to the accumulation and growth of flavonoids and phenolics (Wagay et al. 2020). The capacity of phenolic acids to tolerate drought varies substantially among plant genotypes (Wagay et al. 2020). These phenolic molecules might be employed as stress indicators in areas where the drought is severe.

Less than four irrigation regimes and the changes in total phenolic content (TPC) and total flavonoid content (TFC) were tested. It was discovered that the total flavonoid and phenolic content was dependent on the percentage of water stress in three *Achillea* spp. (*A. nobilis*, *A. filipendulina*, and *A. millefolium*) under 25% FC (severe stress), 50% FC (moderate stress), 75% FC (low stress), and 100% FC (field capacity as normal irrigation) conditions. TPC increased in all *Achillea* spp. under drought stress, although the rate of growth varied between treatments. Total phenolic content rose considerably from low to moderate stress in all three of the aforementioned species, whereas no significant change was seen between low stress and control species. TPC of *A. nobilis* was the greatest in extreme drought stress, followed by *Achillea millefolium* and *Achillea filipendulina* (Gharibi et al. 2016). Several studies have documented a similar reaction in other plant species subjected to stress of drought (Yordanov et al. 2000; Reddy et al. 2004). A decrease in biomass was seen in all genotypes under drought stress, with a substantial rise in total phenolics and phenylalanine ammonia-lyase (PAL) activity, and also increase in lignin production in all genotypes, although it was more obvious in transgenic plants (Silva et al. 2010). Studies on tomato and cherry have also confirmed that drought stress enhanced TPC and TFC (Al Hassan et al. 2015); however other studies showed no effect during stress on total flavonoids or polyphenols (Cherit-Hacid et al. 2015).

The concentration of phenolics increased dramatically in stressed *pea* plant, but the number of anthocyanins (anthocyanin concentration and product of biomass) was about 25% higher in the drought-stressed plants, although the total biomass of the *Pisum sativum* grown under drought stress is only about one-third that of the plants grown under standard conditions. In contrast, when plants were cultivated in drought stress or well-watered condition or non-stress circumstances, the overall output of total flavonoids was approximately the same (Nogués et al. 1998). It was also shown that when *Hypericum brasiliense* was subjected to the drought stress, the total phenolic concentration and content increased dramatically (De Abreu and Mazzafera 2005). Drought stress enhanced the number of polyphenols in *Larrea* sp. (Varela et al. 2016). Two basil species (*Ocimum basilicum* and *Ocimum ciliatum*) were tested under normal and reduced irrigation, and it was discovered that total phenolic was greater in the species grown under reduced irrigation than in the species grown under normal irrigation (Pirbalouti et al. 2017). Under drought circumstances, the polyphenolic and flavonoid content of *Thymus vulgaris* increased significantly (Khalil et al. 2018). Caftaric acid and rutin content were increased in lettuce plants during drought stress (Galieni et al. 2015). Griesser et al. (2015) noticed an enhancement in polyphenol in *Vitis vinifera* cv. Pinot noir, including ferulic acid, 4-coumaric acid, catechin, epicatechin gallate, epicatechin, caffeic acid, quercetin-3-O-glucoside and quercetin-3-O-glucuronide, cis-resveratrol-3-O-glucoside, trans-resveratrol-3-O-glucoside, cyanidin-3-O-glucoside, caftaric acid, and kaempferol-3-O-glucoside.

Plant tissue containing anthocyanins is generally drought-resistant (Chalker-Scott 1999), and it has also been discovered in a purple cultivar of chili that resisted water stress better than a green variety of chili (Bahler et al. 1991). Transcriptomic and metabolomic methods have also demonstrated that flavonoid accumulation is critical for drought tolerance in both wild-type and mutant *Arabidopsis thaliana* (Nakabayashi et al. 2014). Drought-resistant tomato had higher levels of kaempferol and quercetin (flavonoids), whereas drought-sensitive cultivars had lower levels (Sanchez-Rodriguez et al. 2011). The comparison of *Cistus clusii* plants cultivated under controlled drought conditions indicated an increase in flavonol levels when compared to the same species obtained from the field of Mediterranean climate, which is characterized by high temperatures and a protracted absence of rain (Hernandez et al. 2004). Kirakosyan et al. (2003) observed similar findings in *Crataegus laevigata* and *Crataegus monogyna*. Ballizany et al. (2012) discovered that the quercetin (a flavonol) content of white clover increased considerably under drought circumstances when compared to drought-resistant genotypes. Nichols et al. (2015) also found that high amounts of flavonols, quercetin, and kaempferol in white clover were associated with higher stress tolerance capability under drought circumstances. Drought enhanced the level of phenolics, anthocyanins, and flavonoids in wheat cultivars that were drought-resistant (C 306) and drought-sensitive (PBW 343) (Kaur and Zhawar 2015). Drought stress has been studied in two canola (*Brassica napus*) cultivars (RGS003 and Sarigol). Drought stress significantly increased flavonoid content in RGS003, whereas total phenol content rose at high PEG (15%) concentrations in these two canola cultivars.

Tocopherol content was enhanced in RGS003 and Sarigol by 5% and 15% of PEG, respectively. In RGS003, the expression of the PAL gene correlated positively with its enzymatic activity and flavonoid, tocopherol, total phenol, and flavonol levels. In Sarigol, PAL and TAL had a favorable connection with flavonoid, anthocyanin, and total phenol (Rezayian et al. 2018). The total flavonoid content (TFC), total phenolic content (TPC), and anthocyanin of two *Chrysanthemum* cultivars ‘Taraneh’ and ‘Azita’ were observed under drought conditions for 7 days, concluding that TFC and TPC in the cultivar ‘Taraneh’ reached their highest levels at the seventh day, whereas ‘Azita’ showed reverse results at fifth day to the treatment of stress – its TPC increased but its TFC decreased. Drought stress was shown to alter anthocyanin content, which rose by 3.5 and 1.71 times on the fifth and seventh days of the stress period in both cultivars, respectively, as per control.

Furthermore, the buildup of anthocyanins in leaves exhibited comparable patterns in both cultivars up to the fifth day of stress, but under normal conditions, the lowest values were obtained, indicating that water stress had a favorable influence on boosting overall anthocyanin levels (Hodaei et al. 2018). Higher (25%) anthocyanin accumulations have also been recorded in grapefruit (Palliotti et al. 2011), wheat (Ma et al. 2014), and *Reaumuria soongorica* under extreme water stress (Liu et al. 2013).

Jaafar et al. (2012) investigated soil field water capacity (SWC) with its impact on secondary metabolites of *Labisia pumila* Benth in two varieties and found differences in anthocyanin accumulation trends, although almost the similar trends have been reported by many studies for TPC and TFC; however in bean an opposite observations were recorded (Telesinski et al. 2008).

Under drought stress, phenolic acids and flavonoids are generated in large quantities in *Triticum aestivum* leaves, along with the production of cell-damaging oxidants (Ma et al. 2014), generating oxidative stress in *Salix* leaves (Larson 1988). The buildup of these antioxidants and sunshields has been linked to plant reaction to drought stress (Nichols et al. 2015). The antioxidant capacity of finger millet mirrored variations of phenolic acid levels during the malting process (Subba Rao and Muralikrishna 2002). The radical-scavenging capacity of two rice varieties, black-hulled and red-hulled, was shown to be reliant on anthocyanin and proanthocyanidin concentrations, respectively (Oki et al. 2002).

Also, concerning terpenoids, there are some instances in which drought stress-related rise in their concentration is related to the reduction in their dry weight. Nowak et al. (2010) revealed that drought stress causes a large rise in monoterpenes in sage (*Salvia officinalis*) that is significantly greater than the corresponding drop in biomass. As a result, when well-watered controls were compared to plants suffering from moderate drought stress, the total quantity of monoterpenes was found to be considerably greater in plants suffering from moderate drought stress. The increase in essential oil concentration in parsley leaves is more or less offset by the associated loss in biomass during drought stress, affecting overall essential oil contents in drought-stressed and well-watered plants. Manukyan (2011) found just a small rise in monoterpene concentrations in catmint and lemon balm as a result of drought stress (see Table 13.1).

However, certain studies reported effects of water stress as stress-induced decreases in the overall content of flavonoids and total phenolic content in certain plant species during drought stress conditions (Wegener et al. 2015; Carvalho et al. 2021; Krol et al. 2014; Rihan et al. 2017), and similar observations of stress-induced decreases in the content of terpenoids have been observed in *Salvia officinalis*, *Nepeta cataria*, and *Melissa officinalis* (Manukyan 2011). Rezayian et al. (2018) found a substantial drop in anthocyanin concentration in both canola cultivars (RGS003 and Sarigol) following varied levels of drought exposure (see Table 13.2).

However, as previously documented in earlier research, genotype was regarded as the key factor leading to variance in plant TPC (Cao et al. 1996; Zheng and Wang 2001). Unfortunately, total information of records is not present in most published studies, and this information gap is mostly attributable to the fact that most

Table 13.1 Response of various plant species with effects during drought stress

Plant species	Response to drought stress	Effect on parameters	Reference(s)
Brassica napus	Total phenols, flavonoids, and flavonols increased	Increased PAL enzyme activity is accompanied by increased PAL expression	Rezayian et al. (2018)
Nicotiana tabacum	Total phenol content, kaempferol, and quercetin levels increased	Expression of PAL, IFR, DFR, C4H, CHS, 4CL, CHI, and IFS increased	García-Calderón et al. (2015); Silva et al. (2018)
Triticum aestivum	Total phenols, flavonoids, and anthocyanins all increased	Induction of gene expression in ANS, DFR, CHI, CHS, F3H, FNS, and FLS	Kubota et al. (1988); Ma et al. (2014); Kaur and Zhawar (2015); Guo et al. (2020)
Camellia sinensis	(−)Epigallocatechin gallate and (−) epicatechin quinone levels increased	Plants' antioxidant properties improve, and they provide protection against microbial diseases	Hernaéndez et al. (2006)
Echinacea purpurea	Increase in total number of phenolic acids	Increase in chicoric acid levels and root dry weight	Gray et al. (2003)
Hypericum brasiliense	Increased levels of 1,5-dihydroxyxanthone, isouliginosin B, quercetin, and rutin	Antioxidant property induced	De Abreu and Mazzafera (2005)
Labisia pumila	Total phenolic compounds, total flavonoids, and anthocyanin levels increased	Increased PAL activity, anti-inflammatory, and antioxidant response	Jaafar et al. (2012)
Helianthus annuus	Massive increase in chlorogenic acid (CLA)	–	Del Moral (1972)
Prunus persica	Total phenol increased	–	Kubota et al. (1988)
Thymus capitatus	Phenolics increased	–	Delitala et al. (1986)
Echinacea purpurea	67% increase in total phenol	–	Gray et al. (2003)
Crataegus spp.	Massive increase (2- to 6-fold) in chlorogenic acid	–	Kirakosyan et al. (2004)
Hypericum brasiliense	80% increase in total phenols	–	De Abreu and Mazzafera (2005)
Mentha piperita L.	2–2.6-fold increase in total phenols	–	Chiappero et al. (2019)

(continued)

Table 13.1 (continued)

Plant species	Response to drought stress	Effect on parameters	Reference(s)
Cucumis melo L.	Total phenols (massive increase, 196%)	Superoxide dismutase (SOD) activity increase and ascorbate peroxidase (APX), guaiacol (POD), catalase (CAT) activity increase	Ansari et al. (2019)
Salvia sinaloensis	Total phenols (massive increase, 139%)	–	Caser et al. (2018)
Vitis vinifera	Massive increase in anthocyanin (35–57%) and increase in polyphenolic content (4-coumaric acid, caffeic acid, ferulic acid, cis-resveratrol-3-O-glucoside, trans-resveratrol-3-O-glucoside, quercetin-3-O-glucuronide, catechin, quercetin-3-O-glucoside), epicatechin, caftaric acid, kaempferol-3-O-glucoside, epicatechin gallate, cyanidin-3-O-glucoside	Induction in gene expression (F3H, DFR, CHS1, CHS2, LDOX, CHS3, F3′H, CytB5), Myb transcription factors (Myb5a, MybD, MybC, and MybB), and ABA-, drought-, and sugar-related genes	Castellarin et al. (2007); Savoi et al. (2016); Griesser et al. (2015); Moayedinezhad et al. (2020)
Oryza sativa Indigenous aromatic rice cultivars (IARCs)	249.37% increase in rutin and 68.75% increase in kaempferol, as well as de novo production of apigenin and myricetin Significant upregulation of phenolic acids such as chlorogenic acid (14.51%), caffeic acid (5.65%), and p-coumaric acid (31800%)	Increased endogenous ROS and H_2O_2 levels	Dey and Bhattacharjee (2019)
Pisum sativum	45% increase in flavonoids; over 80% increase in anthocyanins	–	Nogués et al. (1998)
	Total phenolic content increased	–	Duval and Shetty (2000)
Lactuca sativa	Increase in levels of chicoric acid, caffeic acid, caftaric acid, and rutin	–	Galieni et al. (2015)

Lotus japonicas	Kaempferol and quercetin content increased	Expression of CHI, PAL, C4H, CHS, DFR, IFS, 4CL, and IFR is upregulated	García-Calderón et al. (2015)
Achillea millefolium, *A. filipendulina*, and *A. nobilis*	Total phenolic and total flavonoid compounds increased	Antioxidant properties improved	Gharibi et al. (2016)
Achillea pachycephala	1,3-Dicaffeoylquinic, luteolin, chlorogenic acid, rutin, luteolin-7-O-glycoside, acid, apigenin, caffeic acid, and kaempferol concentration increased	CHI, PAL, CHS, F3′H, F3′5′H, F3H, and FLS transcript levels were increased	Gharibi et al. (2019)
Chrysanthemum morifolium	Total phenolic, luteolin, anthocyanin, ferulic acid, chlorogenic acid, rutin, quercetin, and apigenin content increased	Total rutin, phenolic, anthocyanin, apigenin, chlorogenic acid, luteolin, ferulic acid, and quercetin content increased	Hodaei et al. (2018)
Fragaria ananassa	–	FLS, PAL, C4H, ANS, 4CL, DFR, and UFGT transcript levels were increased	Perin et al. (2019)
Larrea spp.	Increased polyphenol content, including flavonoids, flavonols, and proanthocyanidins	–	Varela et al. (2016)
Ocimum spp.	Increase in total phenols	–	Pirbalouti et al. (2017)
Thymus vulgaris	Increased concentrations of total flavonoids and polyphenols	–	Khalil et al. (2018)
L. divaricata	Increase in the total flavonoid and total phenol content	Enhancement of antioxidant ability	Varela et al. (2016)
Cistus clusii	Flavonoid content has increased (epigallocatechin gallate, epicatechin, and epicatechin gallate)	Enhancement of antioxidant ability	Hernandez et al. (2004)
Vigna subterranean	Slight increase in total phenolics	–	Inuwa and Muhammad (2017)
Amaranthus tricolor	Total phenolics and total flavonoids have increased	Enhanced antioxidant activity	Sarker and Oba (2018)

Table 13.2 Exceptions to the increase in phenolic compounds during drought stress

Plant species	Response to drought stress	Effect on parameters	Reference(s)
Solanum tuberosum	There was no discernible increase in total phenolics or total flavonoids	There was no discernible increase in antioxidant activity	Wegener et al. (2015)
Vigna unguiculata	Decrease in total phenolic contents	Increased antioxidant activity (has no effect)	Carvalho et al. (2021)
Vitis vinifera	Total phenolic content decreased (p-coumaric acid, ferulic acid, and caffeic acid)	Antioxidant capacity has been reduced	Krol et al. (2014)
Matricaria chamomilla	A significant reduction in total phenols and total flavonoids was observed	–	Rihan et al. (2017)

researchers are only interested in roots, leaves, or seeds. The entire composition of natural goods on a whole plant basis has never been emphasized.

13.5 Pattern of Gene Expression During Drought Stress for Gene Phenylpropanoid

Drought stress is an inescapable factor that manifests itself in a variety of circumstances with no defined limitations and no obvious warning, reducing plant biomass yield, quality, and energy. Water accounts for roughly 80–95% of the plant body's fresh biomass and plays an important role in a variety of physiological activity like plant growth, plant metabolism, and plant development (Brodersen et al. 2019; Abbasi and Abbasi 2010). As a result, some researchers believe that drought stress is the most significant environmental stress in many plants, especially in drought-prone areas (Anjum et al. 2011; Diatta et al. 2020a, b), the only serious threat to the global food security in the future, and responsible factor of major famines in the past in world history (Okorie et al. 2019). Studying pathways of genetic expression and regulation from wild relatives, drought-tolerant varieties and landraces are known to contribute to drought tolerance in major crops and would improve our insights into drought tolerance, and progression in understanding and application of physiological and genetic processes of plant varieties that are stable and have yields in water-scarce environments is the need of the hour.

Perin et al. (2019) evaluated the direct effect of drought on strawberry fruit, finding a favorable relationship between overexpression of phenolic-related genes. It was recorded that dryness increases the quantity of anthocyanins and phenolic compounds by phenylpropanoid pathway. During stress, there is a buildup of phenylalanine ammonia lyase (PAL) transcription with a rising transcript level at the beginning of this phenolic metabolic pathway. The gene primers were constructed for simultaneous amplification for the all known PAL genes, the expression of which indicated the total expression of PAL. The same expression was shown for dihydroflavonol 4-reductase (DFR) (associated with leucoanthocyanidin production), flavonol synthase (FLS) (for flavonol synthesis), cinnamate 4-hydroxylase 2 (C4H2), and ρ-coumarate ligase (4CL) (related to the synthesis of coumaric acid). Furthermore, only drought stress increased the activity of anthocyanidin synthase (ANS), which is responsible for the production of anthocyanidins. The UDP flavonoid glycosyltransferase (UFGT) gene, which is involved in the glycosylation of anthocyanins and flavonols, was shown to be downregulated by both biotic and abiotic stressors. ANS and cinnamate 4-hydroxylase 1 (C4H1) were both downregulated in drought stress, as was flavanone 3-hydroxylase (F3H), which is responsible for the production of dihydroflavonols.

Gharibi et al. (2019) evaluated the gene expression for their molecular processes in the phenylpropanoid pathway (FLS, CHS, F3H, CHI, F3′H, PAL, F3′5′H) during drought stress with the help of qRT-PCR. The samples were harvested at 7-day intervals (0, 7, 14, 21, and 28 days) after being subjected to drought stress and determination of change in the flavonoid and phenolic compounds such as caffeic acid, chlorogenic acid, rutin, apigenin-7-O-glycoside, luteolin, 1,3-dicaffeoylquinic acid, luteolin-7-O-glycoside, and kaempferol, and apigenin-7-O-glycoside, luteolin, 1,3-dicaffeoylquinic acid and kaempferol were analyzed by high performance liquid chromatography (HPLC). It was discovered that the quantities of the majority of the chemicals rose as the duration of the drought stress increased. The majority of the phenolic acids accumulated routinely as the period of stress continued; however, flavonoids declined drastically by the 28th day. At the start of the trial, chlorogenic acid (04.97 mg/100 g dry weight (DW)) was the most abundant phenolic acid, but it decreased on the seventh day and then started to increase again on the 21st day. However, for other flavonoids, such as apigenin, distinct patterns were seen. At the start of the stress treatment, high levels of free radicals (H_2O_2) resulted in increased expression of the majority of flavonoid genes. On the 28th day, MDA enhanced from 22.66 to 43.28 μmol g^{-1} of dry weight. On the seventh day, CHS gene expression increased, whereas CHI gene expression remained steady.

PAL is a key gene in the earliest steps of the phenylpropanoid biosynthesis pathway, as well as the conversion from phenylalanine to cinnamic acid. The transcription of the PAL2 gene increased considerably after 7 days of drought stress. Significant alterations in the transcriptional gene activity of flavonoid were identified during drought stress, and p-coumaric acid was also enhanced. Cinnamate 4-hydroxylase (C4H) activity converts cinnamate to top-coumaric acid, and subsequently, 4-coumaroyl-CoA is produced by 4-coumaroyl-CoA ligase (4CL) (Teixeira et al. 2013).

Ma et al. (2014) studied the expression pattern of flavonoid biosynthesis genes (TaCHS, TaCHI, TaF3H, TaFNS, TaDFR, TaFLS, and TaANS) and the accumulation of flavonoids in *Triticum aestivum* leaves during drought stress. Under drought stress, quantitative real-time PCR analysis revealed enhancement in the expression levels of these genes in two wheat cultivars, Chinese Spring (CS) and Aikang 58 (AK). During drought stress treatment, the cultivar CS had greater levels of

TaCHI, TaF3H, TaCHS, TaFLS, TaDFR, and TaANS gene expression, whereas the cultivar AK had higher levels of TaFNS gene expression. CHS and CHI are the first two genes that encode the unbranched early section of the flavonoid biosynthesis pathway. The relative expression of TaCHS and TaCHI all increased under stress treatment and reached an optimal expression level after 12 h. When compared to CS, the rates of gene expression (TaCHS and TaCHI) were more in AK. Drought stress enhances total flavonoids, total phenolics, and anthocyanin content with schaftoside concentration in leaves of wheat, with cultivar CS wheat which had relatively greater accumulation.

The significance of water stress in the regulation of polyphenol production was investigated by comparing the expression levels of these important genes in two *C. morifolium* cultivars based on their phytochemical attributes using qRT-PCR. Previous research regarded flavonoid biosynthesis key enzymes including PAL, CHI, and F3H to be essential water stress signalling response indicators that might be upregulated in response to diverse environmental pressures (Liu et al. 2013; Li et al. 2015). These genes' mRNA levels changed significantly when water was scarce, although the range of activation of gene expression was extremely cultivar-dependent. Among all of these genes, PAL is essential at the start of the phenylpropanoid biosynthesis pathway (Huang et al. 2016). The relative expression of PAL was much greater in 'Taraneh' than in 'Azita'. The expression of PAL was dramatically increased in 'Taraneh' following 5 days of water stress, with the maximal expression level on day 7 of the stress phase being 3.15 times greater than in control plants. After a minor rise on day 5 of the water stress phase, gene expression in 'Azita' declined considerably. This implies that PAL's sensitivity to water scarcity was entirely cultivar-dependent. PAL and F3H genes were mostly inhibited in 'Azita' during water stress. Furthermore, transcription of F3H in 'Azita' fluctuated less than in 'Taraneh', with a nearly sevenfold rise on day 5 of the water stress phase. After 3 days of exposure to water treatment, the expression of CHI rose fast in both cultivars; however, no significant rise in 'Taraneh' was noticed, and it showed a declining trend (Hodaei et al. 2018). Higher expression of flavonoid pathway genes (CHI and F3H) was also seen in potatoes under water stress, indicating that water stress may have stimulated the expression of these genes (Andre et al. 2009). Xu et al. (2013) found that water stress downregulated CHI transcripts in the *Chrysanthemum* cultivar 'Fall Color' with pink flowers, indicating that changes in expression levels of this gene during water stress are cultivar-dependent and that no consistent trend has been suggested for modulations of this species under water stress. This variance might be attributed to differences in the function of CHI genes in various cultivars under water stress. Different gene expression patterns were discovered as a consequence of interactions between the cultivar and genes under stress conditions. Some genes involved in the flavonoid biosynthesis pathway are upregulated under stress in rice, potato, and birch, indicating the involvement of the flavonoid pathway (Liu et al. 2013). This further conclude that the genes F3H and PAL gene is not regulate works in *Chrysanthemum*, and it was susceptible to a moderate level of water stress. Furthermore, F3H gene transcription was similar as it is under normal conditions, suggesting that gene expression might be repressed under extreme drought stress conditions. Such environmental and genetic interactions result in trait-dependent gene correlations (Sgro and Hoffmann 2004).

With the normal or less level of water stress (at day 3 of experiment), CHI expression was significantly correlated with phytochemicals such as luteolin, chlorogenic acid, and apigenin, whereas PAL expression was negatively correlated with these compounds except for rutin ($r = +0.881$). Water stress increased the synthesis of luteolin, quercetin, and rutin in ‘Taraneh’ and luteolin and apigenin in ‘Azita’ on day 3 of the experiment via upregulating CHI. As a result, it is possible to deduce that the CHI product (naringenin) in ‘Azita’ was mostly employed as a precursor to the synthesis of luteolin and apigenin, whereas it was used in ‘Taraneh’ to synthesize quercetin and rutin.

García-Calderón et al. (2015) used real-time qRT-PCR analysis on *Lotus japonicas* to study and evaluate changes in the expression of genes for the production of phenolic compounds discovered in transcriptomics studies under drought. qRT-PCR found a significant increase in the expression of multiple genes involved in the production of several branches of the phenolic biosynthetic pathway. The analysis of qRT-PCR data shows that the common enzymes of the phenolic biosynthesis pathway (PAL, C4H, and 4CL) were strongly upregulated under drought or active PR treatments, particularly in mutant plants, and that CHS, CHI, DFR, IFS, and IFR expression were also elevated. They also saw a rise in kaempferol and quercetin levels.

In two consecutive years, Castellarin et al. (2002) discovered that total anthocyanin content rose by 37–57% at harvest in water-stressed (WS) fruits. The linear relationship between the integral of mRNA accumulation of the specific anthocyanin biosynthetic gene UDP-glucose:flavonoid 3-O-glucosyltransferase (UFGT) and metabolite content during time series from version to ripening explained at least 84% of the total variation in anthocyanin content. The flavonoid pathway genes chalcone synthase (CHS2, CHS3) and flavanone 3-hydroxylase (F3H) also exhibited a substantial connection. Genes encoding flavonoid 3,5-hydroxylase (F35H) and O-methyltransferase (OMT) were also upregulated in berries from dehydrated plants with anthocyanin compositions enriched in more hydroxylated and methoxylated derivatives like malvidin and peonidin, the grape anthocyanins with the highest affinity for human gastric bilitranslocase.

13.6 Conclusion

Phenolics are a significant and varied collection of secondary metabolites that participate in a variety of metabolic and defense activities. The rise in phenolic content and associated substances such as flavonoids, anthocyanins, and so on by diverse plant species during drought stress or water scarcity is genetically linked to the genes that govern the phenylpropanoid pathway. However, a reduction in phenolic compounds has been recorded during drought stress situations. The actual mechanism explaining the upregulation or downregulation of genes controlling the biosynthesis of phenolic compounds during drought conditions remains a mystery, and unravelling this mystery will be extremely beneficial in crop improvement and management in the future, as well as our better understanding of the genetic and physiological mechanisms of drought-tolerant species.

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Interactive Role of Phenolics and PGPR in Alleviating Heavy Metal Toxicity in Wheat

14

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Abstract

The most essential food crop wheat (*Triticum aestivum*) is having more nutritional value than any other cereal crop. It is cultivated in tropical as well as temperate environments worldwide. Wheat is rich in secondary metabolites, thus enhancing its nutritional value and antioxidant activity against various stresses. Among the several abiotic stresses, wheat is mostly affected by the heavy metal stress such as cadmium, chromium, lead, etc. present in the contaminated soils which in turn results in the negative impact on photosynthesis and growth and causes nutritional deficiency in plants. Phenolics are an important class of secondary metabolites found in wheat that play a key role in scavenging radical oxygen species generated due to heavy metal stress conditions, thus helping in alleviating the stress. Phenolic compounds, because of carboxyl and hydroxyl groups, are able to chelate heavy metals, eliminating ROS and preventing peroxidation induced by ROS and heavy metals. Heavy metal stress is also alleviated by the plant growth-promoting rhizobacteria which secrete several chemicals, amino acids, and proteins, thus assisting the plants against the deleterious effects of stress due to heavy metals. In the present chapter, we put an emphasis on the role of phenolics and PGPR in alleviating the negative impact of heavy metal stress in wheat.

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Phenolics · PGPR · Heavy metal

14.1 Introduction

Wheat (*Triticum aestivum*) is among the most significant crops of the world, supplying more protein and calories than any other cultivated food crop both nutritionally and economically (FAOSTAT 2017). It is a main diet for roughly 35% of the global total population. In spite of being a vital crop, wheat is particularly susceptible to heavy metal poisoning and is more harmed by irrigated water containing heavy metals (Karatas et al. 2006). Nowadays, contamination of soil and water by heavy metals has become a severe problem all over the world. Metal contamination can arise as a result of growing industrialization, mining, fossil fuel burning, petrochemical leakage, increased metal waste disposal, industrial emissions, and agricultural processes (Wang et al. 2013; Mohammadi et al. 2018). The most prominent heavy metals present in soils are cadmium (Cd), arsenic (As), lead (Pb), nickel (Ni), chromium (Cr), zinc (Zn), etc. (Nagajyoti et al. 2010; Clemens and Ma 2016).

In recent times, the deposition of heavy metal contamination in soil because of the widespread industrialization is having a substantial effect on agricultural methods and crop output. The accumulation of toxicity of metals in soil is also due to the increased pace of anthropogenic activity (Hassan and David 2014). The concentration of heavy metals in plants and in soil causes visible structural damage, development inhibition, and a decrease in plant biochemical and physiological activity. The impacts and bioavailability of heavy metals are determined by environmental aspects such as soil texture, pH, fertilization, nutrient element, and plant species. Stress caused by heavy metals poses a severe danger to crop productivity across the world (Panuccio et al. 2009).

According to a survey, industrial effluent is used to irrigate over 20 million hectares of agricultural land around the world (Iram and Akhtar 2012). The occurrence of heavy metals (e.g. Pb, As, Ni, Cr, and Cd) in industrial waste and sewage waterways and their buildup accumulate in crops irrigated by such water, and accumulation beyond the threshold levels can be detrimental to human health (Ahmad et al. 2014). The heavy metals enter the food chain via plant absorption and thus have an impact on human health (Friesl-Hanl et al. 2009). Heavy metal-polluted food when consumed on regular basis results in major health problems such as cancer, cardiovascular, neurological, renal, and mutagenesis concerns in the body of humans (Jarup 2003; Steenland and Boffetta 2000; Radwan and Salama 2006). The mobility of these trace minerals in soil is well known, and as a result they end up in the human food supply chain (Malik 2004). Soil pollution by heavy metals is caused by a variety of human and industrial activities (Chibuike and Obiora 2014). Hazardous metal contamination has significantly expanded in the environment, as a result of several human-made actions carried out in changing industry and urban life.

Despite the fact that these activities have significantly enhanced human living standards, they have also harmed the ecosystem (Singh et al. 2013). Since heavy metals are hard to eliminate from the environment, their toxic effects poses a serious threat to ecosystems (Etesami 2018; Ahemad 2012). Several heavy metals are just required at small quantities for various metabolic activities in organisms, but at larger levels in the soil than permissible level, these metals have a harmful impact on microbial community's growth and composition (Ahemad 2012). The heavy metals pose adverse impact on heavy metal-stressed plant's growth, photosynthesis, and biomass (Nagajyoti et al. 2010; Ali et al. 2015). The heavy metals also cause insufficiency and imbalance of vital nutrients in plants by their interference with the intake and supply of vital nutrients and minerals (Sharma and Archana 2016; Etesami 2018). Furthermore, heavy metals are primarily deposited in soil and transmitted to the food chain by plants that thrive in that soil (Etesami 2018).

Phytoremediation is a useful approach for controlling heavy metal contaminants (Ma et al. 2013). The phytoremediation/assisted phytoremediation is the removal of heavy metals and mitigation of their harmful effects utilizing plants and their associated microbes (Ullah et al. 2015). The phytoremediation procedure can also be used to remove hydrocarbons, pesticides, and polychlorinated biphenyls, in addition to heavy metals. Plants normally deal with toxins through a variety of processes and keep the soil fertile without damaging the topsoil (Mench et al. 2009). Bacteria-aided phytoremediation is the process of using bacteria to remediate pollutants from soils (Glick 2010). Morphological abnormalities, chlorosis, reduced plant growth, yield loss, and metabolic diseases all are caused by higher levels of Cd, Pb, Zn, Cr, Ni, and Co in soil (Mariem et al. 2014; Amari et al. 2014; Taamalli et al. 2014). To minimize heavy metal contamination in soil by using plant growth-promoting rhizobacteria (PGPR) is a realistic, environmentally friendly, and cost-effective solution (Ahemad 2014; Upadhyay et al. 2011).

14.2 Role of Plant Growth-Promoting Rhizobacteria (PGPR) in Alleviating Heavy Metal Stress and in Increasing Nutritional Status in Wheat Plant

Plant growth-promoting rhizobacteria (PGPR) are a type of helpful bacteria that are present in soil ecosystems (Kloepper et al. 1989). Many different plants have PGPR associated with their roots. The impacts of PGPR on plant development can be facilitated by indirect or direct processes (Glick 1995). Synthesis of plant hormones like cytokinins, gibberellins, and auxins, biological nitrogen fixation, and inorganic phosphorous solubilization, among other things, have been blamed for the direct consequences. Indirect strategies include the formation of siderophores, antibiotics, HCN, volatile metabolites, ammonia, and other compounds that reduce phytopathogens, as well as inducing acquired systemic resistance and challenging with the pathogen for nutrition and colonization space (Glick 1995). A rhizobacteria could employ one or more of these strategies to influence development and growth in plants (Montesinos 2003). The practice of using PGPR has expanded dramatically in recent years in several regions all over the world reducing the overall need of using chemical fertilizers for sustainable agriculture. Current research suggests that PGPR increases plant's tolerance to various abiotic stresses like chilling injury (Ait Barka et al. 2006), drought (Timmusk and Wagner 1999; Sandhya et al. 2009), metal toxicity (Dell'Amico et al. 2008), salinity (Han and Lee 2005), and elevated temperature stress (Ali et al. 2009).

Plant growth is affected by PGPR in three ways: (1) by producing and supplying certain specific substances to plants (Glick 1995), (2) increasing the intake of particular nutrients and minerals from the environment (Cakmakçi et al. 2006), and (3) safeguarding plants against disease (Khan et al. 2002). PGPR colonizes plants by secreting a variety of compounds like amino acids, proteins, and antibiotics that assist plants to deal with heavy metal toxicity (Khanmirzaei et al. 2013). The PGPR have the ability to decrease the harmful consequences of heavy metals by oxidizing, reducing, compartmentalization, methylation/demethylation, and converting to a less hazardous form (Nazir et al. 2011).

Biologically based procedures are now widely used by scientists to manage and eliminate toxic contaminants from environmental units such as soil, air, and water and to make them less damaging for the ecosystem (Mishra et al. 2017). In heavy metal-polluted soil, microbes aid plant growth by producing a variety of growth-regulating chemicals such as siderophores, organic acids, enzymes, and hormones. Redox reactions, precipitation acidification, and chelation are some of the methods that these compounds use to promote plant development. Similarly, roots exude helpful nutrient elements to help bacteria colonize and thrive successfully (Taj and Rajkumar 2016). Heavy metals existing in soil can be mobilized/immobilized by numerous plant growth-promoting rhizobacteria (Gadd 1990). The effect of heavy metal-tolerant PGPR in reducing the impact of heavy metals on plant biomass, growth, and development is being researched all over the world (Belimov et al. 2005). Phytoremediation technology uses plants and their rhizospheric microbes to eliminate toxins at a cheaper cost and in an environmentally sustainable manner (Fig. 14.1). Plant colonization by PGPR has helped the plants in repairing heavy metal toxicity facilitated by secretions of various amino acids, antibiotics, chemicals, and proteins (Khanmirzaei et al. 2013). Another way by which heavy metal-resistant PGPR are capable to lessen the detrimental consequences of heavy metals on plants is by enhancing the uptake of important nutrient elements like calcium, magnesium, nitrogen, phosphorus, sulphur, zinc, iron, manganese, etc. (Guo and Chi 2014; Etesami 2018; Sharma and Archana 2016; Saravanan et al. 2011) and as a result improves the systemic acquired resistance of plants to heavy metal exposure (Gomes et al. 2012; Etesami 2018). For example, siderophores generated by heavy metal-resistant PGPR have potential to alleviate stress induced by heavy metals by providing nutrients (mainly Fe), decreasing the formation of radicals across plant roots, and shielding microbial phytohormones from harmful oxidative damage caused by heavy metals in heavy metal-stressed plants (Zloch et al. 2016; Rajkumar et al. 2010). Effects of PGPR in alleviating heavy metal stress in various crop plants have been summarized in Table 14.1.

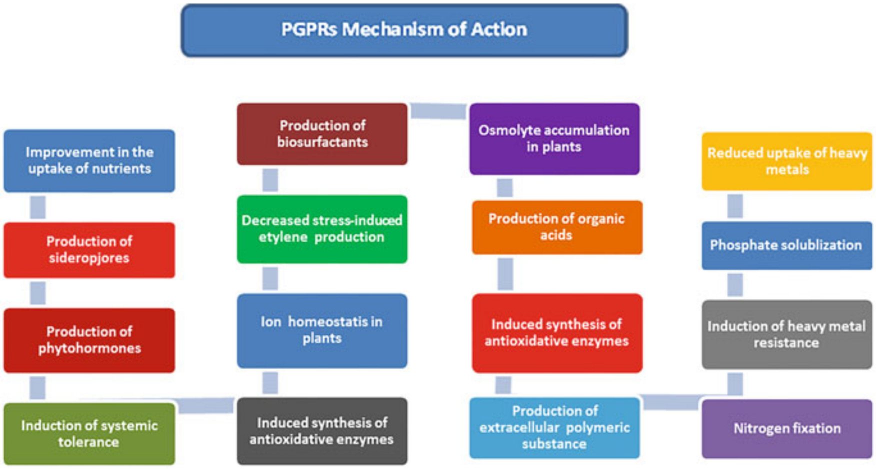

Fig. 14.1 The multiple action mechanisms of PGPR on alleviating heavy metal stress in plants

Numerous heavy metals have different effects on biomass, growth, and development of plants (Ahmad et al. 2012). Cadmium (Cd) is one of the common and dangerous heavy metals because of its high water soluble property (Hassan et al. 2013). Plant development is slowed as the rate of photosynthesis and transpiration is reduced due to Cd stress (Lamoreaux and Chaney 1978). Furthermore, in plants, Cd can cause ethylene buildup (Hassan et al. 2016), chlorosis, lipid membrane instability (Khan and Lee 2013), changes in membrane permeability, and water imbalance (Hassan et al. 2016; Azevedo et al. 2012). Excessive Cd absorption might also result in nutritional imbalances (Khanmirzaei et al. 2013; Greger et al. 1991; Dong et al. 2006; Larbi et al. 2002). Because of the inverse relationship of cadmium (Cd) with iron (Fe) in terms of bioavailability to plants, most plants become iron (Fe) deficient. It also reduces potassium and magnesium bioavailability in plants (Dong et al. 2006; Larbi et al. 2002; Greger et al. 1991).

Understanding the reaction of wheat to Cd stress and how to regulate it in order to limit Cd intake and increasing concentration in wheat may aid in improving grain quality and wheat growth. Wheat can be made more resistant to Cd stress by using exogenous microorganisms. Cd-tolerant bacteria isolated from rhizospheric soil containing tannery effluent lower oxidative stress in cadmium-exposed wheat plantlings by improving plant development, weight, and relative water content (Ahmad et al. 2015). However, bacterial strains' response to Cd stress differs in terms of decreasing Cd intake and increasing wheat growth. Another study found that applying arbuscular mycorrhizal fungi and root endophytes to Cd-exposed wheat enhanced chlorophyll content, growth, and Cd in roots but decreased Cd in shoots, particularly at greater Cd concentrations (Shahabivand et al. 2012). It is generally known that Cd toxicity inhibits root and shoot growth and also affects plant homeostasis and nutrient uptake (Fiaz et al. 2014; Sanita di Toppi and Gabbrielli 1999). Abiotic stress generally increases the amount of ethylene

Table 14.1 Effects of PGPR in alleviating heavy metal stress in different crop plants

PGPR used	Plant	Alleviated heavy metal stress	Effects	References
Azotobacter and *Azospirillum*	Bread wheat	Reduced Pb content	Improved growth and physiological processes	Janmohammadi et al. (2013)
Bacillus cereus	*Trifolium repens*	Improved heavy metal toxicity of Fe, Mn, Zn, and Cd	IAA production and improved plant biomass by increasing P, N, and K acquirement in plants and requisition of heavy metals	Azcón et al. (2010)
Serratia sp.	*Lupinus luteus*	Improved metal toxicity of Cd, As, and Cu	Enhanced plant resistance to metals by decreasing transformation of heavy metals from roots to shoots	Aafi et al. (2012)
Bacillus sp.	*Solanum nigrum*	Reduced Cd phytotoxicity	IAA synthesis, siderophore generation, and ACC deaminase activity	Luo et al. (2011)
Bacillus sp.	*Brassica napus*	Improved metal toxicity of Pb, Cd, and Zn	Enhanced metal toxicity via bioabsorption	Ma et al. (2015)
Ralstonia eutropha	*Zea mays*	Improved heavy metal toxicity of Cd	Reduced metal buildup in plants due to heavy metal restriction and low translocation to shoots	Moreira et al. (2014)
P. aeruginosa	*Chickpea*	Improved heavy metal toxicity of Cr	Reduced metal uptake by reducing Cr^{6+} to Cr^{3+} in the soil	Oves et al. (2013)
Rahnella aquatilis and *Enterobacter aerogenes*	*Brassica juncea*	Declined the toxicity of Cr and Ni	Increased plant growth and development	Kumar et al. (2009)

production in higher plants, which has a harmful effect on growth characteristics (Glick 2014). Under varied levels of Cd toxicity, an enhancement in the basic structural parameters of growth of wheat plants (shoot and root length, shoot and root dry and fresh weight) could be because of decline in ethylene production (Zafar-ul-Hye et al. 2014; Salehuzzaman et al. 1998; Ganesan 2008). Growth-promoting rhizobacteria like *Stenotrophomonas maltophilia* and *Agrobacterium fabrum* help in mitigating Cd-induced stress in wheat plantlings. The inoculation of seeds with ACC deaminase containing PGPR *Agrobacterium fabrum* and *Stenotrophomonas maltophilia* could increase wheat development under Cd toxicity and results in lower Cd levels in their roots and shoots. Both strains are able to inhibit Cd uptake in wheat plants (Zafar-ul-Hye et al. 2018).

Chromium (Cr) is a dangerous heavy metal that poses negative impact on living beings. It is mostly released into the soil because of various industrial operations

(Zeng et al. 2020). Cr is widely utilized in industry, and its release into the surroundings is hazardous because of its higher toxicity and quick buildup in soils (Ashfaque et al. 2017). The compounds of chromium (Cr) are widely used in a variety of sectors, including electroplating, metallurgy, tanning, wood chemical manufacturing, pigment and paint manufacturing, paper and pulp manufacturing, and preservation; hence it is also released as an environmental pollutant (Zayed and Terry 2003). Chromium contamination in soil is increasing as a result of the usage of industrial effluents and wastewater as irrigation source for crop cultivation, primarily in metropolitan areas (Mushtaq and Khan 2010). Chromium's toxicity is greatly reliant on its oxidation state. Chromium is found mostly in soils in the most stable forms of Cr^{6+} and Cr^{3+}. Cr^{3+} is thought to be less harmful than bioavailable Cr^{6+} compounds such as dichromate ($Cr_2O_7{}^{-2}$) and chromate ($CrO_4{}^{-2}$) which are very toxic and have been proved to be carcinogenic and mutagenic (Messer et al. 2006; Srivastava et al. 1999). Low Cr^{6+} concentrations cause interveinal chlorosis in immature leaves, which progresses to necrosis at later growth stages. Cr^{6+} reduces root length, seedling growth, total chlorophyll content in shoots, shoot length, transpiration rates, net photosynthesis rates, and stomatal conductance in wheat (Dey et al. 2009). Cr^{6+} treatment in wheat has shown considerable impact on the enzymatic activities of superoxide dismutase, catalase ascorbate peroxidase, and glutathione reductase (Subrahmanyam 2008). A study by Sharma et al. (1995) has shown that wheat grain yield was greatly impacted by chromium supply. Different physicochemical and biological techniques can be used to reduce hazardous effects of chromium on plants. To reduce chromium toxic effects on plants, among the major cheap and environmentally acceptable biological approach is to use plant growth-promoting rhizobacteria (Khan et al. 2012a, b). Inoculation with bacteria capable of surviving Cr^{6+} stress and converting Cr^{6+} to Cr^{3+} may be very advantageous in developing plant growth in chromium-polluted soil, possibly through various complex procedure of increase in plant growth, particularly formation of growth regulator and controlling stress-led physiological functions of plants (Khanmirzaei et al. 2013). Cr^{6+} reduction may occur for a variety of reasons, including intracellular mechanisms involved in Cr^{6+} detoxification, the interaction of chromate in intracellular metabolic activities as a final electron acceptor for attainment of energy (Wani et al. 2007), and the efflux of waste byproducts by bacteria that reduce Cr^{6+} into Cr^{3+} (Fude et al. 1994). The enzymatic activities of bacterial isolates could also be responsible for the reduction (Cheung and Gu 2003). According to Mistry et al. (2009), the chromium-resistant bacterial strain *Pseudomonas oleovorans* was capable of converting Cr^{6+} to Cr^{3+}, and it was also discovered that this bacterium could bioremediate Cr^{6+} comprising waste material. Morales et al. (2007) discovered *Streptomyces* species which were Cr^{6+} tolerant and capable of converting Cr^{6+} to Cr^{3+}. This could be a natural reaction of plants against toxicity, or it could be because of Cr^{6+} immobilization in root cell vacuoles resulting in increased accumulation in roots (Shanker et al. 2004). The absorption and movement of Cr^{6+} from soil to aerial and root portions of the plant were reduced after wheat seeds were inoculated with Cr^{6+}-resistant bacterial isolates. This drop in Cr^{6+} concentration in wheat plant roots and shoots could be due to bacterial isolates converting Cr^{6+} to Cr^{3+} (III), lowering Cr^{6+} levels in soil (Salunkhe et al. 1998). Wheat plants inoculated with *Pseudomonas* species reduced chromium absorption and concentration in the shoot and root system (Hasnain and Sabri 1997). After harvesting the wheat crop, the Cr^{6+} content in the soil declined dramatically from the original Cr^{6+} concentration. This decrease could be attributed to the uptake and concentration of Cr^{6+} levels in the wheat plant's shoot and root system (Mishra et al. 1997), as well as bacterial isolates converting Cr^{6+} to Cr^{3+} (Salunkhe et al. 1998; Cheung and Gu 2003).

Wheat stems accumulate the maximum levels of Cr followed by leaves and grains (Awan et al. 2019). As per the research, enhanced heavy metal concentration in plant tissues has become a major contributor to food chain impurity, which can induce major disorders in living systems (Abbas et al. 2017). Crops may also be able to lower Cr levels from Cr^{6+} to Cr^{3+}. As a detoxifying mechanism, this reduction process is expected to occur in roots (Lytle et al. 1998). Toxic metal-contaminated areas are treated using various remediation approaches. Microorganisms have the capability to change their gene sequences in response to changes in their environment (Ryan et al. 2009), and chromium-reducing bacteria can alleviate Cr toxicity in the rhizosphere by converting Cr^{6+} to Cr^{3+} via bioaccumulation and biosorption processes (Mishra and Bharagava 2015). *Staphylococcus aureus* is a round-shaped, Gram-positive facultative anaerobic microbe that forms a biofilm on surfaces and develops in clusters. It can grow at temperatures ranging from 7 to 48 °C with 37 °C being the ideal temperature for its proper growth (Wirtanen and Salo 2016). It was identified as a chromium-reducing bacterium after being isolated from tannery effluent. Phytoremediation combined with Cr-tolerant bacteria for Cr^{6+} reclamation has been contemplated as an effective, safe, and economical alternative to traditional methods (Ahemad 2015; Jing et al. 2013). The *Staphylococcus aureus* strain aids in alleviating Cr stress in wheat plants by enhancing antioxidant enzymatic activities and declining oxidative stress through Cr transformation from Cr^{6+} to Cr^{3+} and biosorption (Zeng et al. 2020).

Industrialization has resulted in an increase in heavy metal pollution of agricultural soils. Mercury is a very dangerous heavy metal that has become a widespread contaminant because of industrial contamination, which has resulted in its deposition in the ecosystem (Gontia-Mishra et al. 2016). Industries related to pulp and paper, paints, disinfectants, bactericidal agents, medicines, and fungicides are few examples of anthropogenic sources of mercury. Mercury is also released into the atmosphere by mercury mining, gold smelting, fuel burning, and instrument production (Moreno et al. 2008). It's a big environmental contaminant that's categorized as a bioaccumulative toxin, meaning it lasts a long time in the environment (Dash and Das 2012). It has put plants, animals, and humans in grave danger (Patra et al. 2004; Bridges and Zalups 2004). Mercury exposure has an impact on development and growth in plants at all stages. It results irregular germination, inhibits photosynthesis, lowers biomass output, disrupts water uptake, and interferes with protein function (Patra and Sharma 2000). Mercury discharged into the soil is found to be mostly in the solid phase due to adsorption onto sulphides, soil particles, and organic compounds. The ionic state of mercury (Hg^{2+}) is the most common in agricultural soils (Han and Supanjani Lee 2006). Because mercury is mostly employed in fertilizers and herbicides, its interaction with plant systems is critical (Liu et al. 2010). Mercury resistance is found in a wide variety of microbes (bacteria) isolated from mercury-polluted environments and the rhizospheres of numerous plants (De et al. 2008; Abou-Shanab et al. 2007; Ruiz-Diez et al. 2012). Under metal stress, two bacterial strains, *Klebsiella pneumoniae* and *Enterobacter ludwigii*, supported the growth of wheat seedlings (Gontia-Mishra et al. 2016). These considerably promote longer roots and shoots, increased dry weight of root and shoot, and increase in relative water content. It is reasonable to conclude that all of these factors combined in presence of PGPR promote plant growth and development under mercury stress (Gontia-Mishra et al. 2016). As a result, these PGPR could be viable candidates for enhancing plant growth as well as bioremediation of mercury-contaminated soils. Mercury is known to interact with electron transport chain in chloroplasts, which affects oxidative metabolism and photosynthesis. Chlorophyll accumulation is reduced during heavy metal exposure because of interaction with chlorophyll synthesis process (Sharma et al. 2010). Furthermore, the involvement of PGPR enhanced chlorophyll content and reversed losses caused by metal stress. It's worth noting that the PGPR enhances protein content of plants developing under mercury stress. These proteins might have a direct link to metal resistance. Metal stress damages cell membrane in plants, resulting in an increase in membrane permeability. As a result, the electrolytes in the cell membrane pass out and concentrate in the tissues around it (Zhou et al. 2009). Under mercury stress, PGPR-inoculated plants showed lower electrolyte outflow from shoot tissue of wheat plants, implying that PGPR protected the integrity of cell membranes from the detrimental effects of mercury (Iti Gontia-Mishra et al. 2016).

In some areas, iron poisoning has become a problem for wheat as wheat cannot withstand high levels of iron, especially in acidic soils. Excess iron poses a threat to plant growth in Asia, Africa, and South America's wet tropical regions, where soils are often acidified or flooded (Khabaz-Saberi et al. 2010; Guo et al. 2010). Iron toxicity has been witnessed in wheat shoot tissues, and it was observed that there is a substantial contradictory association between iron accumulation and shoot dry weight in wheat plants (Khabaz-Saberi et al. 2010; Setter et al. 2008). In addition, excess iron reduces shoot and root elongation, as well as affects wheat grain production adversely (Khabaz-Saberi et al. 2012; Kumar et al. 2017). Iron transport in wheat-related PGPR could be categorized in two categories based on the types of substrate: organic iron and inorganic iron. The first category comprises of carbonyl iron, dissociative Fe^{2+}, and Fe^{3+} compound, while the second category includes siderophores and ferric citrate. Many bacteria in soils rely on the production of siderophores and on the absorption of mixed organic iron compounds (Fukushima et al. 2013). As a result, the development of a siderophore-dependent organic iron uptake system could establish competitiveness at the time of bacteria-wheat communism and is significant for its plant growth-promoting characteristics. Bacillibactin is a widely known siderophore of bacilli, which are prominent to wheat-linked PGPR, and its production requires the involvement of adenosine vinyltransferase. However, many *Bacillus* species have altered this gene over time and now only create a pro-bacteriocin precursor which has enough affinity for Fe^{3+} (Segond et al. 2014). Regardless of the fact that siderophore productions have been reported in *Bacillus* species and in another PGPR strain *Paenibacillus* species, genomics investigation has revealed that siderophore production gene group is present only in a few species (Hertlein et al. 2014; Raza and Shen 2010). Wheat grain production is likewise harmed by too much iron content (Khabaz-Saberi et al. 2012). In soils heavy metal phytoextraction is thought to be aided by siderophore-producing microorganisms (Yue et al. 2020). To control the wide availability of iron in plant rhizospheres, metal chelating agents such as microbial siderophores were used (Sharma et al. 2015). Sun et al. (2017) had separated a number of endophytic bacteria from wheat roots; *B. altitudinis* one of the isolated strains has strong potential of absorbing iron and enhances iron resistance in wheat by enhancing the expression of ferritin-encoding genes. The bacteria strain produces siderophores and IAA and has enough phytase and 1-aminocyclopropane-1-carboxylate deaminase activity (Yue et al. 2020). The Pb and Co concentrations of soil and plant parts are significantly reduced by injection of PGPR without or with carrier materials. The reductions in heavy metal concentration in plant root system imply that excess heavy metals were fixed in cell walls or structured into vacuoles (Sofia et al. 2012). *B. cereus* strain and certain other bio-inoculants were also noted to decline the Cd and Ni toxicity (Madhaiyan et al. 2007; Zaidi et al. 2006; Ma et al. 2009). Wheat leaves with *Pseudomonas putida* have been found to have lower Cd, Cr, and Ni levels (Weyens et al. 2015). Treatments with PGPR accelerated root exudation, phytoremediation potential, and mutually supportive root connection, which together enhanced heavy metal bioavailability (Jing et al. 2007). Resistance to heavy metals is linked to the exudation of acids (malate) in the wheat roots (Yang et al. 2013).

Plant nutrition is promoted by plant growth-promoting rhizobacteria because they aid in fixing nitrogen and dissolve phosphorus (Richardson et al. 2009). Through epiphytic or symbiotic connections, certain PGPR inhibit infections and create a variety of metabolites (Masum et al. 2018; Lee et al. 2018). Furthermore, the ACC deaminase enzyme can impact plant growth by supplying plant hormones like indole acetic acid (IAA) or lowering ethylene synthesis (Glick 2014). PGPR strains are resistant to the deleterious impacts of heavy metals on plants growing in metal-polluted soils (Long et al. 2013) and have a favourable influence on plant growth. By synthesizing ACC deaminase and the modification of hormone levels, PGPR strains improve plant growth by providing a suitable nutrient (P, Fe, N, and K) to their host plants. Moreover, they control plant growth under heavy metal stress by creating chelating agents, an expanded root system, stress-induced resistance to abiotic stress, and enhanced bioavailability of critical nutrients through direct or indirect mechanisms. PGPR strains also influence the development of related microorganisms in soils by creation of biofilms (Bhattacharyya and Jha 2012; Ma et al. 2016a, b). These stress-tolerant PGPR strains will be highly valuable in the rehabilitation of metal-contaminated soils because of this mechanistic approach. PGPR inoculation considerably improved nutrient uptake under abiotic stress by promoting root elongation (Safronova et al. 2006). It has also been illustrated that

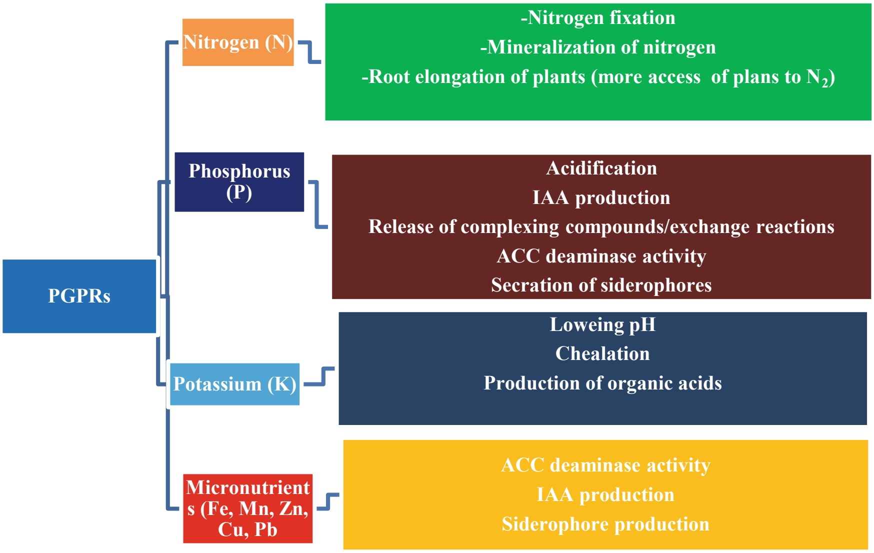

Fig. 14.2 Action mechanism of PGPR in increasing nutritional status under heavy metal stress

injecting plants with beneficial microorganisms reduces heavy metal toxicity by enhancing the activity of antioxidant enzymes (Pérez-Montaño et al. 2014). There was a considerable increase in chlorophyll b, chlorophyll a, and total chlorophyll synthesis. Excess chromium in soil inhibits growth of plants because of Cr toxicity, and this chromium-induced growth retardation has been documented in a variety of plant species (Sharma and Sharma 1996; Bishnoi et al. 1993). Greater concentrations of Cr^{6+} have an adverse impact on root function and growth causing damage of roots, decline in dry and fresh weight, and a reduction in water and nutrient uptake (Terry and Banuelos 2000). Infection of wheat seeds with Cr^{6+} resistance bacterial isolates increased plant health under Cr^{6+} stress and improved all development indices of wheat. Seed inoculation with Cr^{6+}-tolerant rhizobacterial isolates promoted plant yield and health. Several studies have found that rhizosphere bacteria help plants grow and develop in stressful situations (Jacobson et al. 1994; Glick et al. 1998; Gupta et al. 2002). By recycling organic waste, rhizobacteria that promote plant development also improve nutrient availability (Asghar et al. 2006). Plant growth-boosting bacteria *Rahnella aquatilis* and *Enterobacter aerogenes* have been shown to decrease the toxicity of Cr and Ni in Indian mustard (*Brassica juncea*) and improved plant development (Kumar et al. 2009). The favourable effects of *Azotobacter* and *Azospirillum* have the potential to lower Pb concentration and increase wheat development and physiological responses (Janmohammadi et al. 2013). When plants were exposed to various hazardous metals, bio-inoculants increased growth, chlorophyll biosynthesis, and metabolic activities (Gupta et al. 2007; Ganesan 2008) (Fig. 14.2).

14.3 Role of Phenolics in Alleviating Metal Toxicity and Enhancing Nutritional Status in Wheat

In plants secondary metabolites are key chemicals for reacting to stressful conditions and assisting plants in adapting to distinct ecological conditions at various phases of development (Pichersky and Lewinsohn 2011; Boettcher et al. 2014). Secondary metabolite biosynthesis and accumulation rise significantly under stress like a method of adapting to severe situations. This shows a strong relationship among secondary metabolite synthesis and stress resistance capabilities of plants (Kaur and Ganjewala 2019). Phenolic substances are a type of secondary metabolite found in plants that serve significant biological functions all through the life cycle of plants (Sharma et al. 2019). Phenols, one of the main three types of secondary metabolites generated in plants, have been divided into the subcategories, namely, lignins, coumarins, phenolic acids, flavonoids, and tannins (Gumul et al. 2007). Plants synthesize phenols under ideal and inadequate circumstances, and they play important functions in physiological mechanisms such as cell proliferation, hormone control, photosynthesis, reproduction, and nutrient assimilation (Sharma et al. 2019). Phenolic aggregation in plants is a continuous characteristic of plants during stress, and it serves as a protective process to deal with a variety of abiotic challenges (Cheynier et al. 2013). Phenolics are important family of aromatic plant secondary metabolites that have redox characteristics and might operate as promising antioxidants during stress circumstances (Vallverdú-Queralt et al. 2014). Phenolic chemicals have been demonstrated to be beneficial in protecting living organisms from several oxidative stressors, serving an important part in regulating redox homeostasis, and providing prospective strategies for enhancing plant's resistance to stress (Kiani et al. 2021). Plant cells produce a variety of phenolic chemicals as nonenzymatic reduced molecular mass antioxidants that help in the removal of reactive oxygen species (ROS) (Hodaei et al. 2018). Phenolic chemicals in plants are produced biosynthetically via a shikimate/phenylpropanoid mechanism, while terpenoids are produced via a mevalonate mechanism (Sharma et al. 2019). The phenylpropanoid system that is required for the manufacture of numerous phenolic metabolites like phenolic acids, rosmarinic acids, lignins, phytoalexins, and flavonoids begins with phenylalanine (Ali et al. 2006). Phenolics containing an aromatic ring(s) generated in a broad range of plants are created from the phenylalanine amino acid using the L-phenylalanine ammonium lyase (PAL) (Colaka et al. 2019). Erythrose 4-phosphate is coupled with phosphoenolpyruvate (PEP) amid the production of phenolic chemicals to produce phenylalanine. The reaction is subsequently catalysed by phenylalanine ammonia lyase (PAL), which converts phenylalanine to trans-cinnamic acid. This process, technically termed as the phenylpropanoid route, produces a variety of different phenolic components including lignans, flavonoids, hydrolysable tannins, coumarins, monolignols, and lignins (Lattanzio 2013; Cheynier et al. 2013; Saltveit 2010; Naikoo et al. 2019). Phenolic compounds, because of carboxyl and hydroxyl groups, are able to chelate heavy metals, eliminating ROS and preventing peroxidation induced by ROS and heavy metals (Michalak 2006). Metal stress resistance in plants could be enhanced by altering secondary metabolite production and aggregation (Anjitha et al. 2021). Plants use phenolic chemicals for a variety of purposes, and variations in the quantities of phenolic substances have been observed during various environmental and stress circumstances (Sanal 2019). Plants that thrive in stressed circumstances can synthesize higher phenolic substances than plants that grow in ideal circumstances (Selmar 2008). Whenever plants are wounded or diseased, as well as under extreme circumstances like poor nutrition, cold temperature, or heavy metal toxicity, isoflavones and certain related flavonoids are activated (Sanal 2019). However, increased phenolic production in plants during metal toxicity helps in the prevention of plants against peroxidation (Kohli et al. 2018). Many flavonoids have been shown to defend against heavy metal toxicity by transitional chelation of metals (e.g. Fe, Zn, Ni, Cu) that creates hydroxyl radicals through Fenton's reaction (Mira et al. 2002; Williams et al. 2004), and this is consistent with the discovery that metal overload enhances the concentrations of plants' flavonoid (Kaur et al. 2017; Handa et al. 2018). Certain ions of heavy metals could be chelated by anthocyanins, limiting oxidative stress and toxic heavy metal ion transfer (Landi 2015). Under mild Cd toxicity, anthocyanins in the wheat seedlings' coleoptiles were found to have a preventive effect (Shoeva and Khlestkina 2018). Anthocyanin concentration in the cv. 'Saratovskaya 29' coleoptile increased with brief cadmium therapy of wheat seedlings (Tereshchenko et al. 2012). A secondary metabolite, SA (salicylic acid) which is a phenolic molecule generated by plants, regulates various biological functions and the stimulation of plant immunity (Venkatesh and Park 2014; Kovács et al. 2014; Rahmani et al. 2015). SA-boosted biological activities explicitly or implicitly assist wheat crops in overcoming the oxidative harm inflicted by Pb poisoning. External administration of SA has also been shown to benefit proliferation and maturity of wheat plants by mitigating the negative impact of excessive metal toxicity (Alamri et al. 2018). Carotenoids are low molecular mass lipophilic chemicals that function as antioxidants and perform an important role in reducing ROS levels (Sytar et al. 2013). Apart from that, they function as a signalling molecule, detecting environmental stimuli and communicating those towards the plants (Li et al. 2008). Phenolic acids, alkylresorcinols, and flavonoids are all examples of phenolic compounds in wheat. Several phenolic acids found in wheat flour and wheat bran include caffeic acid, ferulic acid (the primary wheat phenolic acid), sinapic acid, vanillic acid, protocatechuic acid, p-hydroxybenzoic acids, syringic acid, and p-coumaric acid (Piironen et al. 2013). Ferulic acid, the primary phenolic acid found in wheat, seems to have a significant level of antioxidant potential (Khan and Shewry 2009). Ferulic acid is the most extensive phenolic component in wheat grains. There are soluble-conjugated and free ferulic acids found in wheat. Anti-inflammatory and antioxidant activities are thought to be specific to conjugated phenolics (Ma et al. 2016a, b). The primary phenolic acids (PAs) in roots included p-coumaric, syringic, and ferulic acids in free, ester, glycoside, and ester-bound states, and their contents were significantly raised by heavy metal applications exclusively in contrast to untreated seedlings in wheat (Colaka et al. 2019). The capability of phenolics to assimilate metals contributes to their antioxidant activity. Phenolics have carboxyl and hydroxyl units that can trap iron and copper in particular (Jung et al. 2003a). These electron-donating molecules, singlet oxygen quenchers, and hydrogen donors operate as antioxidants and stop the formation of reactive oxygen species (Jung et al. 2003b). As a result, metal ion chelation with phenols allows for metal ion immobilization and decreased absorption by aerial plant organs (Anjitha et al. 2021). The synthesis of phenolics has been observed to be increased in wheat plants by nickel poisoning, in the maize plant by aluminium intoxication, and in the bean plant by cadmium toxicity. Modifications in phenolics biosynthesis are considered to happen because of conjugate hydrolysis during heavy metal exposure. It is claimed that an elevation in soluble phenolics is required for the creation of a structural obstacles that prohibit heavy metal entrance through the cell via enhancing cell membrane resilience (Bubna et al. 2011). During a study by Colaka et al. (2019), total phenolic content (TPC) values have been observed to rise in reaction to heavy metal exposure (Cu, Hg, Cd, and Pb). Rozylo et al. (2017) during their study concluded that enhanced accumulation of phenolics (cross-talk reaction to stress events) in wheat was induced by the activation of plant's inherent tolerance by certain sludge constituents, particularly Pb^{2+} and Cd^{2+}. Phenolic molecules are certainly among the most important and dynamic plant ligands. Plant cells additionally chelate and retain heavy metals via cell surface or free phenolics, and heavy metal movement across cell wall to cytosol, as well as root to shoot and also grain, is reduced (Michalak 2006). The aggregation of phenolics is caused by the activation of phenylpropanoid cascade enzymes such as cinnamyl alcohol dehydrogenase, shikimate dehydrogenase, polyphenol oxidase, glucose-6-phosphate dehydrogenase (G6PDH), chalcone synthase, and phenylalanine ammonia-lyase (Zafari et al. 2016; Chen et al. 2019). This, in fact, is reliant on the modification of transcriptional activity of genes that encode metabolic enzymes in the presence of metal toxicity (Handa et al. 2019; Leng et al. 2015). In stress response, mRNAs expressing 3-deoxy-arabino-heptulosonate 7-phosphate synthase, a shikimate network enzyme, essential for phenylalanine production and G6PDH, a carbohydrate biosynthesis enzyme which supplies shikimate network substrates, were strongly stimulated (Cheynier et al. 2013). Furthermore, polyphenol oxidase (PPO) aids in the mechanism of ROS elimination and increases a plant's resilience to environmental stress situations such as heavy metals (Mishra and Sangwan 2019; Mishra et al. 2014). Glucose-6-phosphate dehydrogenase (G6PDH) and shikimate dehydrogenase (SKDH) are two key enzymes that catalyse the biological process necessary for the formation of phenylpropanoid mechanism intermediates (Kovácik et al. 2009). Cinnamyl alcohol dehydrogenase (CADH) is another enzyme that catalyses metabolic events that create substrates for lignin formation (Mishra and Sangwan 2019).

Secondary compounds have attracted considerable interest from researchers owing to its ethnomedicinal potential, besides assisting plants to tolerate environmental stressors (Davis and Milner 2009; Liu 2013; Arcanjo et al. 2018). Nutritive benefits of wheat, high in secondary compounds, too have gotten considerable emphasis. Wheat is among the globe's three primary agricultural crops, as well as a good dietary fibre (DF) supplier for man (Shewry and Hey 2015; Islam et al. 2020). The phenolics can be linked, free, or insoluble attached configuration (Andersson et al. 2014), but around 95% of cereal phenolics (PC) are ester- or ether-linked to cell wall polysaccharides and bridge them intra- and/or structural configuration to create networks. They're also referred to as dietary fibre-phenolic compounds (DF-PC) (Vitaglione et al. 2008). DF may increase intestinal muscular contractions, which is good for health (Anderson et al. 2009), and it also affects metabolic activities (Palafox-Carlos et al. 2011). According to a new study, phenolics along with fibre could be accountable to most of the nutritional benefits of whole cereals (Marín et al. 2018; Sevgi et al. 2015; Tomas-Barberan and Andres-Lacueva 2012; Zeng et al. 2016), and other constituents represent around one-third of our overall phenolic consumption (Parada and Aguilera 2007). The occurrence of phytonutrients in wheat, such as vitamin E, carotenoids, polyphenols, and lignans, contributes to the nutrition benefits of whole grain or whole flour foods (Berger et al. 2005). Wheat (*Triticum aestivum* L.) is a good provider of hydrophilic vitamins, proteins, minerals, and fibre (Liu et al. 2012). The germ, endosperm, and bran are the three primary components of a wheat seed. The bran, the outermost part, is made of B vitamins, antioxidants, fibres (50%), and minerals (50–80%) consisting of magnesium, zinc, copper, and iron (Sramková et al. 2009). Wheat is also an excellent provider of fibre, protein, and carbs, as evidenced by past research (Shewry et al. 2013). The aleurone and germ layers constitute 30% of the total protein, while the pericarp includes 10% of the entire protein. Despite the significant protein concentration of germ and aleurone components of wheat, the proportion of endosperm to overall kernel protein level is considerably larger, around 74% (Brouns et al. 2012). Cereal bran is high in phenolic antioxidants, minerals, and fibres, but aleurone is a crucial element that is often disregarded in favour of non-digestible fibre. Nevertheless, it has the greatest number of bioactive chemicals with substantial antioxidant capacity (Laddomada et al. 2015), especially ferulic acid serving as the primary antioxidant (Lillioja et al. 2013). Secondary metabolites can influence the behaviour of essential substances in plants (Hu et al. 2018). The overexpression or downregulation of various chelating compounds might result in variations in trace component levels (Baxter and Dilkes 2012). Microelement stabilization is critical for development of plant, and the interplay among ROS and microelements has already been explored (Chen et al. 2015). Variations in trace minerals also have an impact on wheat's nutrient content. Conversely, there is a scarcity of evidence on the reactions of secondary metabolism and nutrition to environmental stress (Bao et al. 2021). Phenolics boost absorption of nutrients by chelating metals, increasing functional uptake areas, and increasing soil permeability, resulting in faster mobilization of elements such as iron (Fe), manganese (Mn), potassium (K), calcium (Ca), zinc (Zn), and magnesium (Mg) (Seneviratne and Jayasinghearachchi 2003). Wheat polyphenol contents are greatest in the testa, aleurone, and pericarp regions. So far, numerous studies have been undertaken to demonstrate the wheat polyphenols and their capacity to prevent oxidative stress illness (Habauzit and Morand 2012). Whole wheat contains phenols, which can serve as antioxidants or antibiotics (Poudel and Bhatta 2017). Phenolic substances of wheat are classified as hydroxycinnamic acid or hydroxybenzoic acid equivalents. Diverse chemicals are found in derivatives of hydroxybenzoic acid, such as syringic, vanillic, hydroxybenzoic, p-coumaric, and gallic acids, while hydroxycinnamic acids include various derivatives, like dehydrodimers, ferulic acid, dehydrotrimers of ferulic acid, and p-coumaric acids (Barron et al. 2007; Antoine et al. 2004). The antioxidant potential of wheat grain segments is inversely linked to the aleurone level given the significant quantity of hydroxycinnamic acids, ferulic acid being the most important (Calinoiu and Vodnar 2018). Cinnamic acids have been classified as biologically active dietary components since these are linked to cell wall structural constituents (Wang et al. 2014a, b; Shahidi and Chandrasekara 2010). Ferulic acid (4-hydroxy-3-methoxycinnamic acid) is found in many components of fruits, grains, and vegetables, and it also supports health-improving viewpoints (Kandil et al. 2012; Guo and Beta 2013). Ferulic acid's bioavailability in cereals is restricted because of its tight border with non-digestible components of cell wall (Calinoiu and Vodnar 2018). High diversity in flavonoids and phenolics was discovered among wheat varieties; hence, selecting wheat varieties with greater amounts of phenolic acids might be a viable way of having a favourable effect on human health (Dicko et al. 2005). The existence of phenolics and their relationship to antioxidant properties might aid in the creation of cereal-based nutritious products (Pang et al. 2018). Phenolic molecules have a sensitive reaction to nutrient insufficiency, which helps identify nutritional problems before obvious symptoms develop. Deficits in N, S, P, and K typically lead to higher amounts of phenolic chemicals, whereas plentiful N prevents phenolic synthesis (Gershenzon 1913; McClue 1977).

14.4 Interactive Role of Phenolics and PGPR

Plants communicate through secondary metabolites with their surroundings (Sharma et al. 2019). Plant roots communicate with a community of soil microorganisms within the rhizosphere. Root-linked rhizobacterial populations perform a vital function in maintaining plant viability during abiotic stressors (Khan et al. 2021). Plant roots create a variety of organic chemicals exuded as secretions and recruit soil bacteria such as PGPR, which are an effective provider of carbon within soil (Pothier et al. 2007; Drogue et al. 2013). The beneficial "rhizosphere effect" could also impact microbial populations in bulk soil near roots, causing a comprehensive increase in soil fertility (Caracciolo et al. 2020). Modification in root exudation (time, quantity, and/or contents) offers a method via which the soil physicochemical characteristics are adjusted by plants, as a result, modifying the composition of microbial diversity just at the root interface (Bechtold and Field 2018; Yang et al. 2009; Backer et al. 2018). This robust rhizosphere-rhizobacterial association protects root secretions that include a variety of chemical substances that recruit microorganisms to the root's proximity (el Zahar Haichar et al. 2014; Semchenko et al. 2014). Rhizomicrobiome microorganisms have essential functions in nutrient absorption and processing, better soil characteristics, secreting and modifying extracellular compounds like hormones, secondary metabolites, antibiotics, and other signal chemicals, all of which contribute to increased plant development (Backer et al. 2018). Plant development is dependent on the availability of nutrients that are recyclable. External availability of nutrients and soil microorganism nutrient metabolism contribute to nutrient demand (Naikoo et al. 2019). PGPR promote plant development and yield by improving root development and therefore enhancing the availability of micronutrients to the host plant roots (Khan et al. 2020). Such microbes have the capability to modify the production of plant compounds and increase their carbohydrate, photosynthetic, and protein levels, hence increasing yield-associated characteristics during stress (Ismail et al. 2021). They promote plant development by increasing water and nutrient intake from the ground, especially in demanding conditions (Ahkami et al. 2017). Root exudates aid plants in nutrient acquisition through acidifying or altering the redox state of nutrients found in the rhizosphere (Badri and Vivanco 2009). Exudates are considered to be primarily composed of organic acids, sugars, and amino acids, which are abundant in the plant's cytoplasm, but they also contain trace quantities of intricate secondary metabolites like phenols, flavonoids, and terpenes, which could attract particular microbes in the rhizosphere (Jones et al. 2004; Bais et al. 2006; Musilova et al. 2016). The accessibility of nutrients does have an important impact on exudates of root and plant needs nutrient components to thrive normally. Plants react to nutrient limitation by changing root secretions, which alters the rhizosphere's microenvironment (Lareen et al. 2016). The most significant nutrients of plant are phosphorus and nitrogen. Plants modify root exudates to guarantee phosphorous and nitrogen accessibility. They may absorb nitrogen as NO^{3-} and NH^{4+} ions as well as modify root secretions based on the type of N accessible in rhizosphere (McNear Jr 2013; Liu et al. 2016). The organic acids are more significant of such root secretions; they also serve as the basis of energy supporting microbial-cellular activity and also as intermediate chemicals in biogeochemical cyclic processes occurring inside the rhizosphere (Yang et al. 2013; Wu et al. 2013). Root secretions can operate as electron donors, and several substances could be utilized to eliminate heavy metals via bacteria which reduce metals (Simon et al. 2019). Organic acids influence a number of activities inside the soil's rhizosphere, including but not restricted to metal elimination, plant development control, and nutrient absorption out of the soil (Lu et al. 2007). Organic acids also have an effect on the soil structure, enhancing heavy metal dissociation (Asad et al. 2019). Exploring microorganism tolerance pathways and their interactions with plants could lead to the development of the highly effective and targeted heavy metal bioremediation solutions for agricultural use (Jin et al. 2018). Secondary metabolites and other complicated pathways are among the resistance strategies that involve a chemical conversation between plants and bacteria. Plants in polluted soils produce variations in microbial populations, boosting biomass, variety, and productivity while also improving decontamination of heavy metals by bacteria (Teijeiro et al. 2020; Sun et al. 2020; Hou et al. 2017; Zeng et al. 2018). Phenolic chemicals produced in the rhizosphere confer metabolic flexibility, which is required for sensing and reacting to abiotic and biotic stresses (Baetz and Martinoia 2014). They are believed to have multipurpose functions inside the rhizosphere, specifically in interactions of plant-microbe (Philippot et al. 2013). Polyphenols are engaged in signalling pathways through the root towards the shoot as well as aid in nutrient mobilization (Sharma et al. 2019). Polyphenols alter the availability and movement of organic and inorganic nutrients of soil accessible to plants and/or microorganisms. Phenolic chemicals enter the soil in the form of leachates from below- as well as above-ground plant components and also inside below- and above-ground plant debris (Hattenschwiler and Vitousek 2000). The exudates from the roots include phenolic chemicals that change rhizosphere's physiological and biochemical characteristics. Soil bacteria convert phenolics into chemicals that aid in the mineralization of nitrogen and the production of humus (Halvorson et al. 2009). Polyphenols influence the organization and function of decomposers, hence regulating disintegration rates and cycling of nutrients (Lattanzio et al. 2006). Rehman et al. (2018a) discovered that Zn administration and PGPR application increased the concentration of phenolics and organic acids (methylmalonic acid, tartaric acid, malic acid, citric acid, succinic acid, malonic acid, oxalic acid, oxaloacetic acid, and pyruvic acid) in root secretions of wheat that aided in the mobilization as well as absorption of Zn, N, and Ca nutrients (Rehman et al. 2018a, b). Phenolic molecules also aid in the fixation of nitrogen in legumes. Legumes produce a number of secondary metabolites via their roots, the most important of which are flavonoids (flavanols and isoflavonoids), that perform an important function in the formation of Nod factors as well as the generation of infection tubes throughout nodulation because they restrict auxin mobility and promote division of cells (Zhang et al. 2009). Bacterial secondary metabolites as well as volatile organic compounds (VOCs) could increase stress resistance and/or promote plant development. Chemicals are discharged via roots into the nearby soil beginning once the seed imbibes and germinates, and once the roots expand and eventually senesce. In the rhizosphere, these chemicals promote functioning of microorganisms and growth (Nelson 2004, 2017; Schiltz et al. 2015). Flavonoids are required for chemical communication between rhizobacteria and mycorrhizal fungus (Tanaka et al. 2015; Del Valle et al. 2020). These operate as chemotactic and have the ability to effectively activate bacterial expression of genes (Ling et al. 2016). Flavonoids are a class of compounds that could exhibit an antibacterial effect on fungal and bacterial infections of root (Cho and lee 2015; Gorniak et al. 2019) as well as help crops survive stress (Caracciolo and Terenzi 2021). Microorganism-to-plant signalling molecules have been proven to boost plant development in a variety of species, especially while plants are developing under extreme stress (Subramanian and Smith 2015; Subramanian et al. 2016; Zipfel and Oldroyd 2017). Certain nutritional components, like Zn and Fe, could have a negative impact on crop production. For example Fe and P may be plentiful in soils yet inaccessible to plants. Organic compounds or siderophores are produced by several bacterial strains to improve Fe accessibility (Ahmed and Holmstrom 2014). Siderophores assist plants not just in delivering critical nutrients (like iron) under stress situations, but additionally in detoxifying heavy metals from the soil (Caracciolo and Terenzi 2021). Low molecular mass organic acids are particularly prevalent in soil naturally, and the root secretions are a key reservoir of their production. Siderophores can also be used to suppress harmful bacteria by denying them of Fe (Saha et al. 2016). Siderophores may attach a variety of metals, including Cd^{+2}, Pb^{+2}, Al^{+3}, Zn^{+2}, Cu^{+2}, and Cr^{+3}. Heavy metal ions are sometimes stored outside of cells (Chen et al. 2017; Saha et al. 2016; Zloch et al. 2016; Sepheri and Khatabi 2021). In some circumstances, like the rhizospheres of metal-accumulating plants, metal mobilization could be improved by siderophores, enhancing plant absorption and aiding in phytoextraction (Grobelak and Hiller 2017; Braud et al. 2009; Ma et al. 2015). Furthermore, PGPR-produced siderophores comprise several chelating functional units (carboxylate, phenolics, and hydroxyl) that combine to iron, thus boosting plant resistance to abiotic or biotic stressors, particularly heavy metal contamination (Rajkumar et al. 2009). Toxic metals inside the rhizosphere have negative impacts on root development (Zia et al. 2020). Lead (Pb) is by far the most common heavy metal, inducing suppression of cell proliferation at the tip of root and fast suppression of root development (Dessaux et al. 2016). Chromium (Cr) poisoning produces chlorosis in early emerging leaves and harms root (Asseng et al. 2011; Boo et al. 2011). Likewise, excessive quantity of cadmium (Cd) inside the rhizosphere produces obvious shoot and root damage, discoloration of root system, and chlorosis in shoots of plant (Sharma et al. 2021; Mommer et al. 2016; Li et al. 2011). During metal contamination, certain compounds are released towards the soil as root secretions, increasing the outer detoxifying methods of metals within plants (Bali et al. 2020). Substances having low molecular mass such as organic acids, phenolics, sugars, amino acids, as well as similar secondary metabolites are included, as are high molecular mass secretions such as proteins and mucilage (Bais et al. 2006). Secretion of such organic compounds in plants could serve as an important resistance strategy against contamination by metals (Montiel-Rozas et al. 2016). Metals are excluded from the rhizosphere or apoplastic region by chelation, preventing their passage through the symplast (Nigam et al. 2001). Metal mobilization inside the rhizosphere is linked to acidification and formation of complexes using organic acids found in secretions (Rengel 2002; Luo et al. 2017). Rhizobacteria are documented to influence the accessibility and mobility of heavy metals through the release of different chelating compounds or through the processes of phosphate dissolution, acidification, and electrochemical reactions, hence increasing heavy metal phytoremediation (Ali et al. 2011). Sulphate-reducing microorganisms may transform sulphate to hydrogen sulphate that subsequently interacts with toxic metals, converting these to impenetrable metal sulphides (Ullah et al. 2019). Rhizospheric fungi's oxalate crystals are similarly reported to immobilize and eliminate heavy metals (Ghosh et al. 2019).

14.5 Conclusion

Phenolics are the most intensively researched plant compounds. They are found to have a significant function in various abiotic stresses. Wheat is rich in phenolics which add to its nutritional value and also act as an antioxidant. Heavy metal stress causes the synthesis of these secondary metabolites particularly phenolic compounds in plants which in turn reduces the levels of ROS. The phenolics secreted in the rhizosphere are found to perform an important part in microbe and plant association in alleviating heavy metal stress in plants. Exudates of roots could operate as donors of electron, and several substances could be utilized to eliminate heavy metals via bacteria which are metal-reducing. However much research is needed to be done on the function of several polyphenols under heavy metal stress in wheat and also their upregulation as well as mechanism of their synthesis during heavy metal stress in wheat. A deeper comprehension of root exudation mechanisms, particularly the bacterial as well as plant elements engaged in various development phases and stress reactions, might be valuable for subsequent crop management.

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Phenolics: Accumulation and Role in Plants Grown Under Heavy Metal Stress

15

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Abstract

Heavy metals such as Fe, Mn, Cu, Ni, Co, Cd, Zn, Hg and As have long been gathering in soils as a result of variety of anthropogenic activities particularly after the setup of industrial sector. Plants exposed to high levels of these heavy metals undergo number of changes in their physiology and metabolism. The most typical and visible manifestation of heavy metal toxicity includes reduced plant growth, leaf chlorosis, leaf necrosis, turgor loss, instant drop in seed germination rate and a defunct photosynthetic apparatus, which is frequently associated with progressive senescence processes or ensuing plant death. In plants, heavy metal stress also increases the generation of free radicals and many other detrimental species. To defend themselves against heavy metal stress, plants employ a various avoidant or tolerant mechanisms. One such mechanism that provides plants with a defensive strategy to deal with severe heavy metal toxicity is the synthesis of phenolics, which are secondary natural metabolites originating biogenetically from either the shikimate/phenylpropanoid pathway or acetate/malonate pathway. The present review lays focus on the structure, synthesis, accumulation and role of phenolics in ameliorating the detrimental effects of heavy metals in plants.

Keywords

Phenolics · Heavy metals · Secondary metabolites · Antioxidants · Stress · Senescence

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15.1 Introduction

From roughly 300,000 recorded species of higher plant species, around 200,000 chemical entities have been extracted and identified (Fiehn 2002). Metabolites such as sugars, fatty acids, amino acids and nucleic acids that are required by all plants for growth and development are known as primary metabolites (Wu and Chappell 2008). Plants, apart from these primary metabolites, produce structurally and chemically countless and varied array of compounds known as secondary metabolites. These compounds occur in specialized and distinctive cells and are not vital for photosynthesis and respiration, but are believed to play role in plant persistence in specific environment (Boudet 2007; Harborne and Green 1980). There are vast numbers of secondary metabolites in plants which have the potential of responding to biotic and abiotic stresses. The pathways responsible for their synthesis have frequently been recruited from vital primary metabolism pathways following initial gene duplication, which resulted in the new functions and diversified roles of these duplicated genes, and have become fundamental part of the plant developmental programme. The onset of developmental stage is often accompanied by accumulation of secondary metabolites. This accumulation pattern of secondary metabolites is strictly controlled by gene expression both spatially and temporarily. The transportation of the metabolic intermediates further provides an extra level of regulation. Ontogeny and circadian clock-controlled gene expression also play vital role in synthesizing these metabolites. Phenolics are one of the most prevalent categories of secondary metabolites generated by plant kingdom members (Boudet 2007; Harborne and Green 1980). Phenolic compounds have piqued the interest of scientists due to their biological activity, which has been shown in in vitro and in vivo studies to be advantageous to human health (Vazquez-Olivo et al. 2020). When it comes to plant phenolics, the term “phenol” is used for the compound that has one or more hydroxyl substituents attached to the phenyl ring. The term “polyphenol” would accordingly be defined as any natural product that contains minimum of two phenyl rings with one or more hydroxyl groups, including their functional derivatives (e.g. esters and glycosides). However, this definition would include several compounds which have terpenoid origin, e.g. gossypol, oestrone, etc., thus making the definition unsatisfactory (Harborne 1989). According to Quideau et al. (2011), phenolics should only be used for secondary metabolites that are generated biogenetically by the shikimic acid/phenylpropanoid pathway, which directly makes available phenylpropanoids (Fig. 15.1), or the acetate/malonate pathway, which is also referred to as the polyketide pathway and can yield simple phenols, or both of the pathways. Both of these routes synthesize a huge collection of monomeric as well as polymeric phenol structures that play a variety of roles in plants, ranging from structural components of cell walls to involvement in plant development and survival under diverse abiotic and biotic stress situations. The term polyphenols is used with regard to structure containing more than one phenolic ring. Therefore, the plant phenolics are an extremely diverse assemblage which already contains tens of thousands of members with varied structures, and the number is continuously increasing (Quideau et al. 2011).

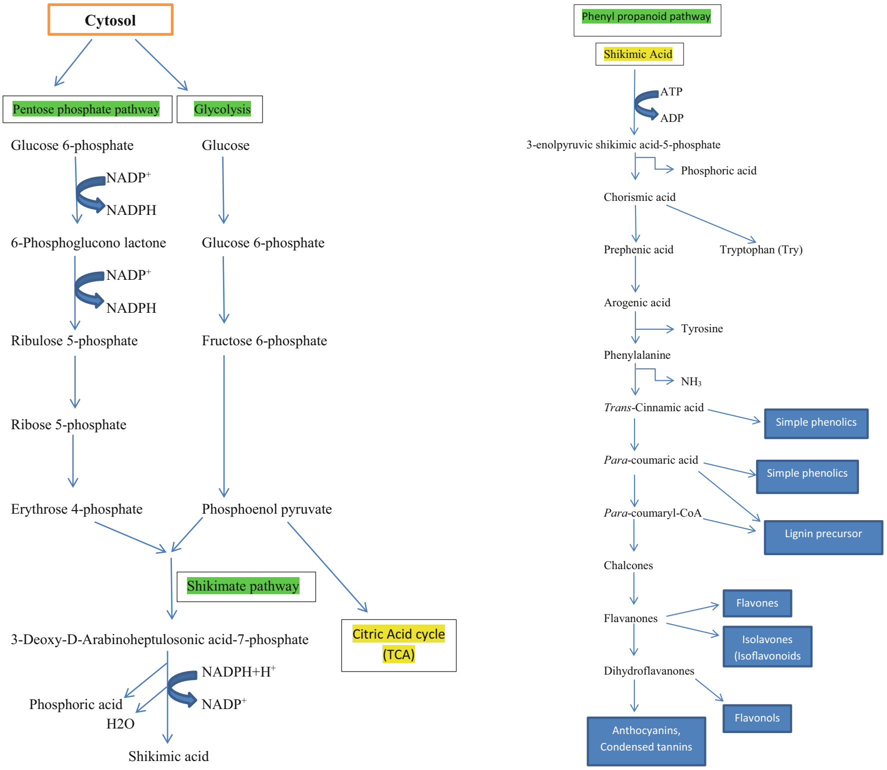

Fig. 15.1 The biosynthetic pathway of phenolic compounds. A diagram depicting the biosynthesis of phenolic compounds in plants via the pentose phosphate, shikimate and phenylpropanoid pathways. (Source: Redrawn from Lattanzio, V., 2013. Phenolic compounds: introduction. In: Ramawat, K.G., Mérillon, J.M. (Eds.), Natural Products, Springer-Verlag: Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-22144-6_57 and Lin et al. (2016))

Higher plants are known for synthesizing tens of thousands of various phenolic compounds. In their leaves, vascular plants contain amides, esters and glycosides of hydroxycinnamic acids; glycosylated flavonoids, particularly flavonols; and proanthocyanidins and their relatives. Chlorogenic acid is one of the few examples of soluble phenolics which is widely distributed across plant families. However, the presence of other phenolics is limited to particular genera or families, thereby making them important biomarker for taxonomic analysis. The examples of phenolic-containing polymers include suberin, lignin and sporopollenin of pollen grains (Boudet 2007). Phenolics are not so common in bacteria, fungi and algae. However, bryophytes regularly synthesize vast array of phenolic compounds that include polyphenols like flavonoids (flavones and flavonols) and proanthocyanidins and their relatives (Swain 1975). It is widely believed that land-adapted plants appeared in the mid-Palaeozoic era, i.e. between about 480 and 360 million years ago. These plants consist of embryophytes (liverworts, hornworts, mosses) and tracheophytes which have arisen from charophycean algae. To cope with the incessantly changing environmental challenges over the evolutionary time, plants synthesized phenolic compounds to address the specific needs. Thus phenolic-producing plants were selected throughout the process of evolution in diverse plant lineages. It provided "phenolic UV light screens" to higher members of Charophyceae which first successfully adapted to the land after emerging from the aquatic environment (Boudet 2007). Apart from this, phenylpropanoid pathway that produces lignin comprises common set of metabolic processes in higher plants, which also showed its presence 400 million years ago with the appearance of stiff vascular land plants. These secondary metabolites have evolved over time to provide the specific adaptations to plants which became one of the reasons for their diversity that we observe today (Boudet 2007). Plant's highly structured interactions with their biotic and abiotic surroundings have been a primary driving force behind the formation of these specialized natural metabolites. In this regard, phenolic buildup in plant tissues is seen as a frequent adaptive response of plants to adversarial environmental settings, hence boosting evolutionary fitness. The plant phenolics are thought to play an important defensive role in plants when environmental challenges like strong light, freezing temperatures, pathogen and herbivore attacks, nutritional shortage and heavy metal stress cause a surge in the formation of free radicals and many other oxidative species. Plants respond to biotic and abiotic stresses by increasing their capacity to reduce reactive oxygen species, according to emerging studies. Secondary metabolism gene expression is frequently stimulated by biotic and abiotic stress by the incorporation of signalling chemicals such as salicylic acid, jasmonic acid and its derivatives (Winkel-Shirley 2002).

15.2 Structure and Classification of Phenolics

Plant phenolics consist of several thousand chemically known members whose structures range from monomeric to dimeric and polymeric phenolics. Harborne and Simmonds (1964) categorized them according to the number of carbons in the molecule as given in Table 15.1.

The phenolics with lower molecular weight are ubiquitous in higher plants. Certain phenolics among them are restricted to some species only, while others are common in higher plants. Proanthocyanidins, which are also referred to as condensed tannins, are the higher molecular weight polyphenols commonly present in woody plants but generally lacking in nonwoody plants. The hydrolysable tannins are found in only 15 of the 40 orders of dicotyledons, making them less common than proanthocyanidins (Ishimaru et al. 1987; Quideau 2009). According to Palanisamy et al. (2020), tannins attach to proteins and other natural substances to precipitate them. The leaves of *Vaccinium* species contain a simple phenol arbutin (hydroquinone b-D-glucoside, I). It is so uncommon that it has been recommended as a signal for pear juice adulteration of other liquids (Kutchan and Dixon 2005).

Phenolic acids are commonly found in complex structures like lignins and hydrolysable tannins as well as bound with carbohydrates or organic acids

Table 15.1 Various classes of phenolics

Phenolics classes	No. of C-atoms	Structure
Simple phenolics, benzoquinones	6	C6
Phenolic acids and related compounds	7	C6–C1
Acetophenones, phenylacetic acids	8	C6–C2
HCAs, phenylpropanoids (coumarins, isocoumarins, chromones, chromenes)	9	C6–C3
Napthoquinones	10	C6–C4
Xanthones	13	C6–C1–C6
Stilbenes, anthraquinones	14	C6–C2–C6
Flavonoids, isoflavonoids	15	C6–C3–C6
Betacyanins	18	
Lignans, neolignans	18	(C6–C3)2
Biflavonoids	30	(C6–C3–C6)2
Lignin		(C6–C3)n
Melanins, catechol	N	(C6)n
Condensed tannins (proanthocyanidins flavolans)		(C6–C3–C6)n

(Tomas-Barberan and Clifford 2000). A C6–C2 compound picein (II), occurring in the needles of spruce trees (*Picea abies*), is also found in many other plant species. Coumarins, C6–C3 derivatives, are benzo-a-pyrones (lactones) produced through the interaction between the o-hydroxy and carboxyl groups and subsequent cyclization. This group is found in several eudicotyledon families either free or in conjunction with sugars heterosides and glycosides (Petersen et al. 1999).

Naphthoquinones, such as plumbagin (VI), are a kind of quinone pigments. There are several higher plant families such as Avicenniaceae, Bignoniaceae, etc. that contain this class of phenolics. They are produced through many pathways such as the polyketide pathway, the shikimate/succinyl-CoA combination pathway and the shikimate/mevalonate pathway (Babula et al. 2009). Xanthones, another class, are present in only a few higher plant families; they have thus high taxonomic importance. Mangiferin (VII) is an unusual natural xanthone in that it has significantly larger natural occurrence than the other members of same class. It was discovered in the leaves of *Mangifera indica* L. for the first time (Bennett and Lee 1989).

Stilbene family is extensively prevalent across the plant kingdom, while certain members of this group are peculiar to specific plant families only. Similarly, different glycosylated and acyl flavonoids and their bound forms comprise a wide range of natural compounds, with over 10,000 distinct structures having been discovered (Veitch and Grayer 2008). They are present in a variety of plant tissues and have chemical structures that are based on a C6–C3–C6 skeleton. The two main families of complicated C6–C3–C6 plant phenolics include bi- and triflavonoids, as well as proanthocyanidins. Because these compounds are the result of oxidative coupling of diverse flavonoid structures, they all have a carbonyl group at C–4 or its equivalent in every component unit.

Lignans and neolignans are plant phenolics generated by the oxidative dimerization of two phenylpropanoid units found in a broad array of plant species. Lignans are phenylpropanoid dimers with C3 side chains that are primarily C–C connected via their C3 side chains (tail-to-tail such as pinoresinol). Eusiderin and other neolignans are phenylpropanoid dimers linked head-to-tail (Moss 2000). Lignin, the key structural polymer of xylem and the second most plentiful organic material in plants after cellulose, is present as an important component of all vascular plant's cell walls. Lignin has a well-known protective effect against phytopathogenic fungi. It possesses antifungal properties, prevents fungal attack by physically stopping their entry and inhibits the spread of their poison (Rashad et al. 2020). The coniferyl alcohol and small quantity of p-coumaryl alcohol are the primary sources of lignins in gymnosperms, whereas coniferyl and sinapyl alcohols are found in about equal amounts in angiosperm lignins.

Plant tannins are high molecular weight phenolic compounds that may form complexes with carbohydrates and proteins. Tannins found in higher plants are metabolites of two types: hydrolysable tannins and proanthocyanidins, which are commonly called as condensed tannins. Proanthocyanidins occur in vast amounts in woody plants but are uncommon in nonwoody plants and usually confined to some specific tissues such as seed coat of *Arabidopsis thaliana* L. or alfalfa. Only 15 of the 40 orders of eudicots contain hydrolysable tannins (Ishimaru et al. 1987), making them less common than proanthocyanidins. A third family of tannins, phlorotannins, was recently discovered in a variety of algal species. The phlorotannins are composed of phloroglucinol subunits connected together either by C–C bonds or C–O–C (aryl-ether) bonds. Acids, bases and, in certain situations, hydrolytic enzymes break down hydrolysable tannins into sugars (often D-glucose) or similar polyols and phenolic acid (tannase). In the case of gallotannins, which are polygalloyl esters, this is gallic acid. Ellagitannins are hexahydroxydiphenoyl carbohydrate esters or cyclitols in a restricted sense, but compounds originating from subsequent oxidative reactions are also included in a broader sense. When the hexahydroxydiphenoyl group is broken down, the parent acid lactonizes quickly to produce the dilactone ellagic acid (IX). Under highly acidic circumstances, proanthocyanidins which are flavan-3-ol oligomers and polymers undergo cleavage of C–C interflavanic linkages to produce anthocyanidins (or C–C and C–O–C in A-type proanthocyanidins). Proanthocyanidins can form polymers with up to 50 units (Quideau 2009). Ishimaru et al. in 1987 reported that flavano-ellagitannins are found in some plants; however, they are far less prevalent (e.g. acutissimin A and B (X–XI), which were initially identified from *Quercus acutissima* Carruthers). Lastly, melanins are high molecular weight dark brown- or black-coloured pigments that are generated from phenolic compounds by the oxidative polymerization. Generally, they are ortho-dihydroxyphenol conjugated polymers (Bell and Wheeler 1986).

15.3 Accumulation of Phenolics in Plants

The buildup of phenolics occurs when plants face the challenges of biotic or abiotic stress such as that of low temperatures, pathogen infection, heavy metals, etc. Several articles have looked at the impact of nonfreezing temperature stress on phenolic metabolism. These researches have revealed that cold stress increases phenolic metabolism and affects its behaviour. However, there is a certain threshold temperature below which a rise in phenolic metabolism occurs, and this temperature is critical at which chilling injury may occur. It was found that cold-induced stress increases the level of phenylalanine ammonia-lyase activity (PAL, EC 4.3.1.5) and other enzymes involved in the phenolic biosynthesis pathway. These low-temperature responses in phenolic metabolism (increased enzyme activity and phenolic compound levels) also affect the shelf life of stored fruit and vegetables by providing an adequate substrate for browning reactions (Lattanzio et al. 1994, 2001). Plant development is dependent on the availability of recycled nutrients, whereas the external nutrient provides only a modest percentage of the overall need. Climate, substrate (litter) quality and decomposer species all have an influence on nutrient mineralization carried out by soil microbes. Polyphenols have been found as soil process regulators, with the potential to affect the total amount and form of nutrients accessible to plants and/or microbes. Polyphenols go into the soil mostly as leachates from above- and below-ground plant parts and/or above- and below-ground plant litter. Phenolic compounds, for example, can have a direct influence on the activity and composition of decomposers, influencing rate of decomposition and nutrient cycling. Furthermore, plants rely on their root's capacity to interact with bacteria. The opposite is also correct; numerous bacteria and fungi rely on relationships with plants, which are frequently controlled by root exudates. Root exudate is teeming with isoflavonoids and flavonoids, triggering certain genes responsible for nodulation and that may be involved in vesicular-arbuscular mycorrhiza colonization. The roots of the host plant initiate nodule formation by releasing flavonoids into the rhizosphere. Because each rhizobia species reacts differently to these compounds, the uniqueness of the symbiotic association is hence defined by the exudate. Flavonoids attract bacteria and activate rhizobia Nod (nodulation) gene expression, resulting in the formation and release of strain-specific Nod factors (NF). The oligosaccharide backbone of NF is composed of N-acetyl-D-glucosamine units connected to a nonreducing sugar by a fatty acyl group. The various NF substituents linked to the oligosaccharide backbone are regarded to be a key factor of host-symbiotic specialization. In most situations, the occurrence of suitable NF is adequate to initiate nodule development (Mathesius 2008). Anthocyanins are kind of flavonoids that provide many flowers and fruits their red and blue/purple hues. These chemical substances act as visual signals to entice pollinators and various animals for seed dispersal. They are housed in vacuole of specialized cells. Anthocyanins are also responsible for the stunning exhibitions of varied red to reddish-orange hue in deciduous tree leaves. Leaf colour dynamics are not just a byproduct of leaf senescence; various concepts have evolved in the last decade to elucidate the evolutionary process of autumn colours which are primarily caused by carotenoids (yellow-orange pigments) and anthocyanins (red-purple). Carotenoids exist in the leaves all year, but they are concealed by the green of chlorophyll in mature leaves; in the fall, they become visible owing to the disappearance of chlorophyll. Anthocyanins, on the other hand, are created in abundance during the autumn season just before the leaves are shed. Hence, red is produced throughout fall and isn't merely a byproduct of leaf withering. Why do leaves that are ready to fall become red? The usefulness of the fall hues is still debated. According to photoprotection hypothesis, red may shield the foliage from the detrimental effects of low temperature, permitting for more effective nutrient resorption, particularly nitrogen. According to coevolution theory, red does serve as a threatening signal to animals, mainly to feeding insects such as aphid. It has also been said that cold, dry and bright sunlight stresses are alleviated by red pigments by the process referred to as light attenuation that lowers the absorption of green sunlight. Recent research on fall and juvenile leaves, on the other hand, suggests that the red pigments prevent leaf injury by making them less appetizing or apparent to animals deficient of red visual receptor, or by indicating poor leaf quality. In their natural habitat, plants are subjected to a plethora of pests and diseases. In response to such creature attacks, the plant may develop tolerance or resistance mechanisms which allow it to thrive. Plants generate diverse phenolic metabolites that perform both functions, i.e. repelling and attracting various organisms in the plant's surroundings. Fraenkel in 1959 identified phenolics as "trigger" molecules that boost or restrict nutrient intake by animal herbivores; plant phenolics have been recognized as significant in chemoecology, particularly in herbivore eating behaviour (Heil 2008). They operate as repellents, inhibitors, natural animal toxicants and insecticides against attacking species (Cornell and Hawkins 2003; Bhattacharya et al. 2010). Preformed antibiotic compounds found in healthy plants are thought to act as intrinsic chemical barriers against herbivorous and fungal adversaries, protecting plants from a wide spectrum of pests and diseases. In contrast, stimulated defensive chemicals are synthesized as plant's reaction to biotic stress both at the location of attack and far away from this site. The latter is signalled by salicylates and jasmonates which soon upon infection are synthesized and prevent further spread and subsequent attacks. A network of interrelated signal transduction pathways governs induced resistance, with phenolic acids functioning as critical signalling molecules (Smith et al. 2009; Runyon et al. 2010). Plant survival in an environment rich in potentially dangerous microorganisms is dependent on effective microbe sensing and quick defensive responses. Plant immunity is dependent on each cell's capacity to identify pathogens. An initial stage of microbe detection is carried out by membrane proteins known as pattern recognition receptors (PRRs) that detect the chemical fingerprints of a broad class of bacteria known as pathogen-associated molecular patterns (PAMPs). As soon as plant PRRs identify prospective pathogens via conserved PAMPs, phenolics are produced, resulting in PAMP-triggered immunity (Nicaise et al. 2009; Zipfel 2008). When a plant recognizes a pathogen, it activates its endogenous multicomponent defensive mechanism. Because a large number of defence-related genes must be activated for plants to respond to pathogen assault, the multicomponent defence response triggered following pathogen infection involves a major investment of cellular resources, including extensive genetic reprogramming. Many defence-related genes form metabolites referred to as phytoalexins, which have antimicrobial property and are synthesized as a result of the interaction between the host's and a fungal parasite's metabolic systems. Phytoalexins formed in the different species of family Leguminosae are isoflavonoids, with pterocarpans such as medicarpin and glyceollin II (XXIII) being the most common isoflavonoid subclass, while phytoalexins from Vitaceae appear to form a rather restricted group of molecules that belong to the stilbene family (3,5,40-trihydroxystilbene). The bulk of plants from which such chemicals have been found are dicotyledonous (Lattanzio et al. 2006; Vermerris and Nicholson 2006). Plants and insects have a complicated ecological connection that includes both physical and chemical interactions. Plant variables, insect factors and certain insect-plant factors, such as hypersensitivity response and plant resistance to insect-borne illnesses, all have an impact on this interaction. Secondary metabolites in sufficient quantity to produce an unpleasant physiological impact are plant elements that make a host unappealing. Plant phenolics are now widely recognized to carry out protection of plants against insects. Tannins may also have an impact on insect development in three different ways: they possess an astringent taste that reduces palatability and in turn consumption; they mix with proteins to create complexes with low digestibility; and they function as enzyme inactivators. Recent research on tannin oxidation in insects by Raymond Barbehenn and coworkers shows that tannin activity cannot be described so easily, since tannin oxidation should also be considered as a plant defence mechanism (Constabel and Barbehenn 2008; Barbehenn et al. 2010).

15.4 Effects of Heavy Metals on Plants

Heavy metals are defined as elements with specific weights more than or equal to 5 g/cm^3. Several of them (Co, Fe, Mn, Mo, Ni, Zn, Cu) are key micronutrients involved in redox reactions, electron transfers and other critical metabolic functions. Non-essential metals (Pb, Cd, Cr, Hg and so on) may be toxic to plants. Human activities such as industrial waste, fertilizer application, smelting and disposal of sewage have been instrumental for accumulation of Fe, Mn, Cu, Ni, Co, Cd, Zn, Hg and arsenic in soils due to the human activities (Wagay et al. 2020; Aydinalp and Marinova 2009). As a result of these operations, metals are leached into groundwater or collected on the soil surface (Aydinalp and Marinova 2009; Gupta et al. 2012; Hakeem et al. 2015; Basheer 2018). All heavy metals are non-biodegradable, which means they can't be removed from the environment naturally. Some are immobile, meaning they cannot be moved from where they have accumulated, while others are mobile, meaning they are often absorbed by plant roots through diffusion, endocytosis or metal transporters (Ali and Jain 2004). However, several of these metals, such as zinc, copper and nickel, are important micronutrients that must be consumed in small amounts as cofactors for specific enzymes. Plants growing in an environment containing hazardous quantities of heavy metals undergo a variety of changes in their physiology and metabolism (Dubey and Naik 2011; Villiers et al. 2011). However, because different heavy metals contain different locations of action inside the plant, the overall toxic effect varies. Their most commonly found visual effect is decreased growth in plants preceded by leaf chlorosis, necrosis, turgor loss, reduction in seed germination and a damaged photosynthetic apparatus and is frequently associated with ongoing senescence processes or eventual plant death (Sharma and Dubey 2007). All of these impacts are connected to heavy metal-induced ultrastructural, biochemical and molecular alterations in plant tissues and cells. Because of the evil ecological consequences, heavy metal pollution of agricultural soil has emerged as a major environmental problem. Such hazardous substances are classified as soil pollutants due to their widespread prevalence and significant negative effects on plants grown in such soils (Gamalero et al. 2009).

15.4.1 Zinc Effects on Plants

Zinc (Zn) is a heavy metal that can remain intact in soil for long periods and can alter several metabolic processes in plants. Zn and Cd phytotoxicity has been investigated in a range of plant species, including *Phaseolus vulgaris*, *Brassica juncea* and tobacco, such as a decrease in growth and development and metabolism and oxidative damage (Cakmak and Marschner 1993; Tkalec et al. 2014). Cd and Zn both have been shown influencing enzyme's catalytic performance in *Phaseolus vulgaris* and pea plants (Van Assche et al. 1988). Zn concentrations in polluted soils typically exceed nutritional requirements, which can lead to phytotoxicity. Warne et al. (2008) demonstrated that Zn concentrations in polluted soils are between 150 and 300 mg/kg. High Zn levels in soil impede several plant metabolic systems, delaying development and causing senescence. Zinc toxicity in plants stopped root and shoot development (Malik et al. 2011). Zinc toxicity also produces chlorosis in the newly formed leaves, which can spread to the older leaves following continuous exposure to high Zn levels in the soil (Ebbs and Kochian 1997). Because hydrated Zn^{2+} and Fe^{2+} ions have comparable radii, chlorosis may be caused in part by an induced iron (Fe) deficit (Marschner et al. 1986). Increased amounts of Zn can also cause deficits in manganese (Mn) and copper (Cu) in above-ground plant parts. These deficits have been linked to a slowed transport of these micronutrients from below- to above-ground plant parts. This impediment stems from the fact that the concentrations of Fe and Mn in plants growing on Zn-rich medium are higher in the root than in the shoot. Another common symptom of Zn poisoning is the formation of a purplish-red hue in leaves, which is caused by a lack of phosphorus (P) (Ebbs and Kochian 1997).

15.4.2 Cadmium Effects on Plants

According to Salt et al. (1995), cadmium (Cd) in agricultural soil has a regulatory limit of 100 mg/kg soil. Plants growing in soil with elevated levels of Cd exhibit evident damage signs such as chlorosis, growth inhibition, root tip browning and eventually death (Mohanpuria et al. 2007; Guo et al. 2008). Cd-induced inhibition of root Fe(III) reductase resulted in Fe(II) shortage, which severely hampered photosynthesis (Alcantara et al. 1994). It has been demonstrated that Cd interferes with the absorption, relocation and use of numerous elements (such as Ca, Mg, P, K) and transportation of water by plants in general (Das et al. 1997). Hernandez et al. (1996) showed that Cd also inhibited nitrate absorption and its transportation from below- to above-ground parts of plants by decreasing nitrate reductase activity in the plant shoots. Plants of *Silene cucubalus* also showed significant suppression of nitrate reductase activity (Mathys 1975). Balestrasse et al. 2003 showed that nitrogen fixation and primary ammonia assimilation in soybean plant nodules reduced under Cd treatments. Metal poisoning can reduce plasma membrane permeability, resulting in decrease in water content. Furthermore, Cd has been shown to interfere with the water balance as was studied by Costa and Morel (1994). Cadmium treatments have been found to impair the activity of ATPase in wheat and sunflower root plasma membrane fractions (Fodor et al. 1995). Cadmium alters membrane functioning by causing lipid peroxidation and disrupts chloroplast metabolism by limiting chlorophyll production and decreasing the activity of enzymes involved in CO_2 fixation (Fodor et al. 1995).

15.4.3 Copper Effects on Plants

Copper (Cu) is a micronutrient for plants that aids in CO_2 uptake along with ATP generation. Cu is required for the formation of several proteins, such as plastocyanin in the photosynthetic system and cytochrome oxidase in the respiratory electron transport chain (Demirevska-Kepova et al. 2004). However, increased industrial and mining activities have contributed to a surge in Cu concentration in ecosystems. Additionally, Cu gets integrated into soils due to several human activities such as mining and smelting of Cu-containing ores. Mining activities produce a significant amount of waste rocks and tailings, which end up remaining on the surface. Cu in excess is cytotoxic, causes stress and kills plants. This slows plant growth and produces chlorosis in the leaves. Plants are harmed by oxidative stress and ROS as a result of excessive Cu exposure (Stadtman and Oliver 1991). Oxidative stress disrupts physiological functions and also causes damage to macromolecules. Copper toxicity impeded the growth of *Alyssum montanum* (Ouzounidou 1994), cucumber (Moreno-Caselles et al. 2000) and *Brassica juncea* (Moreno-Caselles et al. 2000). Copper and cadmium together had affected the germination of seeds, length of seedling and the lateral root number in *Solanum melongena* (Neelima and Reddy 2002).

15.4.4 Mercury Effects on Plants

Hg is an unusual metal since it exists in several forms such as HgS, Hg^{2+}, Hg and methyl-Hg. However, in soil Hg^{2+} predominates. Hg discharged into soil primarily stays in the solid phase due to adherence with sulphides, clay particles and organic materials. An elevated concentration of Hg^{2+} poses threat to plant by causing an apparent damage as well as physiological concerns. For instance, Hg^{2+} attaches to water channel proteins, causing closure of guard cells and hampering the water flow in plants (Zhang and Tyerman 1999). Furthermore, high levels of Hg^{2+} impede mitochondrial activity and induce oxidative stress by producing ROS. As a result, both lipids of cell membranes and plant cellular processes are disturbed (Cargnelutti et al. 2006).

15.4.5 Chromium Effects on Plants

Plants are poisoned by chromium (Cr) compounds, which have a deleterious influence on their growth and development. Because seed germination is altered by Cr, a seed's ability to sprout in Cr-containing medium indicates its resistance to this heavy metal (Peralta et al. 2001). Twenty-five per cent decrease was observed in seed sprouting of the weed *Echinochloa colona* when the medium contained 20 ppm Cr (Rout et al. 2000). In *Phaseolus vulgaris* germination is up to 48% by hexavalent Cr (500 ppm) levels in soil (Parr and Taylor Jr 1982). Similarly, concentration of 40 ppm Cr(VI) in contaminated medium decreased lucerne seeds' (*Medicago sativa* cv. Malone) germination and growth by 23% (Peralta et al. 2001). In another study, Zeid (2001) reported sugarcane bud germination was lowered by 32–57% at 20 and 80 ppm Cr, respectively. Seed germination reduced under Cr stress was because of Cr′s inhibitory effect on amylase function and on the transfer of carbohydrates to the embryo axis. Protease activity rises with Cr treatment that might explain why Cr-treated seeds germinate less well (Zeid 2001). Reduced root development in plants and crops is a well-established adverse effect of heavy metals. In *Salix viminalis*, Prasad et al. (2001) reported that the order of negative impacts of heavy metals on its new root primordia is Cd, Cr and Pb with Cr having a greater effect on root length than the other heavy metals tested. Cr stress is a significant component influencing photosynthetic CO_2 fixation, electron transport, photophosphorylation and enzyme activity (Clijsters and Van Assche 1985). Although the effect of Cr on the process of photosynthesis in higher plants is well established, according to studies it is unclear whether the Cr-induced photosynthesis limitation is due to instability of chloroplast ultrastructure, obstruction of electron transport chain or the action of Cr on activities of Calvin cycle enzymes (Desmet et al. 1975; Van Assche and Clijsters 1983). In peas, Bishnoi et al. (1993) found that Cr(VI) had a stronger influence on the activity of PS I than on PS II in isolated chloroplasts but both were damaged in fully grown plants. In plants, chromium stress causes three kinds of physiological changes as (1) changes in the synthesis of pigments involved in photosynthesis, (2) elevation in the synthesis of metabolites (e.g. glutathione and ascorbic acid) as a direct and immediate response to Cr stress that might harm the plant and (3) metabolic pool changes to channel the synthesis of new metabolites such as phytochelatins and histidine that provide tolerance to Cr stress (Schmfger 2001). Two enzymes such as superoxide dismutase (SOD) and antioxidant catalase are induced as the key metal detoxifying enzymes in plants. It was reported that the activity of these enzymes peaked at lower levels of heavy metal whereas, at higher levels, SOD activity remained unchanged while catalase activity declined (Nematshahi et al. 2012).

15.4.6 Lead Effects on Plants

Lead (Pb) is one of the most common and widely spread toxic heavy metals in soil. It is detrimental to plant structure, growth and physiological activities. Seed germination in *Spartina alterniflora* and *Pinus halepensis* has been demonstrated to be reduced by lead. Germination may be inhibited as a result of lead interfering with key enzymes. Lead also hindered plant elongation, in addition to leaf growth in *Allium* and barley (Grunhage et al. 1985). According to Goldbold and Hutterman (1986), the extent to which root growth is hindered is determined by the medium's lead content, ionic composition and pH. In *Sesamum indicum*, root development has been inhibited in a concentration-dependent manner. Many plant species exhibit aberrant morphology when subjected to high levels of lead in the soil. Apart from lignification of cortical parenchyma, lead also induces unequal radial thickening in pea roots, cell walls of endodermis. Lead at concentrations of 100–200 ppm was applied to potted sugar beet plants, causing chlorosis and growth loss (Paivoke 1983; Hewitt 1953). Lead levels as low as 0.005 ppm resulted in a substantial decrease in lettuce and carrot root development. Pb2+ inhibitory effects on growth and biomass production might be attributed to impacts on metabolic plant processes (Sharma and Dubey 2005). A lead-induced oxidation of IAA (indole-3-acetic acid) is the principal reason of cell growth inhibition. Lead has also been shown to impede photosynthesis by lowering carboxylating enzyme activity (Stiborova et al. 1987). Excess Pb also inhibits enzyme performance, causes water imbalance, affects membrane permeability and interferes with mineral feeding (Sharma and Dubey 2005). According to Reddy et al. (2005), Pb hinders enzyme function by interacting with their sulfhydryl groups at the cellular level. High Pb levels also increase ROS generation in plants, promoting oxidative stress.

15.4.7 Arsenic Effects on Plants

Arsenate (As) is a phosphate (P) analogue that interacts with the same kind of import transporters in the plasma membrane of plant roots (Meharg and Macnair 1992). Arsenate tolerance has been observed in a wide range of plant species, for instance, in grasses; tolerance is produced by the inhibition of a high-affinity P/As absorption route. This inhibition decreases As input to an extent where the plant can detoxify it, most likely through constitutive processes (Meharg and Macnair 1992; Meharg 1994). Within plant cells, As is also converted into less toxic As species (Meharg 1994). Arsenate is converted to arsenite, dimethylarsinic acid (DMA) and monomethyl arsenic acid in phytoplankton and macroalgae (MMA). These methylated forms of As are subsequently broken down into organophospholipids and arsenosugars (Phillips 1990).

15.4.8 Cobalt Effects on Plants

The three forms of cobalt (Co) in which it occurs in soil are cobaltite [CoAsS], erythrite [Co3(AsO4)2] and smaltite [CoAs2]. A trace quantity of Co can be absorbed by plants from the soil. Cobalt absorption and dispersion in plants differ by species and are influenced by a variety of factors (Kukier et al. 2004; Bakkaus et al. 2005). The phytotoxic consequences of increased Co levels are less well understood. A recent phytotoxicity study on Co in barley (*Hordeum vulgare* L.), oilseed rape (*Brassica napus* L.) and tomato (*Lycopersicon esculentum* L.) revealed an adverse impact on above-ground plant growth and biomass. Furthermore, high Co concentrations in cauliflower leaves reduced the activities of Fe, chlorophyll, protein and catalase and also impaired the transport of P, S, Mn, Zn and Cu from cauliflower roots to shoots. Compared to excess Cu or Cr, Co significantly diminished both water potential and transpiration rate. Chatterjee and Chatterjee (2000) discovered that exposing cauliflower leaves to excess Co enhanced their diffusive resistance and relative water content.

15.4.9 Nickel Effects on Plants

Nickel (Ni) is classified as a transition metallic element found in natural soils except in ultramafic and serpentinic soils. However, Ni^{2+} concentrations are rising in certain areas as a result of human activities such as mining, smelter emissions, coal and oil combustion, sewage, phosphate fertilizers and pesticides (Gimeno-García et al. 1996). According to Izosimova (2005), Ni^{2+} concentrations in contaminated soil can be 20–30 times (200–26,000 mg/kg) higher than in normal soil (10–1000 mg/kg). The elevated levels of Ni^{2+} in soil induce metabolic changes and toxicity indications such as chlorosis and necrosis in various plant species including rice (Pandey and Sharma 2002; Das et al. 1997). Vegetation growing in elevated Ni^{2+} soil had impaired nutritional balance, which led in a disruption of cell membrane activities. As a result, Ni^{2+} influences the plasma membrane's lipid content and H-ATPase activity in *Cucumis sativus* shoots. Gonnelli et al. (2001) found that Ni^{2+}-sensitive plants had higher MDA concentrations as compared to Ni^{2+}-tolerant plants. These changes impair membrane function and ion balance in the cytoplasm, particularly for K^{2+}, the most mobile ion crossing the plant cell membranes. Because of the increased Ni^{2+} absorption, the water content of dicot and monocot plant species has been found to decrease. This decrease in water absorption is used to track the evolution of Ni^{2+} toxicity in plants (Pandey and Sharma 2002; Gajewska et al. 2006).

15.4.10 Manganese Effects on Plants

Excessive manganese (Mn) accumulation in foliage slows photosynthetic carbon fixation. Mn is easily transported from below-ground to above-ground plant parts by transpiration; but, once it enters the leaves, it is difficult to remobilize to other plant organs via phloem (Loneragan 1988). The most common symptoms of Mn toxicity are necrotic black spots on leaves, petioles and stems (Wu 1994). The spotting first appears on the lower leaves and then advances to the upper leaves of foliage (Horiguchi 1988). The number and size of the speckles may increase with time, causing necrotic lesions, leaf browning and death. *Cucumis sativus* has shown general leaf bronzing and internode shortening. Apart from chlorosis and browning of tissues, "crinkle leaf" appears in the newest leaf, stem and petiole tissues subjected to Mn toxicity (Wu 1994; Bachman and Miller 1995). Mn-toxic roots are often brown and fragile (Le Bot et al. 1990; Foy et al. 1995). Excess Mn has been shown to limit chlorophyll d production by interfering with a Fe-related process (Clairmont et al. 1986). Mn toxicity in certain species commences with chlorosis of mature leaves and advances to newly formed ones. If the toxicity is mild, then these symptoms develop at the leaf edges and spread to the interveinal regions; but if it is severe, the condition progresses as leaf marginal and interveinal necrosis (Bachman and Miller 1995).

15.4.11 Iron Effects on Plants

Iron, a necessary metal for all plants, is involved in a variety of critical biological processes ranging from photosynthesis to chloroplast development and chlorophyll production. According to Marschner (1995), iron is an important part of many biological redox systems involving haem proteins as well as iron-sulphur proteins. Most soils contain high iron content, but the appearance of iron toxicity symptoms in leaf tissues occurs only when the soil is flooded, owing to the microbial reduction of insoluble Fe3+ to insoluble Fe2+ (Becker and Asch 2005). Therefore, iron poisoning in plants is caused by excessive Fe2+ absorption by roots and transfer to aerial parts via transpiration flow. Excess Fe2+ increases free radical generation, which irreversibly destroys cellular structure and affects membranes, DNA and proteins (De Dorlodot et al. 2005). In tobacco, canola, soybean and *Hydrilla verticillata*, iron toxicity is associated with decreased photosynthesis and yield, as well as increased oxidative stress and ascorbate peroxidase activity (Sinha et al. 1997).

15.5 Role of Phenolics

15.5.1 Physiological Roles of Phenolics in Plants

Phenolic compounds are widely distributed and perform critical functions in plant metabolism as well as in other biological processes (Boudet 2007). There are several growth- and development-related physiological process such as seed germination, cell division and the production of photosynthetic pigments which are influenced by phenolics (Tanase et al. 2019). There are a variety of applications where phenolics are employed such as bioremediation, allelochemicals, plant growth stimulation and food additives as antioxidants (Bujor et al. 2015). Phenolic accumulation in stressed plants is a persistent feature that serves as a defence mechanism against a variety of abiotic stresses. Phenolics enable plant tolerance and adaptability under adverse environment (Andersen 2003; Lattanzio et al. 2009). This class contains many members with antioxidant properties increasing plant performance in stressful conditions (Oszmanski 1995). Plants communicate with their surroundings owing to several metabolites. Polyphenols, in particular, help in nutrient mobilization and signal transmission from root to shoot. The root secretion contains phenolic compounds that modify the physiochemical characteristics of the rhizosphere. Soil bacteria convert phenolics into compounds that help in the mineralization of nitrogen and the production of humus (Halvorson et al. 2009). Furthermore, Seneviratne and Jayasinghearachchi (2003) concluded that phenolics promote nutrient uptake by increasing active absorption sites and soil porosity by rapidly mobilizing mineral elements. Similarly, Rehman et al. (2018a, b) discovered that the increase in the content of phenolics and organic acids in wheat root secretions which aided in Zn, N and Ca nutrient movement and uptake was the result of Zn application and PGPRs (plant growth-promoting rhizobacteria) inputs. In legumes, phenolic compounds also contribute to the nitrogen fixation. Legumes produce and then excrete a large number of secondary metabolites, primarily flavonoid compounds (flavanols and isoflavonoids) through their roots which inhibit auxin transport and stimulate cell division and are hence important in the synthesis of Nod factors and the formation of infection thread during nodulation (Zhang et al. 2009). Flavonoids are required for the development of functional pollen which has been derived from a study in which a trace amount of flavonol, aglycones, kaempferol or quercetin was added during pollination to flowers, which restored fertility in mature pollen (van der Meer et al. 1992; Taylor and Grotewold 2005). Some phenolic compounds, for example, inhibit the enzymes prolyl aminopeptidase and phosphatase, which are required for germination in bean seeds (Shankar et al. 2009). High phenolic acid content, on the other hand, has been found to have a beneficial effect on seed germination. Chen et al. (2016) in canary grass reported a large increase of 1042%, 120% and 741% in free, bound and total phenolic acid contents, respectively, during germination. In *Lycopersicon esculentum*, polyphenol-rich spruce bark extract enhanced seed germination while inhibiting root elongation (Balas and Popa 2008). Phenolics were discovered to lower seed tegument thickness while increasing seed tegument porosity that assists in water absorption and therefore enhance germination rate (Tobe et al. 2001). Polyphenolic-rich spruce bark extracts boosted rate of photosynthesis by increasing chlorophyll a and b pigment production in *Zea mays* and *Helianthus annuus* (Tanase et al. 2015). Phenols reduced the energy required for ion transport by altering the structure of thylakoids and mitochondrial membranes (Moreland and Novitzky 1987). Phenolic compounds also act as antioxidants by scavenging reactive oxygen species (ROS), limiting the action of oxidizing enzymes and catalysing oxygenation processes via the formation of metallic complexes (Amarowicz and Weidner 2009).

In conclusion, polyphenols are generated in plants under ideal and (at higher levels) stress environment, and they play a significant role in development, such as signal transduction, cell reproduction, hormone regulation, photosynthetic activity regulation, seed germination and reproduction rate. Plants that develop more polyphenols in response to abiotic stresses are more adaptable to restrictive environments.

15.5.2 Role of Phenolics on Plants Under Heavy Metal Stress

For dealing with heavy metal stress, plants have a range of molecular and physiological strategies, including complex biochemical and genomic mechanisms. Many of these mechanisms in plants are constitutive since they are part of the homeostatic process. To defend themselves against heavy metals in the soil, plants employ a variety of strategies, including tolerance to them. Other pathways are exclusive that are only triggered in the presence of a certain metal toxicity. All reactions can be described as either avoidant or tolerant. When provoked by heavy metal toxicity, the plant's first line of defence is to reduce metal absorption through the utilization of cells and root exudates. Root exudate increases efflux or biosorption to plant cell walls and keeps metals from entering the cell, therefore classified as an avoidance strategy. Many plants have distinct systems known as metal ion tolerance mechanisms wherein metal ions are housed in compartments and are not allowed to interact with delicate cell components. However, it should be noted that when any cell is constantly subjected to intense stress, its normal defensive systems may become depleted. At this period, metals may be chelated, transported, sequestered or detoxified in the vacuole of plants. Plants have numerous detoxification systems to survive. When any of these processes is activated in a plant, the production of stress-related proteins, hormones, antioxidants, signalling molecules and heat shock proteins begins. Stressed plants also establish symbiotic relationships with mycorrhizal fungi that store metals in the rhizosphere, thereby rendering them inaccessible to the plant. This is another approach for thriving under challenging conditions. Plants have highly developed and complicated defence and control signalling networks that engage several genes at the same time. The mitogen-activated protein kinase (MAPK) cascade is one of the most intrinsic and significant systems engaged in plant abiotic stress. All eukaryotic species have been shown utilizing this mechanism (Jonak et al. 2002; Tena et al. 2001). The MAPK cascade involves phosphorylation, leading to a variety of events such as cell division, differentiation, the production of some stress-related genes or the regulation of the activity of others. MAPK is also associated with hormone responses, which control gene expression in a variety of ways. Surprisingly, the quantity of trace metals in soil is a crucial factor in deciding whether the metals impede or stimulate plant development. Heavy metals typically accumulate in root cells as a result of Casparian strip obstruction or entrapment by root cell walls. Heavy metal accumulation in plants disrupts several biochemical, physiological and morphological activities, interfering with crop output (Shahid et al. 2015). Phenolics serve multiple of roles in plants. Under various environmental and stress situations, there is a rise in phenylpropanoid metabolism and the quantity of phenolic compounds (Diaz et al. 2001; Sakihama and Yamasaki 2002). Isoflavones and other flavonoids are synthesized when plants are injured or when temperatures and nutrition levels are low (Takahama and Oniki 2000; Ruiz et al. 2003). The bulk of them are antimicrobial in nature. To prevent UV-B entering plant's interior tissues, plants store UV-absorbing flavonoids and other phenolics mostly in the vacuoles of epidermal cells (Kondo and Kawashima 2000). Roots of legume plants produce flavonoids that trigger genes in bacteria residing in root nodules (Winkel-Shirley 2002). It has been proven that phenolic compound production is stimulated in wheat and maize when exposed to nickel and aluminium toxicity, respectively (Diaz et al. 2001; Winkel-Shirley 2002). After being sprinkled with copper sulphate, *Phaseolus vulgaris* leaves accumulate soluble and insoluble phenolics; similarly *Phyllanthus tenellus* leaves were found to contain higher levels of phenolics than the control plants (Diaz et al. 2001). Enhanced levels of phenolics were shown to be linked to increased activity of phenolic compound metabolism enzymes, therefore indicating afresh phenolic biosynthesis under heavy metal stress. However, some research suggests that the rise in flavonoid concentration is mostly due to conjugate hydrolysis rather than de novo production (Parry et al. 1994). Rise in soluble phenolics, which are intermediates in the lignin production process, causes increased cell wall endurance and the formation of physical barriers that hinder heavy metals from acting adversely, which thus reflect the normal anatomical changes caused by stressors (Diaz et al. 2001). Metal stress causes the production of harmful ROS that leads to oxidative stress in plants resulting into toxicity and growth retardation (Guo et al. 2017; Pandey and Sharma 2002). The defence against this oxidative stress involves increased phenolic synthesis in metal-stressed plants (Handa et al. 2019; Kohli et al. 2018). Flavonoids can improve metal chelation, which helps reduce damaging hydroxyl radicals in plant cells (Mira et al. 2002), which is consistent with the discovery that metal excess raises flavonoid levels in plants (Kaur et al. 2017a, b). Metal poisoning promotes the production of flavonoids such as anthocyanins and flavonols that help plants defend themselves (Handa et al. 2019; Zafari et al. 2016). The buildup of phenolic compounds is caused by the upregulation of phenylalanine ammonia-lyase, chalcone synthase, shikimate dehydrogenase, cinnamyl alcohol dehydrogenase and polyphenol oxidase (Chen et al. 2019). Flavonoids also scavenge H_2O_2 and are expected to play an essential role in the phenolic/ascorbate-peroxidase cycle (Michalak 2006). According to Kovacik et al. (2009), the phenylpropanoid pathway precursors are synthesized by a process that requires two key enzymes, namely, shikimate dehydrogenase (SKDH) and glucose-6-phosphate dehydrogenase (G6PDH). There is yet another enzyme cinnamyl alcohol dehydrogenase (CADH) catalysing metabolic pathways that produce precursors for lignin synthesis. Heavy metals boost the activity of important biosynthetic enzymes such as PAL, SKDH, G6PDH and CADH, which promotes the phenylpropanoid production pathway in plants (Mishra and Sangwan 2019). Moreover, polyphenol oxidase (PPO) adds to the ROS scavenging process while also increasing a plant's tolerance to abiotic stresses such as that of heavy metals (Mishra et al. 2014) (Table 15.2).

15.5.3 Antioxidant Action of Phenols

The notion of phenolic compound's antioxidant activity is not unique (Bors et al. 1990). There have been several instances of increased buildup of phenolic compounds and peroxidase action in plants facing elevated metal concentrations. The ability of phenolics to chelate metals contributes to their antioxidant activity. Apart from having hydroxyl groups, phenolics have carboxyl groups that can attach to iron and copper (Jung et al. 2003). Plants exposed to heavy metals discharge substantial amounts of phenolics via their roots which can chelate and deactivate the iron (Fe) ions. It can also impede the superoxide-driven Fenton process, which is thought to be the primary source of ROS formation (Arora et al. 1998). Mn chelation protects tannin-rich plants (e.g. tea), which are resistant to Mn overload. Methanol preparations of *Nymphaea* rhizome revealed direct chelation, or adhering to polyphenols, for Cr, Pb and Hg (Lavid et al. 2001). Arora et al. (2000) have showed that flavonoids can change the order of lipid packing and hence affect peroxidation kinetics. Furthermore, they reduce free radical movement, minimize peroxidative reactions and in a concentration-dependent manner help in keeping membranes stable by reducing membrane fluidity (Blokhina et al. 2003). In yet another study by Verstraeten et al. (2003), it was revealed that flavanols and procyanidins can interact with polar head groups of membrane phospholipids via hydrogen bonding in addition to their well-known protein-binding capacity. As a result, these molecules can gather on the surface of the membranes, both within and outside the cells. They also proposed certain flavonoids help retain membrane integrity by preventing hazardous molecules from accessing the hydrophobic section of the lipid bilayer, such as those which may affect membrane rheology and cause damage to several constituents of membrane. In vitro studies have revealed that flavonoids may directly remove the following active oxygen molecular species: $^{\bullet}$O2 (superoxide), H_2O_2 (hydrogen peroxide) and $^1O_2$ (singlet oxygen), OH (hydroxyl radical) or peroxyl radical. Their antioxidant functions are majorly dependent on their potential to transfer electrons or hydrogen atoms (Sakihama et al. 2000; Khan et al. 2000). The polyphenols contain an appropriate molecular chemistry required for this action and have been proven in vitro to be far more effective on a molar basis than vitamins E and C (Rice-Evans et al. 1997). Three structural features of flavonoids, according to Bors et al. (1990), are important drivers of their antioxidant potential:

Table 15.2 Summary of the effects of heavy metal stress on endogenous levels of different phenolic compounds in some plants

Plant species	Heavy metal	Response of endogenous phenolics and related parameters	References
Brassica juncea	Cu	Concentration of total phenols, anthocyanins and other phenolic compounds such as catechin, caffeic acid, coumaric acid and kaempferol increases	Poonam et al. (2015)
	Cr	Rise in the overall levels of phenols, flavonoids and anthocyanins, as well as increased expression of PAL and CHS	Handa et al. (2019)
		A rise in anthocyanins is accompanied by a rise in the activity of CHS gene	Handa et al. (2018)
	Cd	Increased concentrations of total flavonoids and anthocyanins Increased overall flavonoid and anthocyanin concentration, followed by increased expression of PAL and CHS	Kaur et al. (2017a, b)
		Increased total phenolic, polyphenolic and flavonoid content as well as anthocyanins	Kaur et al. (2018)
	Pb	Rise in the overall concentration of phenols, flavonoids and anthocyanins, as well as increased expression of PAL and CHS	Kohli et al. (2017)
		Rise in total phenol, polyphenol, flavonoid and anthocyanin content	Kohli et al. (2018)
Fagopyrum esculentum	Al	Total phenolic, flavonoid and anthocyanin content increases. Increased activity of the PAL enzyme	Smirnov et al. (2015)
Kandelia obovata	Cd and Zn	Increased total phenolic levels are associated by increased activity of phenol metabolic enzymes such as shikimate dehydrogenase, cinnamyl alcohol dehydrogenase and polyphenol oxidase	Chen et al. (2019)
Prosopis farcta	Pb	An increase in total phenol concentration is accompanied by an increase in PAL enzyme activity. Other phenolic molecules, such as ferulic acid, cinnamic acid, caffeic acid, daidzein, vitexin, resveratrol, myricetin, quercetin, kaempferol, naringinine, luteolin and diosmin, were also enhanced	Zafari et al. (2016)
Vitis vinifera	Cu	Transcript levels of numerous genes encoding enzymes involved in phenolic biosynthesis (PAL, C4H, CHS, F3H, DFR) were increased, while UFGT and ANR were downregulated	Leng et al. (2015)
Withania somnifera	Cd	Increased overall flavonoid and phenolic content	Mishra and Sangwan (2019)
Zea mays	Cu, Pb, Cd	Increased levels of total phenols and certain polyphenols, such as chlorogenic and vanillic acid	Kısa et al. (2016)

PAL phenylalanine ammonia lyase, *CHS* chalcone synthase, *CHI* chalcone isomerase, *C4H* cinnamate 4-hydroxylase, *4CL* 4-coumarate-CoA ligase, *F3H* flavanone 3-hydroxylase, *UFGT* UDP flavonoid glycosyltransferase, *IFS* isoflavone synthase, *DFR* dihydroflavonol 4-reductase

(a) The orto 3′,4′-dihydroxy structure in the B ring (e.g. in catechin and quercetin)
(b) The 2,3-double bond in conjunction with the 4-oxo group in the C ring (allowing conjunction between the A and B rings, or electron delocalization)
(c) The presence of a 3-OH group in the C ring and a 5-OH group in the A ring

Among these, the 3-OH group is the most essential predictor of electron-donating activity. When compared to aglycones, glycosylated flavonoids lose action (Rice-Evans et al. 1996). Flavonols were found to be oxidized in situ by hydrogen peroxide in epidermal strips of *Vicia faba* leaves, *Tradescantia virginiana* leaves and V. faba mesophyll cells (Takahama 1988). Plants have two kinds of peroxidases, which may be classified into two different groups: peroxidases (AP X) that employ ASC as an electron donor predominantly and others that preferentially employ phenolics. The AP X is predominantly found in chloroplasts, cytoplasm and peroxisomes, where it scavenges H_2O_2 produced in these cell organelles (Fig. 15.2) (Noctor and Foyer 1998). To detoxify H2O2 in these cellular organelles, AP X oxidizes ascorbate to the short-lived MDA (monodehydroascorbate) radical that gets degraded to ascorbate and DHA (dehydroascorbic acid). DHA is subsequently reduced to ascorbate by glutathione reductase (DHAR) a GHS-dependent enzyme (Sakihama et al. 2002). According to Noctor and Foyer (1998), MDA radical can be converted to ascorbate via the nonenzymatic ferredoxin (Fd) process or the NAD(P)-dependent enzymatic

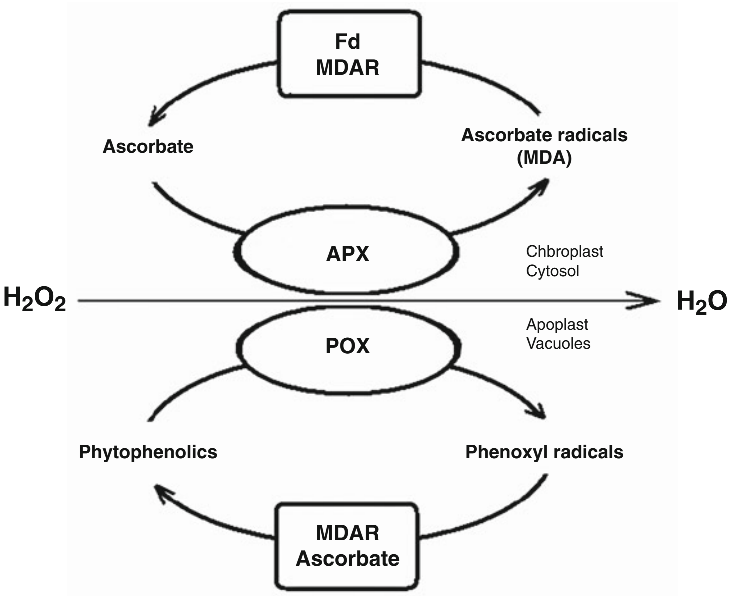

Fig. 15.2 Similarity between APX action (in chloroplast and cytosol) and POX action (in apoplast and vacuole). MDA reductase, according to Sakihama et al. (2000), may act as a phenoxyl radical reductase in the apoplast to renew the redox state of phenols. POX detoxifies H2O2 by using phenolics as a substrate (drawn according to Sakihama et al. (2002), changed)

MDAR (monodehydroascorbate reductase). According to several studies, excessive amounts of heavy metals can impair the activity of AP X (Knorzer et al. 1996). Peroxidases that employ phenolics are classified into three types: soluble and cell wall-bound, apoplastic POXs and vacuolar. The POXs bound to the cell wall are thought to take part in the oxidation of lignin monomers, thereby supplying oxidized substrates for the lignin synthesis and other metabolic processes (de Obeso et al. 2003). According to Rai et al. (2004), peroxidases that contribute to lignin formation and may provide a protection against heavy metal toxicity are involved in the response of cadmium toxicity, wounding and pathogen attack. POXs, which are soluble and apoplastic, can scavenge H2O2 with the help of phenolics and ASC. It has been postulated that H_2O_2 can be detoxified by means of flavonols and phenylpropanoids that occur in vacuoles and the apoplast, by serving as electron donors for phenol peroxidases (guaiacol peroxidases) present in these compartments, resulting in the generation of phenoxyl radicals (Yamasaki et al. 1997). Peroxidases catalyse the initial step in antioxidant activity (reaction 1). Nonenzymatic interaction with ascorbate (reaction 2) can regenerate phytophenolics from phenoxyl radicals while limiting the generation of degradation products (Yamasaki et al. 1997). When monodehydroascorbate radicals develop in vacuoles, they are disproportionately converted to ascorbate and DHA (reaction 3), which can be transferred to the cytoplasm and reduced by DHAR (Takahama and Oniki 2000). Both ASC and DHA have been reported to be transported across tonoplast and between symplast and apoplast (Horemans et al. 2000). Sakihama et al. (2000) speculate that MDA reductase may function as a phenoxyl radical reductase in the apoplast to renew the redox state of phenols.

A scheme of four reactions is:

$$\mathrm{2FlavOH} + \mathrm{H_2O_2} \rightarrow \mathrm{2FlavO}\cdot + \mathrm{2H_2O} \tag{15.1}$$

$$\mathrm{2FlavO}\cdot + \mathrm{ASC} \rightarrow \mathrm{2FlavOH} + \mathrm{2MDA} \tag{15.2}$$

$$\mathrm{MDA}\cdot + \mathrm{MDA}\cdot \rightarrow \mathrm{ASC} + \mathrm{DHA} \tag{15.3}$$

$$\mathrm{H_2O_2} + \mathrm{ASC} \rightarrow \mathrm{2H_2O} + \mathrm{DHA} \tag{15.4}$$

where reaction 4 is the sum of 1, 2 and 3.

When spin-stabilization effectors lengthen the lifespan of the radicals, the oxidized phenolic molecules (phenoxyl radicals) may display cytotoxic and prooxidant activities (Yamasaki and Grace 1998). This also applies to antioxidant compounds such as vitamin C, vitamin E and carotenoids (Rietjens et al. 2002). Because these radicals are unstable and swiftly degrade to non-radical compounds under normal physiological settings, they normally do not cause harm. In reality, they can be beneficial as prooxidants; for example, o-dihydroxy phenolics have anti-herbivore action under specific conditions (Barbehenn et al. 2003). However, due to their potential to generate free radical chain reactions in the membrane and their proclivity to cross-link with range of molecules, phenoxyl radicals are often harmful to biological systems (Sakihama et al. 2002). Metal ions have also been shown to stimulate prooxidant activity. Metal ions have the potential to affect the character of plant phenolics in vivo via modifying the lifespan of phenoxyl radicals. This might explain the harmfulness of metals like Al^{3+}, Cd^{2+} and Zn^{2+} found in the root apoplast (Yamasaki and Grace 1998). Toxic, dark polymerization products of flavonoids may be formed irreversibly if ASC levels are low (Takahama et al. 1999).

15.6 Conclusion and Future Prospects

Plant phenolics are abundantly and ubiquitously found secondary metabolites, consisting of a huge pool of natural compounds with a vast and diverse spectrum of gene regulation and transport mechanisms. As an adaptation response to severe and unfavourable environmental circumstances such as heavy metal stress, in addition to physical injury, pathogen infection, mineral shortages and cold stress, plants build up phenolics in their tissues. Furthermore, these compounds, which are lignin and suberin precursors, undergo polymerization to form cell wall components. Despite a few research findings on the synthesis of phenolic compounds and their accumulation as an adaptive mechanism to heavy metal stress in plants, more research is needed to be done to comprehend their proper mechanism of accumulation, their interactions with other cell metabolites and their amplified expression and conferring tolerance in the face of heavy metal toxicity.

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Role of Phenolic Metabolites in Salinity Stress Management in Plants

16

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Abstract

Abiotic stress has emerged as a major threat to food security, accounting for the majority of crop and agricultural product losses worldwide. Salinity is one of the primary key variables that inhibit plant growth and productivity among other abiotic stresses. Ionic stress, osmotic stress, and the formation of reactive oxygen species (ROS) are all negative effects of high salt levels in the soil. Detoxification of ROS may play a vital role in improving the salinity stress (SS) tolerance of plants. Plants use their receptors to detect risk and activate a protective native defence system to resist ROS. The accumulation of certain protective secondary metabolites such as phenolic compounds (PCs), terpenes, and alkaloids is one of these defensive mechanisms. PCs, in particular, operate as potent antioxidants and are essential for the plant's survival under salt stress. Enhanced PC synthesis ensures the plants' survival, tenacity, competitiveness, and endurance against SS.

Keywords

Abiotic stress · Salinity · Phenolics · Oxidative stress · ROS

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16.1 Introduction

Stress is defined as any unfavourable condition or substance that negatively impacts plant growth, metabolism, development, or productivity. Plants are subjected to a variety of environmental stresses (both biotic and abiotic), which inhibit their growth and alter the quality and amount of agricultural produce (Basu et al. 2016; Wang et al. 2016a, b; Anjum et al. 2017; Hussain et al. 2018). Abiotic stressors, such as drought, salt, cold, and high temperatures, affect 90% of arable lands, resulting in yield losses of up to 70% in the major food crops (Waqas et al. 2019). Drought is expected to reduce production by 17%, salinity by%, high temperature by 40%, low temperature by 15%, and other factors by 8% (Rehman et al. 2005; Ashraf et al. 2008). According to the estimates based on the combination of climate change and agricultural yield models, important crops such as rice, wheat, and maize will lose productivity even further, posing a serious threat to food security (Tigchelaar et al. 2018).

Salinity is one of the most important abiotic stresses, especially in arid and semiarid environments, where it causes several socio-economic concerns. According to reports, nearly 20% of the world's agricultural land is affected by salt (Martinez et al. 2016; Hussain et al. 2019). By 2050, it is anticipated that 50% of cultivable land will be affected by salinity (FAO 2008). A high concentration of soluble salts containing chlorides ($Cl-$) and sulphates of sodium (Na_2SO_4), calcium ($CaSO_4$), and magnesium ($MgSO_4$) characterises salinity ($MgSO_4$). Among them, sodium chloride (NaCl) is the most pervasive, soluble, and superabundant salt on the planet (Munns and Tester 2008; Fageria et al. 2012). Excess salt causes biochemical, morphological, physiological, and molecular alterations in plants, all of which have a negative impact on productivity and plant growth. SS causes disruption in ion!! homoeostasis and osmotic stress and results in the excess generation of ROS and subsequently oxidative damage (Ivanova et al. 2015; Zhu 2016). Plants have evolved an antioxidant defence mechanism that consists of enzymatic and non-enzymatic components that assist scavenge ROS to decrease the toxic effects of ROS accumulation. Among the enzymatic components, glutathione reductase (GR), peroxidase (POX), catalase (CAT), and superoxide dismutase (SOD) are the most important, while the non-enzymatic components mainly include carotenoids, PCs, and flavonoids (Almeselmani et al. 2006; Rivero et al. 2014). In plants, PCs play an important part in their response to SS (Lopez-Martínez et al. 2020). PCs have a strong ROS scavenging capacity, and their build-up is usually thought to be a beneficial self-protection mechanism in plants when they are exposed to salt-induced oxidative stress (Ahanger et al. 2017; Zhao et al. 2015). Honeysuckle leaf PCs, such as chlorogenic acid, were found to be enhanced as a mechanism for acclimatisation to SS was indicated in several studies (Yan et al. 2017). An increase in hydroxycinnamic acid content was reported in tomato plants exposed to SS (Martinez et al. 2016), although the precise role of PCs in combating oxidative stress during SS is still not clear. Therefore, much information about the protective role of plant PCs associated with the SS has been discussed in this chapter.

16.2 Soil Salinity

Soils containing excessive number of water-soluble salts carrying positive charge includes Mg^{2+}, Ca^{2+}, K^+, and Na^+ along with negative charge ions such as CO_3^{2-}, HCO^{3-}, NO^{3-}, SO_4^{2-}, and Cl^- in the root zones are termed as salt-affected soils (Rhoades and Miyamoto 1990). Soluble salts are present in all soils and natural water, and the amount of salts present in the root zone determines whether the soil is normal or salt-affected. When salt concentrations in the root zone approach critical levels, it has a negative impact on seed germination, plant growth, and yield (Conway 2001; Denise 2003). Highly soluble salts like NaCl, Na_2SO_4, $NaHCO_3$, and $MgCl_2$ result in more plant stress when compared to less soluble salts such as $CaCO_3$, $MgSO_4$, and $CaSO_4$. Saline soils can be classified into five major groups based on their salinity levels (Table 16.1). Studies reported that higher NaCl concentrations (200 mM) affected the growth of rapeseed sprouts (Falcinelli et al. 2017). Kaymakanova (2009) also found that germination %, seedlings growth, and respiration rate were decreased in response to NaCl and Na_2SO_4 treatment in bean cultivars.

16.3 An Overview of Salinity Issues Globally

The land surface of the earth is nearly 13.2×10^9 ha, out of which only 7×10^9 ha is arable. At present, the total cultivated area is 1.5×10^9 ha, out of which 0.34×10^9 ha (23%) is saline and 0.56×10^9 ha (37%) is sodic (Massoud 1981). The salinity problem is dynamic, affecting over 100 countries worldwide; no continent is completely free of salinity (Fig. 16.1). Abrol et al. (1988) reported in FAO soils bulletin 39 for different continents, presenting 932.2 Mha of salt-affected soils in the world (Table 16.2).

The majority of countries affected by salinisation are located in arid and semiarid regions, where poor-quality groundwater is used for agriculture (Massoud 1974; Ponnamperuma 1984). The Aral Sea basin in Central Asia, the Indo-Gangetic basin in India, the Indus basin in Pakistan, the Yellow River basin in China, the Euphrates basin in Syria and Iraq, the Murray-Darling basin in Australia, and the San Joaquin valley in the United States are just a few of the prominent regions where salinisation has been widely reported (Qadir et al. 2014). In Asia, salinity affects around 20% of India's cultivable land, primarily in coastal Gujarat, Rajasthan, and the

Table 16.1 Classification of saline soils

Depth of soil	Non-salinity	Weak salinity	Moderate salinity	Strongly salinity	Very strongly salinity
0–60 cm (0–2 ft)	2 dS/m	2–4 dS/m	4–8 dS/m	8–16 dS/m	>16 dS/m
60–120 cm (2–4 ft)	<4 dS/m	4–8 dS/m	8–16 dS/m	16–24 dS/m	>24 dS/m

dS deci-Siemens, pH of saline soil <8.5

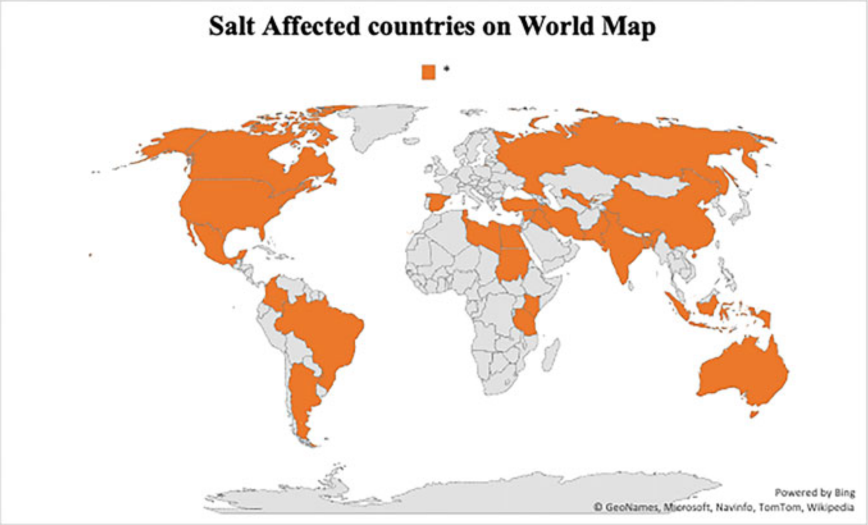


Fig. 16.1 World map depicting countries with salinity problems (adapted and modified from Pavuluri 2014)

Table 16.2 Worldwide distribution of salt-affected areas (Mha)

Area	Sodic soils	Saline soils	Total	Percent
Europe	22.9	7.8	30.8	3.30
Africa	26.9	53.5	80.4	8.60
America	69.3	77.6	146.9	15.8
Asia	121.9	194.7	316.5	33.9
Australasia	340.0	17.6	357.6	38.4
World	581.0	351.2	932.2	100

Source: Abrol et al. (1988)

Indo-Gangetic plains. According to the ICAR-Central Soil Salinity Research Institute, Karnal database, India has a salinity problem of 6.74 million hectares, with 3.78 million hectares of sodic soils and 2.96 million hectares of saline soils (Mandal et al. 2010). Table 16.3 shows the extent and distribution of salt-affected soils in various Indian states. Gujarat (2.20 Mha) and Uttar Pradesh (1.37 Mha) are the Indian states with the most salt-affected soils.

16.4 Causes of Soil Salinity

Because of its negative influence on agricultural production and sustainability, soil salinity is a critical global issue. Salinity issues can occur in any climate and can be caused by both natural and human-induced activities (Flowers 2004; Zaman et al. 2018). Many factors contribute to salinisation, including salt content, soil chemistry, climate, ground topography, and anthropogenic impacts (Blumwald 2000). Also, the

Table 16.3 Distribution of the salt-affected areas in India

State	Coastal saline soil (ha)	Alkali soils (ha)	Saline soils (ha)	Total (ha)
West Bengal	441,272	0	0	441,272
Uttar Pradesh	0	1,346,971	21,989	1,368,960
Tamil Nadu	13,231	354,784	0	368,015
Rajasthan	0	179,371	195,571	374,942
Punjab	0	151,717	0	151,717
Orissa	147,138	0	0	147,138
Madhya Pradesh	0	139,720	0	139,720
Maharashtra	6996	422,670	177,093	606,759
Kerala	20,000	0	0	20,000
Karnataka	586	148,136	1307	150,029
J & K*	0	17,500	0	17,500
Haryana	0	183,399	49,157	232,556
Gujarat	462,315	541,430	1,218,255	2,222,000
Bihar	0	105,852	47,301	153,153
A & N islands	77,000	0	0	77,000
Andhra Pradesh	77,598	196,609	0	274,207
Total	1,246,136	3,788,159	1,710,673	6,744,968

Source: Mandal et al. (2010)

intensity of soil salinisation relies on the type and amount of salts, their relative abundance in the soil, degree of solubility, and effect on soil pH (Dheeravathu et al. 2018). Inherent soil salinity (weathering of rocks, parent material); use of poor-quality irrigation water as well as poor drainage; unsustainable irrigation practices (heavy irrigation); high evaporation; previous exposure of land to seawater; and dumping of industrial brine into the soil are just a few of the main causes of salinity (Shrivastava and Rajesh 2015).

16.5 Salinity Effects on Plants

Salinity in soil and water is major stress induced by higher levels of salts, particularly high Na^+ and Cl. Salt reduces plant growth and productivity at low concentrations, but at higher concentrations, it can inhibit plant growth (Parida and Das 2005). The detrimental effects of SS on the plant are related to low water potential, ion imbalance, nutritional imbalance, and toxicity. They all have negative physiological, biochemical, and molecular effects on plants (Banerjee and Roychoudhury 2018). Ion imbalance is caused by the accumulation of Na^+ and Cl^- in tissues/plants exposed to elevated NaCl concentrations, resulting in an altered Na^+/K^+ ratio. External Na^+ limits the uptake of K+, a critical ingredient for plant growth and development, resulting in lower productivity and even death. Changes in K+ can disrupt osmotic equilibrium, stomatal function, and the operation of certain enzymes (James et al. 2011; Iqbal et al. 2015). Salinity has been shown to increase Na+ and

Cl^- concentrations while decreasing the K+/Na+ ratio in *Vicia faba* in previous studies (Gadallah 1999). Under SS, the mangrove, *Bruguiera parviflora*, showed a significant rise in Na^+ and Cl^- content (Parida and Das 2004). Salinity induces the production of ROS such as singlet oxygen ($^1O_2$), hydroxyl radical (•OH), H_2O_2 (hydrogen peroxide), and superoxide ($O_2^{\bullet -}$) which are toxic to plant metabolism. Salinity-induced ROS generation interferes with the cellular functions of plants and can cause oxidative damage in various macromolecules such as nucleic acids, proteins, and lipids (Gupta and Huang 2014; Del-Rio 2015). Na^+ concentrations above 100 mM are hazardous to cell metabolism, causing critical enzyme inhibition, membrane instability, and osmotic imbalance. SS reduces the quantum efficiency of PSII and Rubisco activity by affecting physiological and metabolic processes such as the photosynthetic pathway, photosynthetic pigments such as chlorophyll, and total carotenoid content. Other physiological functions such as respiration, glycolysis, soluble protein, nitrogen fixation, and disruption of the electron transport system (ETS) in chloroplasts and mitochondria are also affected by SS (Khan et al. 2009; Mittal et al. 2012; Iqbal et al. 2015). Disturbances in photosynthetic ETS due to SS induced the production of ROS into the cells resulting in photoinhibition and photooxidative damages (Gururani et al. 2015). Degradation of chlorophyll in crops like *Thymus* species can also indicate the negative effects of salt (Bistgani et al. 2019). Under high SS, the aminolevulinic acid synthase enzyme, which is the major precursor of chlorophyll production, is altered, resulting in a decrease in chlorophyll concentration (Santos 2004). Growth and metabolism are suppressed by SS, but tolerance limits and growth rate reduction at various toxic salt concentrations vary among plant species (Parida and Das 2005).

16.6 Salt Tolerance in Plants

A plant's ability to develop and complete its life cycle in a medium with a high concentration of soluble salts is known as salt tolerance. During the growth season, salt tolerance is usually quantified as the relative yield of a certain crop in salty soil compared to nonsaline circumstances (Munns 2002). Glycophytes are crop species that are extremely sensitive to soil salt and cannot grow at 100 mM NaCl. On the other hand, halophytes are highly tolerant to SS. They are native to saline soils and can grow at 250 mM NaCl (Hernandez and Almansa 2002; Flowers and Colmer 2015; Parida and Das 2005). Plants vary widely in terms of their tolerance to salinity with different growth stages. Barley (*Hordeum vulgare*), for example, is the most tolerant cereal, whereas rice (*Oryza sativa*) is the most sensitive. Plants that are sensitive to salt are divided into four categories: sensitive, moderately sensitive, moderately tolerant, and tolerant (Table 16.4).

Salinity tolerance is a complex feature that results from a combination of physiological, biochemical, and molecular interactions (Tang et al. 2015). Any changes in morphological appearance during SS are not sufficient to identify the effect and consequently design the management approaches (Ahanger et al. 2017). Plants adopt a variety of physiological, biochemical, and molecular mechanisms to deal with SS

Table 16.4 Classification of some crops based on salt tolerance

Sensitive	Tolerant	Moderately tolerant	Moderately sensitive
Rice	Barley	Sorghum	Chickpea
Sesame	Canola	Soybean	Corn and corn (forage)
Black bean	Cotton	Sunflower	Peanut
Pigeon pea	Guar	Wheat	Sugarcane
Walnut	Oats and forage oats	Barely (forage)	Alfalfa
Mango	Rye and forage rye	Guinea grass	Berseem
Banana	Triticale	Dhaincha	Cowpea (forage)
Apricot	Sugar beet	Rhodes grass	Clover
Banana	Asparagus	Pineapple	Lablab bean
Blackberry	Date palm	Wild rye	Foxtail millet
Carrot	Jojoba	Squash	Sesbania
Grapefruit	Salt grass, desert	Olive	Cassava
Avocado	Bermuda grass	Coconut	Broccoli
Apple	Wheatgrass, tall	Artichoke	Spinach
Orange	Natal plum	Safflower	Sweet potato

to limit toxicity and increase yield (Koyro 2006; Stepien and Johnson 2009). To understand which physiological systems are responsible for plant salinity tolerance, it's necessary to know if the osmotic effect of salt in the soil or the toxic effect of salt within the plant suppresses growth (Munns and Tester 2008). Separation of ions, osmotic adjustment, generation of suitable solutes (proline, glycine betaine), salt exclusion or salt secretions, induction of plant hormones, induction of antioxidant enzymes (SOD, CAT, POX, GR), and accumulation of PCs are some of the biochemical techniques used (Parida and Das 2005; Zheng et al. 2010; Sharma et al. 2019). Few halophytes (*Atriplex*, *Plumbago)* and some mangrove species (*Avicennia and Acanthus*) bear multicellular salt glands which secrete excess salts at leaf surfaces (Hasanuzzaman et al. 2013). Studies on *Brassica napus* cultivars showed increased accumulation of proline during SS (Rezaei et al. 2017). A positive correlation has been noticed between the accumulation of glycine betaine and polyamine in stress tolerance in quinoa varieties (Adolf et al. 2013). Activities of different enzymes such as ascorbate peroxidase (APX), POX, CAT, and glutathione S-transferase (GST) are upregulated in response to SS in *Chenopodium quinoa* (Causin et al. 2020).

Changes in the plant transcriptome, metabolome, and proteome are among the molecular processes of salt tolerance (Banerjee and Roychoudhury 2018). Different families of transcriptional factors, such as activator protein (AP2), basic leucine zipper (bZIP), ERF, MYB, and WRKY, all show strong relationships with SS (Kumar et al. 2017). Several studies noted that different transcriptional factors induce the overexpression of many genes in response to SS. Enhanced expression of *GmDREB2*, *MtCBF4* in *Arabidopsis thaliana* (Chen et al. 2007), bZIP gene in *Tamarix hispida* (Wang et al. 2010) provides tolerance against SS.

16.7 PC Accumulation Under SS

PCs are a diverse group of plant secondary metabolites. PC and its derivatives including anthocyanins, coumarins, isoflavonoids, flavonoids, tannins, and lignins play pivotal roles throughout the life cycle of the plant (Tomar and Agarwal 2013). PCs are aromatic molecules with one or more hydroxyl groups that come from diverse developmental phases and environmental influences, such as shikimate and phenylpropanoid (PP) pathways (Tomar et al. 2015; Patra et al. 2013). Plants rely on PCs for growth, development, and reproduction. They act as defence compounds against abiotic and biotic stresses (Lattanzio 2013). During abiotic stress conditions, the biosynthesis of most PCs such as phenolic acids, flavonoids, lignin, and tannins increases, which helps the plant cope with environmental constraints. Under abiotic stress conditions (drought, heavy metals, salt, high/low temperature, and ultraviolet radiations), the PP biosynthetic pathway is activated, resulting in the accumulation of different PCs that can alleviate oxidative stress and scavenge damaging ROS (Rossi et al. 2016; Borges et al. 2017). Plants under SS vary in composition and PC content, which is both genetically and environmentally controlled (Awika and Rooney 2004). A literature survey reported the increase in PCs in different plant tissues during SS (Table 16.5). The higher PC contents and antioxidant activities were noticed in *Salvia mirzayanii* and red pepper plants in response to SS (Navarro et al. 2006; Valifard et al. 2014). Environmental factors have an impact on PC biosynthetic pathways, as their regulation and gene expression are altered in response to various stresses. In the case of SS, the altered activity of various key enzymes in the shikimate and PP pathways governs PC production (Lattanzio 2013; Martinez et al. 2016; Sanchita 2018). A detailed discussion on how plants manage SS through the accumulation of PCs is discussed in the following section.

16.8 Mechanism of Action of PCs in Salinity Stress Management

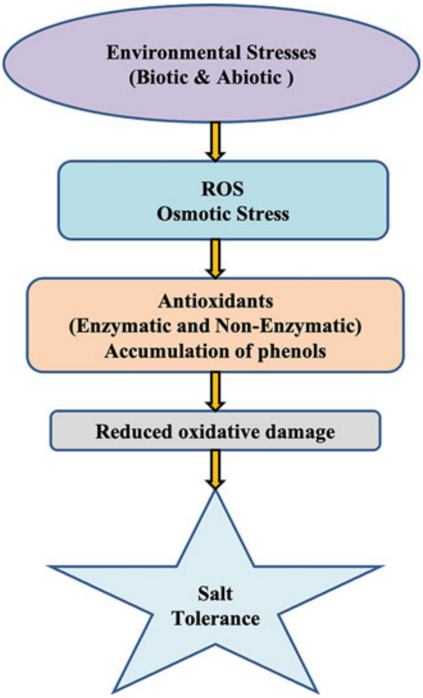
SS causes the production of ROS like H_2O_2, $O_2^{\bullet -}$, and •OH and requires a strong antioxidant system to combat the ROS propagation (Taibi et al. 2016). During SS, PCs act as powerful antioxidants and participate in plant protection against ROS (Bistgani et al. 2019) (Fig. 16.2).

PCs displayed an antioxidant activity by preventing the breakdown of hydroperoxides into free radicals or by deactivating the free radicals (Valifard et al. 2014). Furthermore, the changed activities of numerous important enzymes in PC biosynthetic pathways govern PC production in response to SS (Rossi et al. 2016). Upregulation of enzymes is followed by increased transcript levels of genes encoding important biosynthetic enzymes such as F3RT (flavonoid 3-O-rhamnosyltransferase), F3GT (flavonoid 3-O-glucosyltransferase), FLS (flavanol synthase), F3′H (flavonoid-3′-hydroxylase), F3H (flavanone3-hydroxylase), CHI (chalcone isomerase), CHS (chalcone synthase), C3H (cinnamate 4-hydroxylase), 4CL (4-coumarate coenzyme A ligase), C4H (cinnamate 4-hydroxylase), PAL (phenylalanine-ammonia lyase), SK (shikimate kinase), SDH (shikimate

Table 16.5 Phenolic compounds in salinity stress management

Plant/crop	Response of endogenous phenolics during salinity stress	References
Hypericum pruinatum	Increase of PCs, namely, chlorogenic acid, rutin, quercitrin, isoquercitrin, and hyperoside	Caliskan et al. (2017)
Salvia mirzayani	Accumulation of PCs and antioxidant activity	Valifard et al. 2014)
Rice (*Oryza sativa L.*)	Cell wall-bound PC ferulic acid and 4-hydroxycinnamic acid were increased	Gupta and De (2017)
Thymus vulgaris L.	Increase of PC content and radical scavenging activity	Bistgani et al. (2019)
Honeysuckle (*Lonicera japonica* Thunb.)	Increased production of chlorogenic acid and luteolosid	Yan et al. (2017)
Artichoke (*Cynara scolymus* L.)	Caffeic and chlorogenic acid accumulation increased	Rezazadeh et al. (2012)
Amaranthus tricolor	Gallic acid, vanillic acid, ferulic acid, isoquercitrin content increased	Sarker and Oba (2018)
Asparagus aethiopicus	Increased chlorogenic acid, caffeic acid, and rutin content	Al-Ghamdi and Elansary (2018)
Carthamus tinctorius	Total PC and flavonoid content increased	Wang et al. (2016a, b)
Chenopodium quinoa	Total PC and flavonoid content increased	Aloisi et al. (2016)
Cynara cardunculus	Increased gallocatechin, quercitrin, and leucocyanidin content	Lucini et al. (2016)
Hordeum vulgare	Increased total phenolic content	Ma et al. (2019)
Mentha piperita	Increased total phenolic content	Coban and GokturkBaydar (2016)
Ocimum bascilicum	Increased caffeic acids, cinnamyl malic acid, and quercetin	Scagel et al. (2019)
Olea europaea	Total phenolics, kaempferol, and quercetin	Rossi et al. (2016)
Salvia mirzayanii	Increased total phenolic content	Valifard et al. (2014)
Solanum lycopersicon	Increased total caffeoylquinic acid content	Martinez et al. (2016)
Solanum villosum	Increased caffeic acid, total phenolic, and quercetin	Ben-Abdallah et al. (2019)
White cabbage (*Brassica oleracea* var. capitata)	Increased hydroxycinnamic acids	Linic et al. (2019)
Rapeseed (*Brassica napus* var. oleifera)	Increase in contents of PCs	Falcinelli et al. (2017)
Achillea fragrantissima	Increase in contents of PCs	Abd El-Azim and Ahmed (2009)

Fig. 16.2 Flow chart indicating phenolic salinity stress tolerance mechanisms



dehydrogenase), and DAHPS (3-deoxy-D-arabino-heptulosonate) (Fig. 16.3). The enzyme DAHPS is highly upregulated under all stresses including salinity and is a key determinant governing the carbon flow into the shikimate pathway (Zhang et al. 2015). The other enzymes SHD and SK of shikimate pathway as well as the expression level of their transcripts were also upregulated. L-phenylalanine, an essential amino acid for the formation of hydroxycinnamic acids, is produced by the shikimate pathway. The amino acid L-phenylalanine is generated higher during SS (Hoque et al. 2020). This is also in agreement with the levels of L-phenylalanine produce several folds higher than in control in tomato plants under SS (Martinez et al. 2016). Following the shikimate pathway, L-phenylalanine is transformed into cinnamic acid, which leads to the creation of other phenolic compounds (Fig. 16.3, PP pathway). Several key enzymes, such as PAL, C4H, and 4CL, participate in the synthesis of cinnamic acid, p-coumaric acid, and p-coumaryl-CoA from L-phenylalanine (Besseau et al. 2007; Ferrer et al. 2008). The major enzyme in the PP pathway, PAL, transforms phenylalanine to cinnamic acid and is significantly upregulated in response to a variety of environmental stressors. In olive trees, the number of PAL and their transcripts increases in response to SS, according to studies (Rossi et al. 2016). Under SS, the expression levels of several enzymes such as PAL, C4H, and 4CL were many times greater and were also strongly linked with the concentrations of various substances such as cinnamic acid, p-coumaric acid, and p-coumaryl-CoA (Martinez et al. 2016). p-Coumaryl-CoA produced in PP pathway is

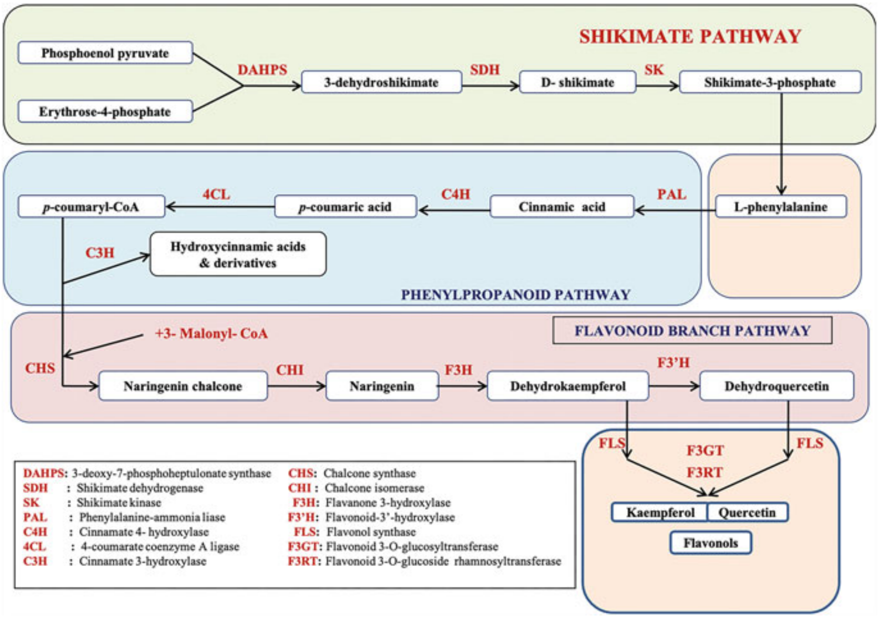


Fig. 16.3 Schematic representation of the regulation of phenol metabolism in response to salinity stress (adapted and modified from Martinez et al. 2016)

used as a substrate for the synthesis of hydroxycinnamic acids or flavonols (flavonol-branched pathway). With the help of the enzyme C3H, p-coumaryl-CoA is transformed into hydroxycinnamic acids and derivatives (Ferrer et al. 2008). SS induces the upregulation of enzyme C3H and resulted in overaccumulation of hydroxycinnamic acids and derivatives. The major factor for flavonoid production is chalcone synthase (CHS). This enzyme CHS catalyses the conversion of p-coumaryl-CoA and three molecules of malonyl-CoA into naringenin chalcone, starting the flavonoid production process (Fig. 16.3, Flavonoid branch pathway). From naringenin chalcone, production of other compounds like naringenin, flavonols, and other derivatives is regulated by different enzymes like CHI, F3H, FLS, F3GT, and F3RT, respectively. Studies reported that higher amounts of PCs like quercetin, caffeic, ferulic, and apigenin are accumulated in response to salinity stress in *Thymus* species (Bistgani et al. 2019). Salicylic acid plays a function in increasing salinity tolerance mechanisms in a variety of crops, including *Vicia faba*, *Brassica juncea*, *Medicago sativa*, and *V. radiata* (Jini and Joseph 2017; Khan et al. 2015).

16.9 Conclusion and Future Prospective

Salinity has become a major environmental issue that has a negative impact on plant growth and development. Because SS impacts plant cellular activity, agricultural output suffers and the farmer loses money. A recent salt stress study has shown that PCs such as phenols, polyphenols, flavonoids, anthocyanin, and phenolic acids increase plant tolerance. PCs protect plants from salt stress in a variety of ways, including reactive oxygen species detoxification, physiological and metabolic process regulation, and cell integrity maintenance. Aside from the vast amount of information available on PCs, more study is needed to determine the involvement of specialised PCs in response to salinity stress and to define the intimal molecular process that switches from primary metabolism to activation of the PP pathway in response to SS.

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Ameliorative Effects of Phenolics in Oxidative Stress Management in Plants

17

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Abstract

Oxidative stress is a result of a changing environment, and it decreases plant development and production due to decreased photosynthesis and other essential cellular functions caused by oxidative damage to biomolecules, which is a result of abiotic or biotic stresses. Stress leads plants to produce reactive oxygen species (ROS) such as superoxide ions, hydroxyl ions, and singlet oxygen, which trigger a chain of degenerative reactions. Biotic and abiotic stressors are the most common causes of extensive agricultural output loss around the world, posing a serious threat to food security. A loss of roughly 50% of major agricultural productivity is believed to be caused by various abiotic stress factors. Plants respond to abiotic stress in three steps which involve perception of the stress stimulus by the oxidative stress (OS) receptors; activation of a chain of protein kinases and other proteins, i.e., signaling; and defense response against the stressors. As part of the body's defense mechanism, terpenes, alkaloids, and phenolics are increased in expression. Phenolic compounds, which have a high antioxidant activity, accumulate throughout OS and play an important role in the regulation of OS in plants. Stress management against oxidative stressors is the primary focus of this chapter. As a bonus, it sheds information on the potential mechanism by which phenolics work to alleviate the symptoms of OS.

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17.1 Introduction

17.1.1 Oxidative Stress (OS)

OS is a state of free radical (FR) burst that occurs when the pace of FR formation surpasses the antioxidant defense mechanisms' capacity, resulting in an imbalance between FR production and neutralization with a shift toward the former. When an atomic, molecular, or ionic compound possesses an unpaired electron, it is referred to as FR. Most FRs are reactive oxygen species (ROS); however, nitrogen species (RNS) and transition metals (or carbon-centered FRs) can also develop. As electrons leak from chloroplast and mitochondrial electron transport pathways, ROS are generated, which are the major FRs. ROS is also formed as a result of various additional metabolic pathways in aerobic organisms (Foyer 1997; Blokhina and Fagerstedt 2010; Heyno et al. 2011). Hydroperoxyl radical ($HO_2^{\bullet}$), hydrogen peroxide (H_2O_2), superoxide anion (O^{2-}), hydroxyl radical ($OH^{\bullet}$), singlet oxygen ($^1O_2$), and hypochlorous acid are examples of radical and non-radical ROS (Collin 2019). At normal concentrations, these FRs are involved in signaling, cellular defense, and maintaining homeostasis. In order to stabilize, they must first react with biomolecules and either give or remove an electron from them, causing oxidative damage to cellular organelles due to their high instability and chemical reactivity (Ali and Alqurainy 2006).

Organelles such as chloroplasts, peroxisomes, and mitochondria are crucial to the production of ROS in plants, as they are involved with electron transport and energy transfer, as well as photorespiration. Secondary sites of ROS generation include the cell membrane, endoplasmic reticulum (ER), cell wall, and apoplast. Due to its unpaired electrons and parallel spin in its ground state, oxygen does not have a great deal of reactiveness. But the physical and chemical activation reactions transform oxygen into its excited or activated state which is detrimental for the plant (Apel and Hirt 2004). Physical activation is caused by the spin reversal on the unpaired electrons by the energy transfer. In plants, the sufficient energy required for inverting the spin may be transferred to oxygen from an excited chlorophyll molecule of photosystem II (PS II) that is formed as a consequence of insufficient energy dissipation during photosynthesis due to low CO_2 concentration caused by stomatal closure that is triggered by environmental stresses such as heavy metals, salt, and drought. As a result of spin constraint, complete oxygen reduction to water does not allow for chemical activation (Halliwell and Gutteridge 1984).

The absorption of sufficient energy causes the spin reversal of one of the unpaired electrons in molecular oxygen, allowing it to engage in two electron transfer processes, resulting in the production of $^1O_2$ due to activation of oxygen through both physical and chemical means. A variety of ROS are produced as a result of energy transfer reactions like $O_2^{\bullet-}$, $OH^{\bullet}$, H_2O_2, and $^1O_2$. By exchanging energy with molecular oxygen, chlorophyll molecules in their triplet state produce $^1O_2$. It causes damage to both PS and thus decreases the photosynthetic efficiency. Additionally, it may cause cell death in its short half-life of 3 μs, by targeting cellular nucleic acids, proteins, pigments, and lipids (Hatz et al. 2007; Wagner et al. 2004; Krieger-Liszkay et al. 2008). $O^{2-\bullet}$ can be produced either by the chemical activation of oxygen or transfer of energy to oxygen. It is generated in the thylakoid membranes of chloroplast at PSI due to reaction of oxygen with the components of ETC other than cytochrome c oxidase. Although it is fairly reactive and has a short half-life, it does not cause much damage on its own but is transformed into more reactive and poisonous FR species, such as $OH^{\bullet}$ and $^1O_2$. After its formation, $O_2^{\bullet-}$ further reacts and forms other ROS either directly or by initiating a cascade of enzyme- or metal-catalyzed chain reactions as it has both oxidizing and reducing properties. By accepting one electron and two protons, $O^{2\bullet-}$ gets transformed into H_2O_2 either nonenzymatically that is induced by low cellular pH or by a reaction catalyzed by superoxide dismutase (SOD). The half-life of H_2O_2 is significantly longer than that of other FR species. Fenton's reaction, a process catalyzed by transition metals (Fe^{2+}, Fe^{3+}) that results in the creation of $OH^{\bullet}$, occurs when H_2O_2 combines with O_2. It causes damage to membranes by peroxidation of lipids and other biomolecules either by removing a proton or by adding to the organic molecules. $OH^{\bullet}$ is the most toxic ROS as it reacts with oxygen in the triplet state due to the existence of single unpaired electron and moreover cell does not possess enzymatic machinery required for its neutralization, and thus it causes cell death when produced in excess.

Aerobic metabolism inevitably leads to the production of FRs. The amount of ROS present in a plant cell determines whether the molecule will have a favorable or negative impact on the plant. While they serve as stress signaling molecules when present in low quantities, they injure cellular components when present in high amounts (Das and Roychoudhury 2014). To keep ROS formation and neutralization in balance, plants use a number of enzymes and nonenzymatic processes. The complete elimination of ROS will lead to loss of an important signaling molecule, and therefore their basal level should be maintained. But when plants get exposed to environmental stresses (abiotic, biotic), that balance gets disturbed leading to a shift of equilibrium toward the production of FRs. Plants, unlike animals, are sessile, making them vulnerable to environmental stresses such as salinity, heat, cold, heavy metal toxicity, and pathogen attack. As a consequence, plants produce ROS as an initial step of their defense response which play a protective role due to their signaling role in activating many defense pathways and also due to their toxicity to pathogens. But continuous exposure to stressful conditions for a long duration enhances the rate of generation of ROS which exceeds the neutralization capacity of cellular defense mechanism resulting in a state of OS (Xie et al. 2019).

17.1.2 Phenolic Compounds

Apart from primary metabolic chemicals, plants also produce a large diversity of secondary metabolites to cope with adverse environmental conditions. A wide class of secondary metabolites known as phenolic compounds helps plants deal with biotic (drought, high temperature, salinity, cold, heavy metals, and low nutritional levels) and abiotic challenges (pathogen attack, herbivory, insectivory). Plant phenolics may be categorized as preformed phenolics and induced phenolics. Preformed phenolics are synthesized constitutively in the plant tissues and are present even in the absence of any stress, whereas induced phenolics are synthesized in response to stress. However, some induced phenolics may also be synthesized constitutively at a basal level, but their synthesis is upregulated when plants encounter stress (Winkel-Shirley 2002). In addition to their role in defense, phenolics also have roles in various metabolic and physiological processes like seed germination, cell division, synthesis of pigments, and many more as they are present at a basal level throughout the life cycle of plant (Senaratna et al. 2000; Nazar et al. 2011). Phenolic compounds in plants are biosynthesized by shikimic acid pathway with erythrose 4-phosphate and phosphoenolpyruvate (PEP) acting as the precursor compounds which react with each other to form phenylalanine which is then converted into trans-cinnamic acid in a reaction catalyzed by phenylalanine ammonia-lyase (PAL). In plants, there are many mechanisms to produce phenolic chemicals. The glycolytic and pentose phosphate pathways produce phosphoenolpyruvate and erythrose 4-phosphate, respectively. These precursors are fed to the shikimate route for the synthesis of phenylalanine, the precursor of phenylpropanoid pathway which produces phenolic compounds and also the precursors for feeding into the diverse flavonoid biosynthesis pathways (Soto-Hernández et al. 2019). Structures of phenolic compounds have aromatic rings and hydroxyl groups (Chirinos et al. 2009; Kumar and Pruthi 2014). There is a great structural diversity in compounds within the class based on the number and position of phenol rings and hydroxyl groups present, and this variation in turn influences the physical, chemical, biological properties and functions of particular compounds. Phenolics have also been categorized in several ways like the number of carbon atoms present in them. The categories of phenolic compounds based on the number of carbon atoms include simple phenol, benzoquinones (C6), phenolic acids (C6–C1), acetophenone, phenylacetic acid (C6–C2), hydroxycinnamic acid, coumarin, phenylpropanes, chromones (C6–C3), naphthoquinones (C6–C4), xanthones (C6–C1–C6), stilbenes, anthraquinones (C6–C2–C6), flavonoids, isoflavonoids, neoflavonoids (C6–C3–C6), lignans, neolignans, (C6–C3)2, catechol melanins (C6)n, condensed tannins (C6–C3–C6)n, and lignins (C6–C3)n. The class also includes flavonoids (C6–C3–C6) and stilbenes (C6–C2–C6), compounds with intermediate molecular weight (Whiting 2001; Ahmed et al. 2020). Flavonoids and phenolic acids, for example, possess antibacterial and other bioactive characteristics in addition to their antioxidant activity (Lone et al. 2020).

17.1.3 Role of Phenolics in OS

The exposure of plants to abiotic or biotic stresses causes change in expression pattern of several genes and thereby diverts the metabolism toward the synthesis of several defense compounds. Phenolic compounds like flavonoids, phenolic acids, tannins, lignins, and hydroxycinnamate esters are the most widely distributed plant defense compounds. The tremendous antioxidant potential of the plant phenolics confers them the ability to act as defense compounds against the oxidative damage caused by various environmental stresses like high temperature, drought, saline soil, herbivore attack, pathogen infection, and many more, since the generation of ROS is enhanced under stress conditions (Dar et al. 2017). Synthesis of phenolic compounds takes place constitutively in most of the plants so as to maintain their basal levels, but their synthesis gets upregulated in response to abiotic and biotic stress stimulus as these compounds play an active role as defense compounds in coping with the stress conditions (Selmar 2008; Sharma et al. 2019). Accumulation of phenolics during stressful conditions results from the enhanced expression and performance of key enzymes involved in their biosynthetic pathway like PAL, 4CL (4-coumarate-CoA ligase), C4H (cinnamate-4-hydroxylase), and chalcone synthase (CHS). Since phenolic compounds have strong antioxidant activity, they neutralize FRs by either scavenging them or chelating redox-active metal ions and thereby terminate the chain reactions responsible for causing lipid peroxidation (Schroeter et al. 2002). The antioxidative properties of phenolic compounds are attributed to their structural features, which make them hydrogen or electron donors, chelators of transition metals, and FR chain breakers (Rice-Evans et al. 1997).

In this chapter, we have thoroughly examined the role of phenolic chemicals in protecting plants against the OS. It begins with the elicitors that cause the OS and then moves on to the treatment for stress relief provided by phenolic chemicals.

17.2 Elicitors of OS

17.2.1 Abiotic Stressors

Every type of abiotic stress like salt, drought, heat, cold, and osmotic stress elicits OS as FRs such as O_2^-, H_2O_2, and $OH^\bullet$ are produced in excess whenever plants are exposed to stressful conditions due to impairment of homeostasis of cellular oxidation-reduction. Plants employ a variety of antioxidant defense mechanisms to scavenge FRs and protect themselves from oxidation-induced cellular damage during stressful situations.

17.2.1.1 Drought

Drought stress causes stomatal closure, which reduces water loss through transpiration but reduces carbon dioxide fixation. Reduced internal levels of carbon dioxide affect the efficiency of Calvin cycle and thereby result in decreased regeneration of $NADP^+$ (electron acceptor). The lack of $NADP^+$ and moreover continuous exposure to sunlight result in leakage of electrons to O_2, and thus enhanced generation of ROS takes place at PSI via the chloroplast Mehler reaction (Asada 2006). H_2O_2 production is triggered by drought stress when there is a mismatch between carbon dioxide absorption and sunshine intensity (Noctor et al. 2002). Role of ROS on plant growth and development is impaired by the damage to biomolecules that occurs when plants are exposed to drought conditions.

17.2.1.2 Salt Stress

As a result of salt stress, plants lower their stomatal conductance in order to prevent excessive water loss, which results in reduced gas exchange and hence a decreased absorption of CO_2. The efficiency of Calvin cycle gets reduced by the decreased cellular carbon dioxide concentration resulting in decreased regeneration of $NADP^+$, the final electron acceptor in PS I, and therefore electrons are instead transferred to O_2 leading to the generation of O^{2-} by Mehler reaction (Elstner 1991). The imbalance between light harvesting and photosynthesis causes insufficient energy dissipation in photosynthesis and thereby results in the formation of excited chlorophyll in PS II that transfers its energy to molecular O_2 and thereby leads to the formation of $^1O_2$ (Krieger-Liszkay et al. 2008). Another reason of ROS generation during salt stress may be the disruption of photosynthetic electron transport chain by Na^+/Cl^- toxicity which causes leakage of electrons to O_2 (Gossett et al. 1994; Slesak et al. 2008). Moreover, reduced intracellular carbon dioxide concentration results in a decrease in the ratio of CO_2/O_2, thereby resulting in photorespiration in C3 plants and thus generation of more H_2O_2 in the peroxisome (Wingler et al. 2000; Ghannoum 2009). Under osmotic stress, photorespiration is responsible for more than 70% of H_2O_2 generation (Noctor et al. 2002). Salinity stress also activates cell membrane-bound NADPH oxidase and apoplastic diamine oxidase, which contribute to the generation of ROS in the apoplastic region (Rejeb et al. 2015; Tsai et al. 2005). Due to the unique methods that each organelle employs to produce ROS, their signaling role varies depending on the location of their production, such as the photosynthetic and respiratory electron transport chains as well as the peroxisome, apoplast, and cell wall.

17.2.1.3 Heat Stress

Peroxidation of membrane lipids, higher levels of ROS scavenging enzymes, and activation of numerous pathways and genes involved in the defense against OS are all signs of ROS formation in response to high temperatures (Davidson and Schiestl 2001; Larkindale and Knight 2002; Rizhsky et al. 2002; Vacca et al. 2004). According to a study, heat treatment caused the activation of pathways or processes involved in preventing oxidative damage in plants (Larkindale and Huang 2004). Since ROS is sensed by heat shock transcription factors (HSFs) and heat shock proteins (HSPs), some studies have indicated the role of ROS in the induction of signal transduction against heat stress involving HSFs and HSPs (Pnueli et al. 2003). A HSF-binding sequence at the promoter of the ascorbic peroxidase (APX1) gene has been shown to link heat stress to ROS production, which suggests that the activation of these heat stress-related proteins has a central role to play in defense against OS as they are involved in activating expression of enzymes like APX1 (Mittler and Zilinskas 1992; Storozhenko et al. 1998). Plants pretreated with ROS scavenging enzyme enhancers (calcium, salicylic acid, abscisic acid, and 1-aminocyclopropane-1-carboxylic acid) have enhanced heat tolerance, suggesting that heat stress induces the generation of ROS in plants (Larkindale and Knight 2002; Larkindale and Huang 2004).

17.2.1.4 Chilling Stress

ATP demand decreases due to slowing down of enzymatic activity as a consequence of exposure to cold conditions resulting in saturation or overflow of electrons during electron transport which in turn increases the generation of ROS (Okuda et al. 1992). Calvin cycle is also inhibited during chilling stress due to reduced activity of the pathway enzymes which causes an imbalance between the absorption of light and its use resulting in enhanced electron flux toward O_2 (Hu et al. 2008). Higher electron flow to O_2 and hence increased ROS formation are caused by a decrease in RUBISCO content and initial activity, as well as a decrease in the amounts of rbcL and rbcS transcripts due to chilling stress. The early RUBISCO activity and photosynthetic rate are adversely connected to H_2O_2 buildup in chloroplasts (Zhou et al. 2006). The presence of ROS, lipid peroxidation, protein oxidation, and increased antioxidant enzyme activity (APX, SOD, GR) in plants are all indications of OS (Zhang et al. 2008).

17.2.1.5 Heavy Metal Stress

Exposure to high amounts of heavy metal ions results in the overproduction of ROS by Haber-Weiss reaction especially accumulation of H_2O_2 which can be converted to highly toxic $OH^{\bullet}$ radicals in a metal-catalyzed reaction (Fenton's reaction) in the presence of redox-active transition metal ions such as copper (Cu) and iron (Fe). $OH^{\bullet}$ is very reactive FR species as it chemically modifies various cellular components irreversibly due to its radical initiating activity. Other heavy metals like zinc (Zn), mercury (Hg), nickel (Ni), and cadmium (Cd) cause OS by inhibiting the enzymatic and nonenzymatic antioxidant system since they do not possess redox activity. Heavy metals also disturb cellular processes in plants by disrupting the electron transport chain, interfering with the metal-catalyzed reactions, inactivating metalloenzymes, and causing peroxidation of membrane lipids (Caregnato et al. 2008). Excessive Cd exposure has been linked to decreased photosynthesis, respiration, and nitrogen metabolism as well as decreased water and nutrient absorption by plants, apart from chlorosis and plant death (Chen et al. 2010). Cd exposure also decreases the level of reduced glutathione (GSH) by converting it into phytochelatin (oligomeric form of glutathione) and sequestering it into the vacuoles (Nazar et al. 2011).

17.2.1.6 UV Light Stress

As a result of their dependence on sunlight for photosynthesis, plants are unable to withstand the sun's harmful UV rays. Plants suffer oxidative damage as a result of high ROS production and low CO_2 absorption by UV-B. UV radiation has been shown to increase the activity of NADPH oxidase, which produces ROS (Naikoo et al. 2019). ROS produced in plant cells disrupt protein structure, cause membrane lipid peroxidation, and create damaging DNA alterations by dimerizing thymine and causing photolytic damage to enzymes.

17.2.2 Biotic Stressors

17.2.2.1 Plant Pathogens

Oxidative burst in plants following pathogen attack is elicited by the pathogen-derived elicitors like bacterial and fungal peptides and carbohydrates (chitin, lipopolysaccharides, β-1-3-glucans). ROS are generated during pathogen attack due to impairment of the functioning of photosynthetic machinery. Several studies have reported that pathogen attack causes damaging effect on photosynthetic function of chloroplast by altering the structure of thylakoid membranes (Torres et al. 2006; Díaz-Vivancos et al. 2008). When pathogens attack a plant, ROS build up, triggering a series of communication cascades that activate plant defenses (Torres et al. 2006). There are a few enzymes that play a major role in the "oxidative surge" that occurs when the body is infected with a virus, such as respiratory burst oxidases (ROBHs) and peroxidases (PRX). Cell wall peroxidase or NADPH/NADH oxidase can be the source of ROS in the plasma membrane (Bolwell 1999). ROS play a defensive role during pathogen attack, but they lead to the death of plant tissues if their excess production is not controlled.

17.2.2.2 Insectivory/Herbivory

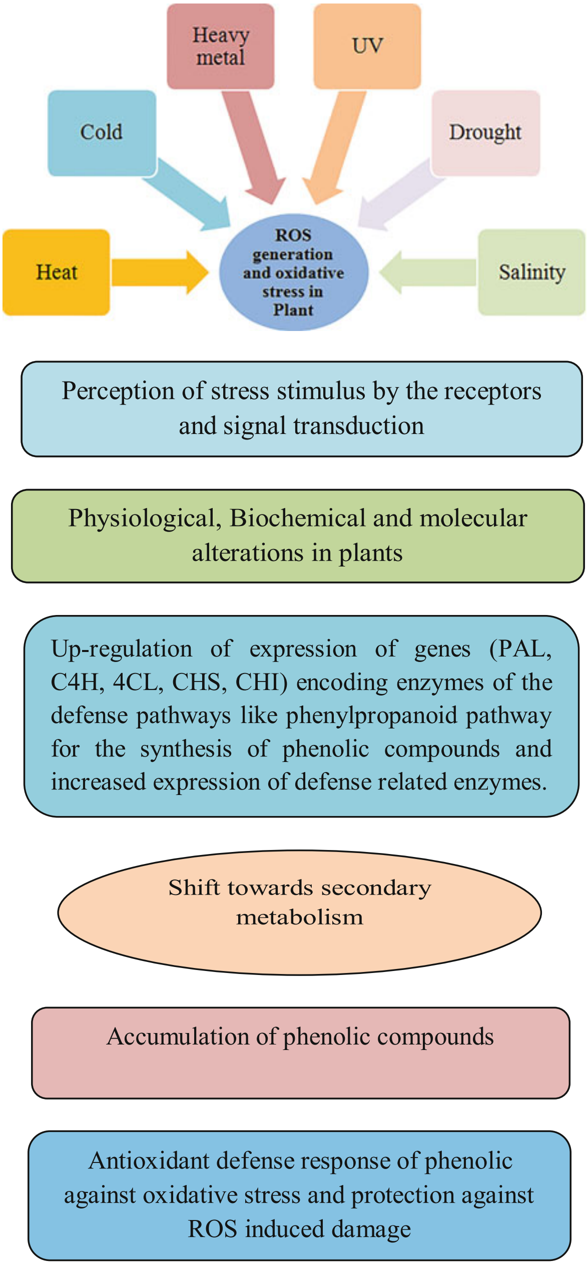
Any type of insect or herbivore attack is recognized by the perception of elicitor molecules either derived from the attacking insect as part of insect oral secretions or oviposition fluid or are produced in the plant tissues in response to the damage (Kessler and Baldwin 2002; Diezel et al. 2009; Bonaventure et al. 2011). The production of ROS like O_2^- and H_2O_2 is a rapid reaction to wounds that occurs in less than 5 min after the attack (Bolwell et al. 2002). With stress, a variety of enzymes, such as the cell wall-localized POX, which produces H_2O_2, and the plasma membrane-localized NADPH oxidase, produce ROS. Many apoplastic amines, diamines, and polyamine oxidase enzymes also create ROS (Sagi and Fluhr 2001; Torres et al. 2002). Insect salivary gland enzymes, such as glucose oxidase, can also produce H_2O_2, which could enhance ROS concentrations at the assault site (Dangl and Jones 2001).

17.3 Role of Phenolics in Combating Oxidative Stress

It is observed that almost every type of abiotic or biotic stress in plants ultimately results in oxidative damage and so most of the defense responses of the plant targets the OS to prevent damage induced by various types of stresses. In most of the cases, it has been found that plants respond to environmental stresses by switching their metabolism toward the synthesis of secondary metabolites especially phenolic compounds as these compounds have antioxidant activity which enable them to neutralize ROS generated by various types of stresses and thus they protect plant cells against the damaging effects of OS caused by stressful conditions (Schroeter et al. 2002; Selmar 2008). Stress-induced enhanced synthesis of phenolic compounds results from the alteration in biochemical and molecular pathways of the stressed plant like upregulation in the expression of genes encoding key enzymes (PAL, C4H, 4CL, CHS) involved in the phenol biosynthesis and enhanced activity of these enzymes due to some metabolic changes. Plant phenolics play a vital role in the defense mechanism when more FRs are produced in response to environmental stressors such as UV radiation, pathogen attack, drought, salinity, and extreme temperatures. Owing to their antioxidant properties, phenolic compounds scavenge ROS and thereby neutralize their damaging effects on plants (Šamec et al. 2021). Salicylic acid and its derivatives, as well as a number of other signal molecules, influence gene expression in response to stressful conditions (Winkel-Shirley 2002; Gould and Lister 2006; Nascimento and Fett-Neto 2010). Phenolic compounds have a crucial role in countering the OS induced by different types of stressors which may be due to their unique ways of antioxidant action. A schematic representation of defense response of plants against oxidative damage is shown in Fig. 17.1.

17.3.1 Role of Phenolics in Drought-Induced Oxidative Stress Management

Drought stress defense is a complex collection of biochemical, physiological, and molecular responses that work together to defend the plant from the deleterious effects of oxidative damage caused by drought. Accumulation of phenolic compounds is one of the nonenzymatic antioxidant defense mechanisms of plants which protect plants from ROS-produced damage as these compounds have strong antioxidant activity. Various transcriptomic and metabolomic studies have shown enhanced synthesis of phenolic acids, flavonoids, and flavonols under drought conditions as a result of drought stress influencing genes that encode important enzymes in the phenylpropanoid biosynthesis pathway (Nakabayashi et al. 2014; Rezayian et al. 2018). For example, increased levels of flavonoids like kaempferol and quercetin have been observed in the drought-stressed tomato plants for the neutralization of H_2O_2 (Sanchez-Rodriguez et al. 2011). *Hypericum brasiliense* grown in drought had 10% more phenolic compounds than the control plants (De Abreu and Mazzafera 2005). Increased flavonol, quercetin, and kaempferol concentration in white clover growing in drought circumstances was linked to drought tolerance in a study by Nichols et al. (2015). In response to water stress-driven OS, Quan et al. (2016) found an increase in the phenolic acids. Phenolic accumulation directly reflects how well the plant is able to cope with drought.



Perception of stress stimulus by the receptors and signal transduction

Physiological, Biochemical and molecular alterations in plants

Up-regulation of expression of genes (PAL, C4H, 4CL, CHS, CHI) encoding enzymes of the defense pathways like phenylpropanoid pathway for the synthesis of phenolic compounds and increased expression of defense related enzymes.

Shift towards secondary metabolism

Accumulation of phenolic compounds

Antioxidant defense response of phenolic against oxidative stress and protection against ROS induced damage

Fig. 17.1 Schematic representation of plant defence response against oxidative stress

17.3.2 Role of Phenolics in Salt-Induced Oxidative Stress Management

Plants produce ROS such as O_2^-, $OH^•$, and H_2O_2 in response to salt stress (Taïbi et al. 2016; Acosta-Motos et al. 2017). In order to counteract the harmful effects of ROS, plants activate a variety of enzymes and nonenzymatic antioxidant mechanisms (Martinez et al. 2016). The buildup of phenolic compounds is a nonenzymatic method for avoiding salt stress-induced oxidative damage (Valifard et al. 2014; Chen et al. 2019). Several phenolic compounds have been observed to accumulate in salt-stressed plants, including cinnamylmalic acid, gallic acid, caffeic acid, vanillic acid, and ferulic acid (Bistgani et al. 2019; Scagel et al. 2019). Anthocyanins and flavone synthase genes were shown to be activated by salt stress in several studies, suggesting that plants battle salty surroundings by increasing their production of antioxidant chemicals (Dkhil and Denden 2012).

17.3.3 Role of Phenolics in Heat-/High Temperature-Induced Oxidative Stress Management

In reaction to heat stress, plants create anthocyanins, flavonoids, flavonols, and phenolic acids, which shield them from oxidative damage and hence help them survive (Ancillotti et al. 2015; Martinez et al. 2016). In response to heat stress, *Festuca trachyphylla* plants increased the production of phenolic compounds such as ferulic acid, cinnamic acid, salicylic acid, benzoic acid, coumaric acid, gallic acid, and vanillic acid. This suggests that they play a role in providing heat stress tolerance (Wang et al. 2019). A number of phenolics such as salicylic acid have been found to promote the synthesis of phenols in plants exposed to high temperatures (Cingoz and Gurel 2016).

17.3.4 Role of Phenolics in Cold-/Low Temperature-Induced Oxidative Stress Management

Plants subjected to nonfreezing chilling temperatures show an increase in phenolic metabolism (Akula and Ravishankar 2011). Since freezing causes dehydration and cell collapse, phenol biosynthesis enzymes are activated at low temperatures, which increases the production of phenolic compounds, which are then integrated into the cell wall as lignin or suberin thickenings and strengthen the cells' resistance to cold injury (Lattanzio et al. 2001; Griffith and Yaish 2004). Phenolic compounds like chlorogenic acids and anthocyanins have been shown to accumulate in the plants during cold stress in order to increase their resistance and adaption (Christie et al. 1994).

17.3.5 Role of Phenolics in Heavy Metal-Induced Oxidative Stress Management

Because of their antioxidant properties, phenolic substances such as flavonoids shield plants against the damaging effects of heavy metal toxicity-induced changes in physiological and metabolic processes (Villiers et al. 2011). Flavonoids decrease oxidative damage caused by metal stress by minimizing the generation of harmful $OH^{\bullet}$ by enhancing the chelation of transition metals, which act as catalysts in the formation of $OH^{\bullet}$ in Fenton's reaction (Mira et al. 2002; Williams et al. 2004). The phenolic compounds catechin and quercetin, which are precursors to the synthesis of lignin, were more in corn plants (*Zea mays* L.) grown under heavy metal stress (Michalak 2006). Treatment with copper induced the accumulation of phenolics in the seedlings of red cabbage as suggested by increased PAL activity and antioxidant capacity which protects the plants to counteract the heavy metal-induced OS (Posmyk et al. 2009). High content of tannins in the tea plants enables them to tolerate high metal salt concentrations as the metal salts will be chelated by tannins and thereby prevent them from catalyzing the generation of $OH^{\bullet}$ (Michalak 2006). To cope with OS, it is possible that heavy metal stress increases the production of phenolic compounds by the phenylpropanoid pathway's key biosynthesis enzymes (phenylalanine ammonia-lyase, chalcone synthase, cinnamyl alcohol dehydrogenase, shikimate dehydrogenase, and polyphenol oxidase) (Mishra et al. 2014).

17.3.6 Role of Phenolics in UV Light-Induced Oxidative Stress Management

Since plants cannot avoid the exposure to UV rays as they are dependent on sunlight for photosynthesis, various mechanisms have been developed by them to counteract the effect of UV exposure. Synthesis of phenolic compounds is one of the mechanisms which provide protection to plants as phenols form a shield under the epidermal cell layer to defend the plants against the harmful effects of UV rays. Phenolic compounds especially flavonoids prevent the light-induced destruction of important coenzymes like NADP and NAD and dimerization of thymine and thus have a protective effect on DNA. Phenolic chemicals' outstanding antioxidant qualities allow them to keep the cell's redox balance in check (Daayf and Lattanzio 2009). UV radiation can also be mitigated by other antioxidants, both enzymatic and nonenzymatic. Exposure to UV causes plants to produce more CHS, a flavonoid biosynthesis enzyme, which suggests that flavonoids can protect plants from UV damage (Koes et al. 1989; Schulze-Lefert et al. 1989). The effect of various abiotic elicitors on the level of phenolic compounds in plants is presented in Table 17.1.

Table 17.1 Effect of various abiotic elicitors on the level of phenolic compounds in plants

Abiotic elicitor	Plant species	Effect on composition of phenolic compounds	References
Drought	White clover	Increase in flavonols, quercetin, and kaempferol levels	Nichols et al. (2015)
	Lycopersicon esculentum	Increase in the level of kaempferol and quercetin	Sanchez-Rodriguez et al. (2011)
	Brassica napus	Increase in the levels of phenols, flavonols, and flavonoids Enhancement in activity and expression of phenylalanine ammonia-lyase (PAL) enzyme	Rezayian et al. (2018)
	Nicotiana tabacum	More PAL activity and lignin content	Silva et al. (2018)
Salinity	*Hordeum vulgare*, *Mentha piperita*, *Triticum aestivum*	Enhanced total phenolic levels	Ma et al. (2019); Kaur and Zhawar 2015
	Salvia mirzayanii, *Salvia macrosiphon*	Enhanced expression and activity of PAL. Rise in total phenolic content	Valifard et al. (2014)
	Thymus spp.	Enhancement in the levels of phenolic acids such as syringic acid, cinnamic acid, gallic acid, caffeic acid, rosmarinic acid, trans-2-hydroxycinnamic acid, and vanillic acid. Rise in content of naringenin, rutin, apigenin, and luteolin	Bistgani et al. (2019)
	Solanum lycopersicon	Rise in the level of caffeoylquinic acid	Martinez et al. (2016)
Heavy metal toxicity	*Zea mays* (aluminum, Al)	Defence against Al toxicity due to rise in catechin and quercetin levels	Michalak (2006)
	Beta vulgaris (copper, Cu)	Synthesis of betalains	Trejo-Tapia et al. (2001)
	Ginkgo biloba (Cu)	Accumulation of flavonoids	Kim et al. (1999)
	Brassica juncea (chromium, cadmium)	Enhanced phenol, flavonoid, and anthocyanin levels, PAL, and CHS genes upregulated	Kaur et al. (2017); Handa et al. (2019)
	Kandelia obovata (cadmium, zinc)	Rise in activity of polyphenol oxidase, cinnamyl alcohol dehydrogenase, and shikimate dehydrogenase leading to increased phenolic levels	Chen et al. (2019)
UV light	*Picea abies*	Increase in flavonol content	Fischbach et al. (1999)
	Catharanthus roseus	Rise in the levels of vinblastine and vincristine (anticancer compounds)	Bernard et al. (2009)
	Oryza sativa	Increase in C-glycosylflavone content	Markham et al. (1998)

(continued)

Table 17.1 (continued)

Abiotic elicitor	Plant species	Effect on composition of phenolic compounds	References
	Vigna radiata	Increase in total phenol and flavonoid content, enhanced activities of PAL and CHI enzymes	Goyal et al. (2014)
	Brassica oleracea	Enhanced gallic acid and sinapic acid content	Moreira-Rodriguez et al. (2017)
	Ribes nigrum	Rise in the levels of anthocyanins, hydroxycinnamic acid, flavonols, and hydroxybenzoic acids	Huyskens-Keil et al. (2012)
Heat	*Lens culinaris*	Enhanced synthesis of of gallic acid, salicylic acid, chlorogenic acid, ferulic acid, and naringenin. Rise in the levels of total phenolics and flavonoids	Swieca (2015)
	Solanum lycopersicon	Rise in the levels of flavonols	Martinez et al. (2016)
	Vigna angularis	Enhanced level of flavonoids and anthocyanins	Zlotek et al. (2015)

17.4 Mechanism of Action of OS Management in Plants

The underlying mechanism of action of defensive properties of phenolic compounds is their antioxidant ability. There are various mechanisms of antioxidant action of phenolics which include trapping of lipid alkoxyl radical for the inhibition of lipid peroxidation, stabilization of membranes, scavenging of FR species such as ROS/reactive nitrogen species (RNS), chelation of FR-generating metal ions, suppression of FR formation by inhibiting some enzymes, and upregulation of the enzymatic antioxidant defense (Cotelle 2001; Rice-Evans et al. 1996). Nevertheless, phenolics' antioxidant activity is influenced by the compound's molecular structure, including the quantity and position of hydroxyl groups (Millic et al. 1998). Phenolic compounds like flavonoids inhibit lipid peroxidation of the membranes by trapping the alkoxyl radicals and modifying the lipid packing order (Arora et al. 2000). FR-induced peroxidation reaction is also prevented by decrease in the membrane fluidity resulting in stabilization of membranes and thereby reduced diffusion of FRs (Blokhina et al. 2003; Verstraeten et al. 2003). The association of phenolics like flavanols and procyanidins with the polar head groups of phospholipids by H-bonding provides additional stability to membranes against lipid peroxidation, resulting in the buildup of these chemicals both inside and outside of the cells. By preventing ROS from diffusing beyond the hydrophobic portion of the bilayer, phenolic chemicals interact with membranes to maintain structural and functional integrity (Verstraeten et al. 2003). By virtue of the presence of OH groups, phenolic substances are able to halt the FR chain reaction and prevent the production of new

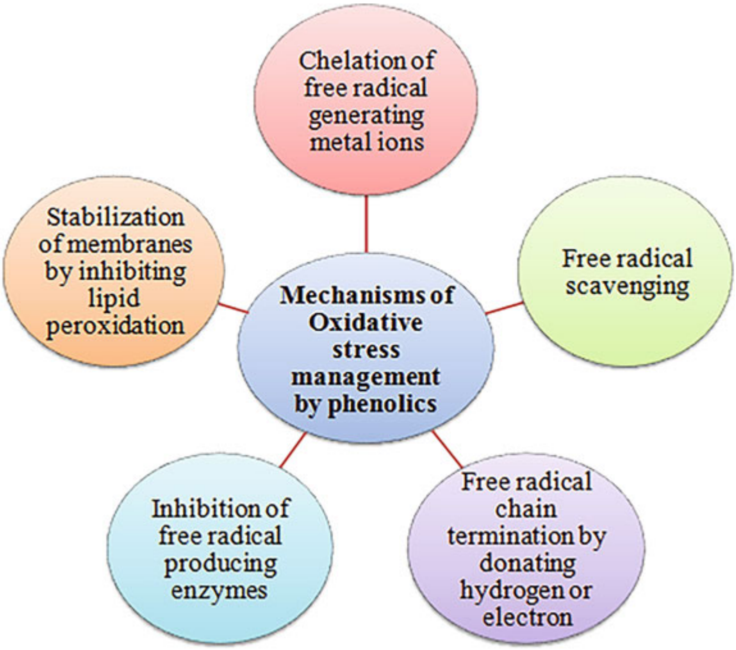


Fig. 17.2 Antioxidant defense mechanisms of plant phenolics

free radicals (Valentão et al. 2003; Heim et al. 2002; Choi et al. 2002). The structural chemistry of the phenolic compounds enables them to donate electron or hydrogen atom which is the main underlying mechanism of their antioxidant activity. They can stabilize and delocalize the unpaired electron, acting as FR chain breakers. Chelation of FR-generating metal ions is another mechanism of antioxidant action of phenols (Yang et al. 2001). By virtue of their hydrophobic benzenoid rings and the H-bonding potential of the phenolic OH groups, phenolic compounds inhibit enzymes involved in the creation of FR species, such as several cytochrome P450 isoforms, cyclooxygenases, lipooxygenases, and xanthine oxidase. Figure 17.2 represents the different mechanisms of action of phenolic compounds in combating OS.

17.5 Conclusion

Sustainability in agriculture is the need of present era as the demand for food and other plant-derived products is increasing at a fast pace due to rapid increase in the world's population, and maintaining high productivity as well as quality amidst of changing weather conditions and decreased land area is a major challenge that the agriculture is facing right now. The changing climate is posing various types of stress (abiotic or biotic) to plants, and the exposure of plants to each and every type of these stresses ultimately results in OS which decreases plant's growth and hence its productivity by causing the impairment of photosynthesis and other vital cellular processes as a consequence of oxidative damage to biomolecules (lipids, nucleic acids, proteins). When the production of ROS surpasses the plant's ability to neutralize them, a free radical burst occurs, causing OS in the plant. However, their production at low concentrations is a normal consequence of aerobic metabolism which does not cause any damage as antioxidant defense system of plants efficiently neutralizes them. ROS not only act as damaging agents; they also protect the plants from further damage by acting as signaling agents in defense response pathways. In order to maintain a delicate balance between ROS generation and neutralization, plants are unable to eradicate ROS totally since they are both a curse and a blessing depending on the quantity of ROS. To protect themselves from environmental stresses, a complex network operates in plants involving stimulus perception, intracellular signaling, and enzymatic/nonenzymatic responses. Phenolic compounds, which protect plants from ROS-induced damage because of their antioxidant activity, are part of the plant's reaction to OS. They have wide occurrence in nature with a broad chemical diversity and antioxidant mechanisms. Oxidative damage induced by ROS overproduction during stressful situations can be prevented by the accumulation of phenolic compounds, which accumulate as an adaptive response to various stressors. Understanding the process of stress-induced upregulation of phenolic compound production would aid in conferring resistance to susceptible plants.

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Anthropogenic Stress and Phenolic Compounds: An Environmental Robustness Diagnostics Compound Family in Stress Ameliorations

18

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Abstract

Natural ecosystems are progressively vulnerable to a number of multiple anthropogenic stressors, particularly with water, ozone, air pollutants, pesticides, heavy metals (HMs), deforestation, artificial lightening, agriculture intensification, and land use pattern changes. All of them have risen in ecosystem imbalance, climate change, global warming, and many other natural disasters as abiotic stresses. These stressors cause imbalance in physiological, biochemical, and molecular traits at different levels and under different environmental components, which they are subjected. Therefore, to diminish the catastrophic consequences on ecological sustainability, the present chapter focuses on the role and mechanisms of secondary metabolites (SMs) especially phenolic compounds (PCs) for environmental robustness diagnostics via adaption or avoidance from these stressors. The prime objective of this chapter tends to explore the functions and responses of PCs in respect to elevated CO_2 (eCO_2), heavy metal (HM) stress, salinity, pollutant translocations, and transformations in ecosystem. For instance, it will help in understanding the different anthropogenic stressors, their impact on environmental components, PC response, and pathway or mechanisms by which these PCs nullify the drastic consequences of anthropogenic stressors.

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18.1 Introduction

Human developmental activities such as overpopulation, industrialization, urbanization, transportation, pharmaceutical, cosmetic industry, mining, manufacturing, energy industry, fishing and farming (use of fertilizer and pesticide), infrastructure building, and drainage of factory and municipal influence the biophysical environments, leading to a change in ecosystem, natural resources, and biodiversity (*https://en.wikipedia.org/wiki/Humanimpactontheenvironment*). In addition to these, deforestation and mining, intensified agriculture, altered land use pattern, excess artificial lightening (AL), and excess pesticides and fertilizers magnify the concentrations of pollutants in water, soil, and atmosphere, becoming the determining factors in affecting the environmental sustainability (Morand and Lajaunie 2017). These factors are known as anthropogenic stressors, and substantially disturb the natural environment by altering the ecosystem services and functions of terrestrial as well as of aquatic one, which lead~~s~~ to ecological imbalances, climate change, global warming, and other abiotic stresses (heat, chilling, freezing, high irradiation, salinity, drought, flooding, and mineral deficiency) (Dukhovskis et al. 2003; Midgley and Thuiller 2011; Häder and Gao 2015).

The plethora of these stresses leaves some pessimistic consequences on biodiversity, human health, as well as plant's survival and also impairs the basic structure, mechanisms, and functions of plants (Dukhovskis et al. 2003). Considering the drastic impacts of growing anthropogenic stress, scientists are continuously working to find the mechanism and novel strategies to mitigate/ameliorate its impacts on ecosystem. The common mechanism, followed by all the plants during stress conditions, is the production of reactive oxygen species (ROS) or oxidative stress. This condition can be mitigated by improving defense mechanism of plants or by improving the level of antioxidant compounds. These compounds have the dexterity to boost up the plant's immune system in coping both biotic and abiotic stresses. Antioxidant compounds such as PCs, terpenes, and alkaloids participate in defense mechanism which are developed by plants in a wide range, under the adverse situation (Isah 2019). In this consequence, phenols are ubiquitous in plant's kingdom, helping in overwhelmed stress constraints and survival under suboptimal conditions. The antioxidant properties and nature of phenolics are by virtue of the ring structure containing phenolic hydroxyl groups and effective against multiple stresses (Edreva et al. 2008). Considering the discussed facts, this chapter covers the response of various anthropogenic stressors such as deforestation, mining, pesticides, fertilizers, and artificial light on plant system and mechanism involved in amelioration of these stressors, especially by phenolic compounds.

18.2 Effect of Various Anthropogenic Stressors on Plant System

18.2.1 Deforestation and Mining

Removing of forest (vegetation) from any part of the planet for agriculture, industrialization, and urbanization purpose leads to diminishing carbon sequestration, and causes imbalance in atmospheric gases by overemission of greenhouse gases especially CO_2 that has increased from 280 to 405 ppm (Houghton 2005; IPCC 2014). This imbalance in gaseous concentration leads to degradation of air quality, acid deposition, ozone hole, sea-level rise, alterations in rainfall, and storm pattern (Keller et al. 1991). These changes are endangered for flora and fauna biodiversity and have drastic impacts on all living organisms. Water scarcity and other unfavorable conditions due to climate change impact on agriculture production system and food security associated with damaging the crops and irrigation systems (Lawrence and Vandecar 2015). Mining of natural resources such as fuels, coals, and ore of metals is a profitable activity for promoting industrial development, but it causes the accumulation of hazardous gases, surface logging, and deforestation (Anonymous 2011; Chakravarty et al. 2012).

18.2.2 Pesticide and Heavy Metal (HM) Accumulation

Due to industrialization, urbanization, and modern agricultural practices, several toxic chemicals like pesticides, herbicides, insecticides, fungicides, and HMs are applied for crop productions in excess quantities (Rashid et al. 2010; Kumar et al. 2021). The use of pesticide significantly increased with time, and it is estimated that 2 MT of pesticides is utilized annually, which can be increased up to 3.5 million tons by 2020. Excess use of pesticides can alter the plant's physiological and biosynthetic reactions and molecular composition. Moreover, it can influence the growth of beneficial rhizosphere microorganism interactions and hampers the soil fertility and productivity (Sharma et al. 2019).

Heavy metals like Cd, Hg, As, Pb, Ni, Cu, Zn, Cr, Co, and Se are highly toxic, and act as nondegradable pollutants and become hazardous for plants as well as humans, even at minute concentrations (Nagajyoti et al. 2010; Singhal et al. 2022). Nevertheless, some metals are essential for normal metabolic activities of plants and considered as micronutrients (Fe, Zn, Mn, Cu, and Mo), which are required in very trace amounts (Hänsch and Mendel 2009). HMs emanate from natural sources such as volcanic eruption, weathering of rocks, and biogenic sources and anthropogenic sources such as industrial waste, burning of fossil fuels, application of fertilizer and pesticide, municipal and agriculture wastewater, and mining and accumulated in soil, water, and air by physical and chemical processes (Mohammed et al. 2011). Heavy metals can be absorbed by crops' rhizosphere, and their accumulation and toxicity are affected by a variety of factors including sand, silt, clay proportions in soil, temperature, cation exchange capacity, pH, organic and inorganic matter content, etc. (Kim et al. 2012).

The native soil fauna is altered by heavy metals which ultimately affects the ability of soil microorganisms to carry out the mineralization process and subsequent nutrient availability. Heavy metal caused oxidative damage and alters membrane permeability and modulates sugar and protein metabolism (Fryzova et al. 2017). Germination of seeds, root and shoot elongation, fresh and dry weight, soluble sugar content, α-amylase enzyme activity, and protein content in various crops are affected by toxic levels of heavy metals resulting in disruption in plant metabolism and growth (Goyal et al. 2020).

18.2.3 Rise of Pollutants in Water, Soil, and Air

Pollution is a widespread problem affecting environmental health. Various substances are responsible for rising pollution (i.e., pollutant) and that have undesired and adversely effects the usefulness of a resource, introducing from various anthropogenic sources like industries by product and sewage seepage, transportation contaminant and agricultural waste disposal, which congregated and remained for ever since in soil, air, and water (Popescu and Ionel 2010; Gheorghe and Ion 2011). Pollutant can be alienated in several categories includes Hg and other HMs, persistent organic pollutants such DDT, polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) (Kodavanti et al. 2017; Rose and Fernandes 2017), ozone (O_3), particulate matter (PM), persistent pharmaceutical pollutants such as tetracycline, ciprofloxacin, ibuprofen, diclofenac, carbamazepine, cetirizine, polycyclic aromatic hydrocarbons (PAHs) like naphthalene, fluorene, anthracene (Maliszewska-Kordybach and Smreczak 2000), secondary metabolites like terpenoids and volatile organic molecules like alkanes, alkenes, alcohols, esters, etc. (Kesselmeier and Staudt 1999). These pollutants are bioaccumulated in the environment and enter in the food web and drastically affect the livings (She et al. 2016).

Discharge of above waste can be excess in soil and water bodies (eutrophication) causes acidity and negatively influences soil and water microorganism and associated plants (Porter et al. 2013). Pollutants have several detrimental effects on plants, including germination and leaf and root damage, which interrupt photosynthetic properties and ultimately caused *stunted* growth and poor biomass production. Pollutants are also responsible for *obstruction in stomata, respiration,* and damage which appears *in the form of chlorosis, bronzing, and mottling at severe conditions (*Maliszewska-Kordybach and Smreczak 2000; Pourkhabbaz et al. 2010; Kreslavski et al. 2017).

18.2.4 Use of Artificial Lightening

The process of photosynthesis can be always affected by a specific spectrum of light within a notable time period, although plants are exposed with a wide range of visible spectrum of light over the lifespan that are responsible for their normal growth and functions; however, excessive visible and UV radiation impairs plant productivity (Häder and Gao 2015). Disturbance in natural cycle of diurnal rhythm affects arguably the ecosystem (Singhal et al. 2019a; Meravi and Kumar Prajapati 2020; Singhal et al. 2021b). Artificial lighting emits a variable intensity of light (Darko et al. 2014). When plants are exposed with continuous street light during dark hours, plants experience stress, and Fv/Fm value of photosystem II was lower (Meravi and Kumar Prajapati 2020). Light pollution strongly depends on source and emission color of light (Falchi et al. 2011). Light pollution significantly influences germination, vegetative growth, and flowering of crop plants (Singhal et al. 2019b; Meravi and Kumar Prajapati 2020; Sodani et al. 2021).

18.2.5 Increase in Agriculture Intensification and Change in Land Use Pattern

Agriculture-intensifying practices promote to fulfill the demand of increasing population (Rodriguez Garcia et al. 2018) by increasing productivity per unit area (Byerlee et al. 2014). As a consequence of intensifying production practices, the demand of inputs like fertilizers, pesticides, water for irrigation, farm machinery, and labor has been increased. Intensification of crops like wheat, rice, and cowpea leads to land sparing (Folberth et al. 2014; Garcia et al. 2020), causing mineral deficit. Emission of CO_2 and N_2O is increased by intensive agriculture practices and leads to global climate change and loss of biodiversity. Altered land use pattern due to overpopulation can lead to alteration in surface temperature (Chakraborti et al. 2019), loss of groundwater quality (Sarkar et al. 2020), and nutrient criteria (Liu et al. 2018), which influence climate (Llopart et al. 2018).

18.3 Modulations of Physiological, Biochemical, and Molecular Traits by Anthropogenic Activity

Release of injurious gases, HMs, and other chemicals such as pesticides into the environment from anthropogenic activities disrupts physiological processes and metabolic functions of plants by forming anthropogenic and natural stress circumstances. Higher dose of pesticides and HMs also acts as stressor and affects the nontargeted plants (Shakir et al. 2018).

According to various reports, these stresses adversely affect crop yield-related attributes and amplify ROS generation which alter the cellular redox homeostasis and affect plant's immune system, causing damage of cell organelles, resulting in hindrance of many physiological functions in plants (Fryzova et al. 2017; Shakir et al. 2016, Shakir et al. 2018). Oxidative stress perturbs the photosynthetic process by generation of singlet oxygen in chloroplasts. Mitochondrial activities also influenced ROS production, where H_2O_2 is rapidly generated (Asati et al. 2016). These ROS also decline phospholipid and saturated fatty acid contents, thus causing membrane damage by lipid peroxidation (Asati et al. 2016; Shakir et al. 2018) among various other biomacromolecular assembly disruptions (Gill and Tuteja 2010).

Nevertheless, plants have evolved several mechanisms at the morphological, physiological, biochemical, and molecular levels to protect themselves via adaptation or avoidance against these unfavorable circumstances and sustain their lifecycle. To diminish the adverse effects of these stresses, plants need to improve their performance and tolerance to these stresses by enhancing antioxidant defense system (Shakir et al. 2018), supporting in detoxifying ROS with using superoxide dismutase (SOD), catalase (CAT), peroxidase (POD), ascorbate peroxidase (APX), glutathione reductase (GR), glutathione peroxidase (GPX), glutathione *S*-transferase (GST), monodehydroascorbate reductase (MDHAR), dehydroascorbate reductase (DHAR), and quinine reductases (QR) enzymes (Ahmad et al. 2008; Das and Roychoudhury 2014; Shakir et al. 2018). Likewise, nonenzymatic antioxidant compounds such as ascorbate (AsA), glutathione (GSH), carotenoids, ascorbate, amino acids like proline and proteins like LEA protein, dehydrins (DHN), antifreezing proteins, mRNA-binding protein, and chaperons (Akula and Ravishankar 2011) stimulate the enduring capability of the system to face the destructive effects of oxidative stress.

Secondary metabolites, consisting PCs like flavonoids, isoflavonoids, and terpenoids, and nitrogen-containing metabolites like alkaloids (dos Reis et al. 2012) are found to contribute in stress-tolerant mechanism (Kumar et al. 2020a, b, c). Plants under stress condition also respond through synthesizing some specific, endogenous, and low-molecular-weight stress hormones such as salicylic acid, jasmonic acid, ethylene, and abscisic acid (Fujita et al. 2006; Hayat et al. 2014). Higher accumulation and activities of these antioxidants in plant tissue impart stress tolerance directly or indirectly (Sharma et al. 2019; Kumar et al. 2020).

18.4 Role and Mechanisms of SMs Especially PCs in Environment Robustness Diagnostics Via Adaption or Avoidance from Stresses

Basic cellular process requires energy and oxygen saturation environment for normal functioning. The energy demand and oxygen are derived from the primary metabolites which are accumulated through photosynthesis and later on yield ATP and oxygen via respiration (Hussein and El-Anssary 2018). Apart from primary metabolites, there are also other low-molecular-weight compounds which do not participate in basic cellular constitution and thermodynamics. The later are known as secondary metabolites and can be often seen as the derived products of primary metabolism (Thirumurugan et al. 2018). Responses to changing environmental cues are mediated by secondary metabolites which make the plants eligible to withstand climate adversaries, and even the plants can maintain optimal growth and development (Isah 2019; Tyagi et al. 2020; Tak and Kumar 2020; Wagay et al. 2020).

Secondary metabolites involve in defense mechanism against pathogens and abiotic stresses such as atmospheric pollution and extreme environmental conditions which represents the main array of innate immune system of plants; these properties of SMs make it essential as primary metabolites (Kliebenstein 2013).

Secondary metabolites involve in several important processes, representing physiological, metabolic, and reproductive ones, and improve biomass production of plants. However, metabolites do not take part directly in growth and developmental processes but execute their roles in signaling, in stimulating and inhibiting enzymatic activities, and in defense mechanism and also involve in an interaction with other organisms too. Secondary metabolites have a wide-ranging importance including pharmaceuticals, agrochemicals, food additives, flavors, fragrances, colors, and other industrial materials and are applicable as antioxidants, bioremediation agents, allelochemicals, plant growth regulators, and metal ion chelators (Tiwari and Rana 2015). Besides antioxidants, it has also an antimicrobial activity and inhibitory role on lipid peroxidation and carcinogenesis (Mojzer et al. 2016). Phenolic compound influences several processes such as seed germination, cell division, growth and development process, and photosynthetic activity of plants. Alteration in germination and photosynthetic activity occurs due to change in germinating enzyme's activity such as amylase, peroxidase, and chlorophyll content. Plant phenolics act as regulatory signal for modulating both physiological and developmental phases through regulation at transcription and translation levels, signal transduction, and modification in membrane dynamics. Taken all together these series of regulation can bring about the tolerance against abiotic and biotic stresses (Cheynier et al. 2013). Phenolic and flavonoid have potential to scavenge free radicals (Chan et al. 2008).

During chemical stress, plants trigger synthesis of phenolics like isoflavones, phenolic acid, and hydroxycinnamic acid derivatives (Akula and Ravishankar 2011). These PCs have potential to inhibit the germination as well as growth process of plants by reducing leaf water and stomatal conductance. The higher production of PCs in plant tissue induces stress condition which inhibits the growth of plants via two ways, either by inhibition of chlorophyll biosynthesis or via accelerating chlorophyll degradation, both of which lead to retardation of photosynthesis and decrease in photosynthates with decreased net assimilation rate (NAR). Phenolic compound is derived primarily from the phenylpropanoid pathway (Dixon and Paiva 1995); during stress situation the activity of phenylpropanoid pathway is emanated; hence, the synthesis of phenolic acid is increased to intensify the detoxifying activity of PCs (Mahdavi et al. 2015). Phenylalanine is involved in biosynthesis of phenolic antioxidant, but under stress condition, a transient decline in phenylalanine is exhibited, which significantly rises at later stage. Similarly, shikimic acid also decreases due to overuse at early phase of stress, which is an essential component of the shikimate pathway (Dixon et al. 2002).

Primary metabolites, having more carbon and nitrogen, may be used for the generation of various SMs as per demand, opting related pathways through phenylpropanoid, mevalonate, glucose, amino acid, and acetate-malonate via acting as a sink, depending upon the requirement; further it can also be recycled again in primary metabolites through the degradation process (Collin 2001). Chemical elicitation also can induce stress responses and stimulate synthesis and accumulation of

SMs in plant tissue (Naik and Al-Khayri 2016). Exogenous application of Ca^{++} affects PC metabolism and influences the activities of enzymes such as phenylalanine ammonia-lyase (PAL), polyphenol oxidase (PPO), and peroxidase (POD) in tobacco (*Nicotiana tabacum* L.) leaves under normal condition (Ruiz et al. 2003), while in wheat, the expression of phenylalanine ammonia-lyase (PAL), 4-coumaric acid-CoA ligase (4CL), cinnamic acid 4-hydroxylase (C4H), caffeic acid O-methyltransferase (COMT), and p-coumarate 3-hydroxylase (C3H) is noted to influence under UV-B radiation, and phenolic contents either free or in bound form significantly increased during germination, which in turn contributes to improved antioxidant capability (Chen et al. 2017, 2019a, b).

18.5 Function and Responses of Phenolic Compounds in Respect to Elevated CO_2, Heavy Metal Stress, Salinity, Pollutant Translocations, and Transformations in Ecosystem

During stressful condition SM content is raised, which indeed confers higher tolerance to plant against stressful situation. Under these stresses, plants have potential to synthesize additional SMs especially phenolic compounds through upregulation of genes conferring synthesis of regulatory enzymes of phenylpropanoid pathway, which are capable of scavenging free radicals and preventing cell membrane damages by peroxidation (Koopmann et al. 1999; Selmar 2008).

18.5.1 Response of Phenolics Under Elevated CO_2 and Their Role

A major portion of available fixed carbon are diverted to form carbon-based secondary metabolites, while the remaining carbon increases the intracellular CO_2 concentration (Becker and Kläring 2016; Huang et al. 2017; Sabagh et al. 2021). Elevated CO_2 affects important plant traits by generating ROS and improves the level of defensive compound (total phenolics) which positively correlated with leaf C:N ratio (Karowe and Grubb 2011). Accumulation of PCs under enriched CO_2 levels is due to the upregulation of phenol biosynthetic (phenylpropanoid pathway) enzymes including PAL, *β-glucosidase, and flavanone-3-hydroxylase* (Peltonen et al. 2005). Elevated CO_2 and UV-B radiation in combination lead to a significant increase in the allocation of carbon between biomass and secondary metabolites (phenolic acids, flavonoids, condensed tannins), due to interrelation of primary and secondary metabolism and triggered by the enzyme activity such as phenylalanine ammonia-lyase (PAL), peroxidase, and PPO (Mattson et al. 2005). Enhanced PCs and flavonoids by elevated CO_2 and UV light levels have indirect and direct impacts on the insect performance and behavior, herbivory rates, and pathogen attack (Bidart-Bouzat and Imeh-Nathaniel 2008).

The enzymatic activity of PAL, biomass production, and lignin content in four plant species, namely, *Spergula arvensis*, *Poa annua*, *Senecio vulgaris*, and *Cardamine hirsuta*, are indicated to alter under elevated CO_2 (Hartley and Jones 2003). Penuelas et al. (1996) observed that in leaves of wheat, the phenolic concentration was increased, while it reduced in pine and no significant change was noted in orange, under enrichment of CO_2, and they also indicated an inverse linear relation between PC content and biomass production. Flavonoid (quercetin, rutin, catechin, epicatechin, kaempferol, naringenin, fisetin, and morin) and phenolic acid (gallic acid, vanillic acid, ferulic acid, tannic acid, cinnamic acid, and salicylic acid) profiles were influenced by elevated carbon dioxide (400–1200 μmol mol^{-1} CO_2), which might upregulate the antioxidant activity in three varieties (alata, pumila, and lanceolata) of Malaysian *Labisia pumila* (Myrsinaceae) (Jaafar et al. 2012). Kim et al. (2005) noted that UV exposure and other environmental factors have critical impacts on cellular damage and aging via working through free radicals and ROS; they further reported that metabolic excess of carbon also rises flavonoid content in *Acer palmatum* and in wheat leaves (isoorientin and tricin concentration) at high CO_2. Impacts of elevated CO_2 and modulation of plant traits and PCs are presented in Table 18.1.

18.5.2 Responses of Phenolic Under Heavy Metal and Their Role

Anthropogenic activity introduces heavy metals (HMs) as one of the persistent abiotic stress factors through overaccumulation which causes oxidative stress by producing ROS that leads to disorganization of lipids in cell membrane and alters physiological and metabolic processes, thus ultimately reducing in growth. However, protective mechanism initiated in that condition enhanced the production of stress-related proteins, antioxidants, SMs, hormone, and signaling molecules (Ghori et al. 2019). Accumulation of phenolic compounds such as flavonoid and phenolic acid in plants has been an effective defense response to heavy metal stress, and the protective role of these compounds might be associated with their ability to scavenge ROS (Izbiańska et al. 2014; Chen et al. 2019a, b). Under HM stress condition, an excess amount of flavonoids and polyphenols was observed in various crops such as in alfalfa treated with Pb (Sima et al. 2012; Maslennikov et al. 2018) and isoflavonoids (like anthocyanin) in cabbage (Posmyk et al. 2009).

Higher synthesis of phenolic compound is depending on the upregulation of PAL and chalcone synthase (CHS) activity, stimulated by HM stress (Winkel-Shirley 2002). Silicon and selenium (Se) enhanced the production of phenolic compound in maize and rice, respectively (Mihaličová Malčovská et al. 2014; Chauhan et al. 2017). Shikimate dehydrogenase (SKDH), peroxidase, glucose-6-phosphate dehydrogenase (G6PDH), PAL, cinnamyl alcohol dehydrogenase (CAD), caffeic acid peroxidase (CA-POD), chlorogenic acid peroxidase (CH-POD), PPO, and b-glucosidase (b-GS) also increase in metal stress condition; these enzymes are associated with synthesis of PCs as well as lignin accumulation (Ali et al. 2006). Flavonoid has the ability to chelate metals (Keilig and Ludwig-Müller 2009) and

Table 18.1 Highlight the impacts of elevated CO_2 on phenolic content and modulation of plant traits

Plants	Trait influenced	Change in phenolic contents	References
Dactylis glomerata and *Bromus erectus*	Biomass, nonstructural carbohydrates	Increase in phenolic acid (gallic acid)	Castells et al. (2002)
Labisia pumila Benth	Increasing radical scavenging activity and ferric reducing antioxidant potential	Increase in phenolic acid and flavonoid (gallic acid, caffeic acid, pyrogallol and quercetin, myricetin, kaempferol, rutin, and naringenin) and enhanced PAL activity	Jaafar et al. (2012)
Strawberry (*Fragaria x ananassa* Duch.)	Alteration in ascorbic acid (AsA), glutathione (GSH), altered ratios of AsA to dehydroascorbic acid (DHAsA) and GSH to oxidized glutathione (GSSG), reduced content of DHAsA with elevated ROS absorbance activity	High anthocyanin and phenolic content (p-coumaroyl glucose, dihydroflavonol, quercetin 3-glucoside, quercetin 3-glucuronide, and kaempferol 3-glucoside contents, cyanidin 3-glucoside, pelargonidin-3-glucoside, and pelargonidin-3-glucoside-succinate content	Wang et al. (2003)
Soybean (*Glycine max* L)	Changes in antioxidant enzyme and growth attributes	Increase in isoflavones like genistein and daidzein and the flavonols like quercetin and kaempferol, and naringenin	O'Neill et al. (2010)
Malaysian herb Kacip Fatimah (*Labisia pumila* Blume)	High ROS production, higher GSH, GSSG, soluble carbohydrate, and antioxidant activities observed	Increase in total phenolics and total flavonoids	Ibrahim and Jaafar (2011)
Labisia pumila Benth.	Decrease in chlorophyll content, total soluble sugar, starch, and TNC	Upregulation in SM production via shikimic acid pathway and increased starch content	Ibrahim et al. (2014)
Rice (*Oryza sativa* L.)	Change in C:N ratio and total nonstructural carbohydrates	Increase in total PC and flavonoid contents under elevated CO_2 at maturity but decrease during germination and flowering stage and total nonstructural carbohydrate contents are increased	Goufo et al. (2014)
Strawberry	Increase in antioxidants like SOD	Increases in total polyphenol such as catechin, pelargonidin-3-glucoside, quercetin-3,4-di-glucoside, p-coumaric, ferulic acid,	Balasooriya et al. (2019)

(continued)

Table 18.1 (continued)

Plants	Trait influenced	Change in phenolic contents	References
		coumaroyl, kaempferol-3-glucuronide, resveratrol, flavonoid, and anthocyanin	
Lettuce	Modulation of antioxidant enzymes and SMs	Increase in flavonoid, quercetin-3-O-glucoside, quercetin-3-O-glucuronide, luteolin-7-O-glucoside, kaempferol, myricetin, chlorogenic, chicoric, gallic, protocatechuic, caffeic, and p-coumaric, vanillic, syringic acids	Pérez-López et al. (2018)

provide protection against HMs (Kidd et al. 2001). Hydroxyl (–OH) and carboxylic acid (–COOH) of PCs help in binding metals (Michalak 2006). Impacts of HMs on plant's growth traits and PCs are represented in Table 18.2.

18.5.3 Responses of Phenolic Compounds Under Salinity and Their Role

Salinity is the consequence of accumulation of salts by anthropogenic activities; it is a major constraint on the survival and synthesis of bioactive compounds of plants (Isah 2019; Singhal et al. 2021a; Sabagh et al. 2021). Salinity intensifies overproduction of ROS that induces oxidative stress and causes alteration in the defense responses and production of antioxidants including plant's SMs (Gill and Tuteja 2010). They have an influential scavenging property to ROS in plant under salt stress. Moreover, the induction of secondary metabolic pathway gets initiated by salt stress, resulting in higher production of SMs that have potential antioxidative capacity.

Biosynthesis of PCs enhanced by the overexpression of transcriptional regulator (gene) such as VvbHLH1 in *Arabidopsis thaliana* (Wang et al. 2016), NtMYB4 mediate NtCHS1 in tobacco (Chen et al. 2019a, b) and NHX in *Olea europaea* (Rossi et al. 2016); results in upregulation of key genes of the phenylpropanoid pathway PAL, cinnamate-4-hydroxylase (C4H), 4-coumarate-CoA ligase (4CL), chalcone synthase (CHS) and chalcone isomerase (CHI); DFR, FLS, and ANS (Wang et al. 2016; Rossi et al. 2016) that significantly enhanced the biosynthesis and accumulation of flavonoid like kaempferol and quercetin (Wang et al. 2016). Bistgani et al. (2019) reported that total phenolic contents increased up to 20%, leaf flavonoid (38.6%), cinnamic acid (31.4%), gallic acid (20.4%), rosmarinic acid (27.6%), in *Thymus vulgaris* and *Thymus daenensis* after application of 60 mM NaCl and suggested that increased PCs associated with enhanced antioxidant property under salinity stress. Similarly, Linić et al. (2019) suggested that PCs are associated with short-term adaptation to salinity tolerance, although it is species

Table 18.2 represents the impacts of heavy metal on phenolic contents and modulation of plant traits

Heavy metal	Plant	Growth trait	Phenolic contents	Reference
Chromium (Cr)	Rice (*Oryza sativa*)	High MDA, high proline, increased antioxidant enzymes such as GST, APX, and SOD including DPPH	Higher phenolic and flavonoid content evaluation	Dubey et al. (2018)
Lead (Pb)	Lupine (*Lupinus luteus* L.)	Significant increase in the root length and accumulation of both H_2O_2 and O_2 and TBARS content	Increased flavonoid contents	Izbiańska et al. (2014)
Copper (Cu)	Cabbage (*Brassica oleracea*)	Enhanced in TBARS content, and SOD, CAT, POX, APX, GPX, and GR	Levels of anthocyanin and sinapoyl derivatives	Posmyk et al. (2009)
Cadmium and zinc (Cd and Zn)	*Kandelia obovata*	Effects on antioxidant capacity and growth	Increase in phenolic acids including pyrogallic acid, coumaric acid, protocatechuic acid, chlorogenic acid, and salicylic acid	Chen et al. (2020)
Copper (Cu) stress	Pepper (*Capsicum annuum* L.)	Decrease in the plant growth	Increase in SKDH and peroxidase, and isoperoxidases, PRX-B, and PRX-A3	Diaz et al. (2001)
Aluminum and cadmium	Blueberry (*Vaccinium corymbosum* L.)	Increase in MDA and H_2O_2 contents and antioxidant SOD	Increase in PCs (gallic, chlorogenic and ellagic phenolic acids)	Manquián-Cerda et al. (2018)
Lead (Pb)	*Prosopis farcta* shoots	Increase in aspartic acid and glycine content but glutamic acid significantly decreased	Enhanced PAL activity, increase in phenolic acids and flavonoids; daidzein, vitexin, ferulic acid, and SA	Zafari et al. (2016)
Zn and Cd	*Arabidopsis thaliana*	Reduced antioxidant enzyme	Induction of phytochelation genes (*AtPCS1*, *AtPCS2*) by flavonoid (quercetin and naringenin)	Keilig and Ludwig-Mueller (2009)
Copper (Cu)	*Panax ginseng*	Increased cysteine, NPSH contents and DPPH activity; the induced activities of substrate-specific peroxidases like caffeic	Increase in activities of G6PDH, SKDH, PAL, and CAD; increase in accumulation of phenolics (phenolic	Ali et al. (2006)

(continued)

Table 18.2 (continued)

Heavy metal	Plant	Growth trait	Phenolic contents	Reference
		acid peroxidase, and CA-POD; chlorogenic acid peroxidase (CH-POD), polyphenol oxidase (PPO) and b-glucosidase (b-GS)	acid and flavonoids) and lignin	

specific. Effects of salinity stress on plant functional traits and PCs are represented in Table 18.3.

18.5.4 Responses of Phenolics by Pollutant and Their Role

Systemic pesticide generates the chemical stress in soybean that triggers the production of phenolic compound, and it is observed that total phenols in leaf, shoot, and fruit are noted to increase by 114 and 220% at vegetative stage and 50, 166, and 163% at late fruiting stage (Siddiqui and Ahmed 2006). Nitrogen and phosphorus are key nutrients, and both play an imperative role in the plant growth and development and application of nitrogenous and phosphoric fertilizers, which have potential to change the flavonoid content in St. John's Wort plant (*H. perforatum*) (Azizi 2004). Impacts of different pesticides on plant traits and PCs are represented in Table 18.4.

Furlan et al. (1999) reported that the valley of Piloes River (no air pollution) and valley of Mogi River (severely affected by air pollutions) showed the increase in N, leaf palatability and nutrition value and a decrease in SMs (phenol and tannins) production in valley of Mogi River weaken the defense capacity and future fitness. In *Lotus corniculatus* L., *Trifolium montanum* L., *T. pratense* L. and *T. repens* L. While the leaves were subjected to pollution, generated by human activities and cement factories, then the accumulation of PCs in epidermis, assimilatory mesophyll, and vascular tissue is noted to be associated with ensuring tolerant capacity, and plants have shown less injury (Gostin 2009). Similarly, it was suggested that a progressive shift in ozone-treated leaves leads to a faster senescence, and most surface phenolic compounds showed a declining trend, although some metabolic shift toward few phenolics is associated with higher antioxidant capacity (Saviranta et al. 2010; Khoddami et al. 2013). Herbicide and nitrate enrichment are major problems of aquatic ecosystem and affect plant growth, structural integrity, and PCs (Nuttens et al. 2016). Acid rain influences physiological, biochemical, and molecular change and leads to degradation of pigments, cellular components, and structure by the overproduction of ROS. This kind of digastric effects can be coped with the accumulation of vitamin C, carotenoids, and phenols and exogenous application of polyamines, salicylic acid, and β-aminobutyric acid (Xalxo and Sahu 2017).

Table 18.3 highlights the impacts of salinity stress on plant traits and phenolic compounds

Plant	Plant trait influenced	Phenolic compounds	References
Phaseolus vulgaris L.	Decreased biomass and photosynthetic pigment, increased MDA content, antioxidant enzymes, and ascorbic acid	Increase in amounts of total flavonoids	Taïbi et al. (2016)
Sesuvium portulacastrum L.	Accumulated high contents of proline	Higher polyphenols, anthocyanins and carotenoids at moderate salinity	Slama et al. (2017)
Roselle (*Hibiscus sabdariffa* L.)	Decreased plant height, fresh weight of shoot and flower	Increase phenolic and anthocyanin content	Hashemi and Shahani (2019)
Lettuce	High antioxidant enzymes SOD, POD, CAT; and enhanced carotenoid	Increase in phenolics biosynthesis (phenolic acids and flavonoids);	Mahmoudi et al. (2010)
Thymus vulgaris L. and *T. daenensis* Celak)	Decreased plant dry matter production	Increased total phenolic and flavonoid content (Cinnamic acid, gallic acid)	Bistgani et al. (2019)
Lettuces	p-Hydroxybenzoic and syringic acids, caffeic acid, gallic, protocatechuic, caffeic, p-coumaric, and ferulic acids	Induce flavonoids quercetin, quercetin-3-O-glucoside, quercetin-3-O-glucuronide and quercitrin.	Sgherri et al. (2017)
Amaranthus tricolor	Enhanced pigments (anthocyanins, carotenoids, β-cyanin, β-xanthin, and betalain); β-carotene, vitamin C	Increase in phenolic acids and flavonoids (Salicylic acid, vanilic acid)	Sarker and Oba (2018)
Clary sage (*Salvia sclarea* L.)	Decrease in fatty acid such as palmitic, stearic, and arachidic acids; linolenic at appreciable percentage	Increase in total phenolic contents	Taârit et al. (2012)
Salvia mirzayanii	Higher in amount of volatile oil components, oxygenated monoterpenes comprising of α-terpinyl acetate, 1,8-cineole, and sesquiterpene hydrocarbons	Increase in total phenolic content	Valifard et al. (2014)
Rapeseed (*Brassica napus*)	Reduced growth and yield attributes	Increase in total phenolics, non-flavonoids	Falcinelli et al. (2017)

Table 18.4 Impacts of different pesticides on phenolic compounds and plant's growth traits

Pesticide used	Plant/ vegetation	Phenolic compounds	Trait observed	Reference
Emamectin benzoate, alpha-cypermethrin, and imidacloprid	Tomato (*Solanum lycopersicum*)	Decline in secondary metabolic synthesis	Loss in cell viability and decrease in total soluble sugar (TSS) and total soluble proteins (TSP). Higher cell injury due to high ROS (H_2O_2) production and TBARS content. Increases in antioxidant activities SOD, CAT, GR, POD, APX, and proline	Shakir et al. (2018)
Topsin, benlate, Demacron, and chlorsulfuron	Soybean (*Glycine max*)	Total phenol contents increased leaf (114%) and shoot (220%)	Decrease in leaf area ratio, leaf area index, specific leaf area, net assimilation rate, leaf weight ratio, leaf area duration, RGR, CGR Increase in total phenolic	Siddiqui and Ahmed (2006)
Pyridine; IPP	Wheat (*Triticum aestivum* L.)	Modulation of polyphenol oxidase activity	Increase thiobarbituric acid (TBA), PPO, total protein, water-soluble carbohydrate	Wang et al. (2014)
Imidacloprid (IMI)	*Brassica juncea* L.	Modulation of the expression of nonylphenol isomers, (1E)-1-ethylidene-7a methyloctahydro-1H-indene	Synthesis of phytochemicals such as nonylphenol isomers, linoleic acid, ethyl 2-isopropylphenyl ester, oxalic acid, etc.	Sharma et al. (2015)
Diazinon	Rice (*Oryza sativa* L.)	Expression of valine, ferulic acid, sinapic acid, and phenylalanine	Biosynthesis and metabolism of 30 sugars, amino acids, organic acids, and phenylpropanoids, 31 metabolites including (hydroxybenzoic acid and ferulic acid)	Mahdavi et al. (2015)

Therefore, different atmospheric pollutants influence plant traits, and PC modulation helps in tolerance capacity up to a certain extent.

18.6 Summary

Human activity will exacerbate climatic conditions. Allelopathic nature of phenolic compounds could solve numerous ecological problems with respect to sustainable development of agriculture, forestry, natural resources, and environmental conservation. Every stress condition produces highly reactive oxygen species, responsible for oxidative stress. These PCs have potential to reduce the drastic adverse effects of oxidative stress in various plant species by elevating antioxidant defense. However, PCs are ubiquitous compounds generated during stress situations, and their higher expressions provide tolerance capacity. Although PCs are very less studied in this respect, more research should be carried out to understand the molecular mechanisms of these PCs. This chapter signifies on PCs under various anthropogenic stresses and concludes the mechanism of tolerance under this circumstance.

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UV Light Stress Induces Phenolic Compounds in Plants

19

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Abstract

Among the different types of abiotic stress, one of the most important is irradiation stress. Ultraviolet (UV) irradiation represents between 7 and 9% of total solar radiation, and and is composed between 100 and 400 nm of the electromagnetic spectrum. It is mainly divided into UV-A (315–400 nm), UV-B (280–320 nm), and UV-C (200–280 nm). This type of irradiation can affect DNA, proteins, and plant cells. This could affect the development, morphology, and photosynthesis. To counteract these harmful effects, plants use their defense mechanisms, mainly the production of secondary metabolites, among which phenolic compounds stand out (phenolic acids, flavonoids, stilbenes, tannins, lignins, and coumarins). These are of great interest for its antioxidant, anticancer, antimicrobial properties, among others. However, the responses in the increase of the different phenolic compounds will depend on factors such as intensity, type of UV light and exposure time, which is reflected in the different investigations carried out on this topic. In this sense, it is interesting to review the variety of phenolic compounds that have been reported through induction by UV irradiation.

Keywords

UV light · Phenolic compounds · Irradiation · Stress · Secondary metabolites

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19.1 Introduction

The environment of plants is constantly changing and can be stressful, which can limit their development. Different types of stress can be classified into two categories, such as biotic and abiotic stress. The former stress includes pathogens, nematodes, bacteria, and herbivores, among others, while the latter stress involves extreme temperature, heavy metals, salinity, drought, flood, and radiation (Verma et al. 2017). In response to different types of stress, the levels of reactive oxygen species (ROS) are increased, with the possible consequence of lipid peroxidation, DNA damage, and inactivation of enzymes (Khare et al. 2020). To counteract stress, plants have defense mechanisms such as antioxidant systems that participate in the prevention and balance of oxidative damage.

The enzymatic system consists of the participation of different enzymes such as superoxide dismutase (SOD), ascorbate peroxidase (APX), glutathione peroxidase (GPX), catalase (CAT), glutathione reductase (GR), monodehydroascorbate reductase (MDHAR), and dehydroascorbate reductase (DHAR), among others. On the other hand, the nonenzymatic system depends on the biosynthesis of compounds such as the accumulation of secondary metabolites, ascorbic acid, and glutathione (Gill and Tuteja 2010; Redondo-Gómez 2013).

Irradiation stress is one of the most common in plants, since light is essential for its development; in this sense, it is known that plants use photoprotection strategies to avoid the damaging effects of excessive absorption of visible light and UV light (Younis et al. 2010). The UV light has been a subject of interest in recent decades since UV light is present in solar radiation and is divided depending on its wavelength as UV-A (315–400 nm), UV-B (280–320 nm), UV-C (200–280 nm), and UV vacuum (100–200 nm). All UV types (A, B, and C) present several responses in plants; depending on the intensity and exposure, they can be stressors on plants that could limit plant development and growth (Isah 2019; Gómez-López 2012).

In response to UV stress, various studies have shown that plants can induce the biosynthesis of phenolic compounds, which are derived from secondary metabolism and have a variety of structures. The interest in these compounds is due to their biological effects as antioxidants, antitumor, antimicrobial, and anticancer, among others (Haminiuk et al. 2012; Roleira et al. 2015). For these reasons, the objective of this chapter is to review the different responses of UV light in plants by inducing the wide variety of phenolic compounds used as a defense mechanism.

19.2 Electromagnetic Radiation

Electromagnetic radiation is a form of energy that propagates like electric and magnetic waves, contains neither mass nor charge, and travels in packets of radiant energy called photons. For its part, the electromagnetic spectrum (ES) is made up of the different waves of varied energy that interact with matter. Frequency, wavelength, and photon energy are the three factors that represent it. Depending upon the wavelength and frequency, the ES can be classified into different groups such as radio wave, microwave, infrared, visible, ultraviolet, X-ray, and Ɣ-ray (Table 19.1). Energy is proportional to frequency and inversely proportional to wavelength (Percuoco 2014; Funk et al. 2016; Allison 2013).

Electromagnetic radiation is usually divided into two classes, such as ionizing radiation and nonionizing radiation. The first one is characterized by having enough energy to remove electrons from an atom or molecule; some examples are X-rays, Ɣ-rays, and electron beams (Kuan et al. 2013; Funk et al. 2016). While nonionizing radiation is insufficient to ionize molecules or break chemical bonds, it is represented by radio wave, microwaves, visible, and ultraviolet light (IARC 2002; Dyro and Morris 2004). Both types of irradiation are used for a significant number of purposes from the development of technological innovations in food preservation, communications, and medical applications. On the other hand, some types of nonionizing irradiation and ionizing irradiation can produce radicals in a living matter through interaction with biomolecules or water. It is believed that these free radicals are the main causes of biological effects by irradiation (Skalická et al. 2012). In this sense, ultraviolet light can affect plants despite having defense mechanisms to counteract, like protecting cells from DNA and membrane damage (Stefi et al. 2016).

19.2.1 Ultraviolet Light

It is estimated that between 7 and 9% of the total energy of the radiation that reaches the earth's surface corresponds to ultraviolet (UV) light. UV light is the part of the electromagnetic spectrum with wavelengths from 100 to 400 nm, comprising different classes that vary in their wavelengths. The classes are divided into UV-A (315–400 nm), UV-B (280–320 nm), UV-C (200–280 nm), and UV vacuum (100–200 nm); each type of UV can have different effects on plants. UV-C light is considered the most harmful; however, the majority is absorbed by the ozone layer. Inside the UV light and belonging to solar radiation, UV-A represents 95%, while UV-B alone 5%. UV levels may vary depending on the season, time, latitude, altitude, and solar zenith angle (Solovchenko and Merzlyak 2008; Maharaj 2015; Verdaguer et al. 2017; Gómez-López 2012).

UV-C light has been used as a postharve treatment to delay the loss of quality of fruits and vegetables; it is applied as an antimicrobial treatment, and its use is

Table 19.1 Electromagnetic spectrum (Allison 2013)

Source	Wavelength (m)	Frequency (Hz)	Electron volt (eV)
Radio wave	10^{2}	10^{6}	10^{-8}
Microwave	10^{-2}	10^{10}	10^{-4}
Infrared	10^{-5}	10^{14}	10^{-1}
Visible	10^{-6}	10^{15}	1
Ultraviolet	10^{-7}	10^{16}	10
X-ray	10^{-9}	10^{18}	10^{3}
Ɣ-ray	10^{-12}	10^{20}	10^{6}

approved in the USA within 240–260 nm for disinfection of surfaces in food. UV-C light used at doses of 0.5–20 kJ m^{-2} can damage nucleic acids of some microorganisms, through the formation of pyrimidine dimers that distort DNA and block replication (Escalona et al. 2010). It has also been described that in low doses (hormesis), it can stimulate beneficial responses, such as the increase in the production of phytochemicals (Artés-Hernández et al. 2010; Jagadeesh et al. 2011).

Similarly, UV-B is energetic so it can have harmful effects on DNA, proteins, and plant cells, affecting the development, growth, and morphology, and affect the photosynthesis of plants. However, some plants do not seem to be affected by this type of irradiation and seem to stimulate their growth. Also, plants can present positive responses as an improvement of the antioxidant system and the biosynthesis and accumulation of phenolic compounds, carotenoids, and glucosinolates (Morales et al. 2013; Zlatev et al. 2012; Takshak and Agrawal 2019). Similarly, UV-A can activate different types of responses in plants on morphology, plant growth, leaf size, photosynthesis, and the accumulation of phenolic compounds. Phototropins and cryptochromes can absorb this type of light (Chen et al. 2019; Verdaguer et al. 2017).

19.3 Mechanism of UV Action in the Induction of Phenolic Compounds

The application of different types of abiotic stress such as hyperoxia, wounding, phytohormones, and UV light for the induction of the accumulation of antioxidant compounds in plants has been of interest for some years. These types of stresses coincide in the activation of the defense mechanism of plants with the consequent production of secondary metabolites (Jacobo-Velázquez and Cisneros-Zevallos 2012). Secondary metabolites are organic compounds produced by plants that, for the most part, do not participate in the processes of development, growth, and reproduction. Their taxonomic group limits some of these, and many of their functions remain unknown (Hussain et al. 2012). However, its participation in the defense against different types of stress is proven; the secondary metabolites are produced through the use of substrates or modification of the pathways of primary metabolism (Kabera et al. 2014).

Among the compounds produced in secondary metabolism, perhaps the most important are phenolic compounds, which have a great diversity of structures and characteristics. Currently, more than 10,000 different compounds have been identified (Li et al. 2014a). Most of them have a common metabolic origin, the shikimic acid pathway, and the metabolism of phenylpropanoids. They are characterized by having at least one aromatic ring with one or more hydroxyl groups. Their structures can be simple or complex polymers of high molecular weight (Haminiuk et al. 2012). They can be classified concerning their structure within phenolic acids, flavonoids, stilbenes, tannins, lignins, and coumarins (Shahidi and Yeo 2018).

Light is essential for plants to carry out photosynthesis and achieve their development; however, depending on its wavelength, it could be an abiotic stress factor, affecting the production of secondary metabolites. Due to the above, the biosynthesis of phenolic compounds, mainly flavonoids, has been reported to be increased due to UV radiation exposure (Agati et al. 2011). There are different studies carried out on this effect for either UV-A (315–400 nm), UV-B (280–320 nm), or UV-C (200–280 nm) (Verdaguer et al. 2017; Schreiner et al. 2012; Urban et al. 2016). However, there is still no clear explanation as to how UV light acts as a signaling agent in the biosynthesis of secondary metabolites, although some progress has been made in this direction.

The concentration of phenolic compounds has been described to be increased by UV irradiation, probably using reactive oxygen species (ROS) as signaling components. In addition to this, some authors suggest that the production of flavonoids under the stress of UV light is mainly carried out by plants to counteract the generation of ROS, since other compounds such as derivatives of hydroxycinnamic acids have a greater molar extension coefficient in the UV range (Fini et al. 2011; Agati et al. 2011).

Similarly, Gonzalez-Aguilar et al. (2010) described that UV-C interacts with atoms and molecules producing ROS, initially superoxide anion ($O_2{}^{-*}$), and then activating the mechanism of antioxidant enzymes [(SOD, CAT, MDHAR (monodehydroascorbate reductase), GSH (glutathione), and GSSG (oxidized glutathione)], by which H_2O_2 is produced. Moreover, H_2O_2 acts as a signaling molecule, activating the expression of genes that encode phenylalanine ammonia-lyase (PAL) and chalcone synthase (CHS), responsible for the synthesis of phenolic compounds. For example, the activation of the defense mechanisms of plants has been observed in peanut seedlings irradiated with UV-C for 1 h, where there is an increase in the levels of hydrogen peroxide (H_2O_2) and superoxide anion ($O_2{}^{-*}$), as well as the consequent enzymatic response with the increase of antioxidant enzymes such SOD, CAT, APX, DHAR, and MDHAR (Tang et al. 2010). Similarly, Kumari et al. (2010) reported an increase in the activity of SOD, CAT, APX, and GR enzymes after the application of two different doses of UV-B (1.8 kJ m^{-2} day^{-1} and 3.6 kJ m^{-2} day^{-1}) in *Acorus calamus*.

The presence of a photoreceptor has recently been described *UV RESISTANCE LOCUS8* (UVR8) specific for UV-B, which controls a variety of genes such as DNA repair, protection against oxidative stress, chloroplast functions, and the keys in the induction of phenolic compounds such as flavonoids. These responses are mediated by transcription factors that regulate CHS as *ELONGATED HYPOCOTYL5* (HY5) and *CONSTITUTIVELY PHOTOMORPHOGENIC1* (COP1) (Coffey et al. 2017; Liu et al. 2015). COP1 degrades the HY5 protein in the dark; however, under UV-B light conditions, UVR8 is divided into monomers, which act with COP1; this UVR8-COP1 interaction allows the response of the genes responsible for the acclimatization of plants as activation of flavonoid synthesis (Singh et al. 2014; Morales et al. 2013). For example, in *Arabidopsis* UVR8, COP1, and HY5 mediate CHS induction (Tilbrook et al. 2013). Likewise, Clayton et al. (2018) found that

UVR8 participates in the induction of flavonoids, which contribute to UV-B tolerance in *Marchantia polymorpha.*

In the case of UV-A, there are few studies compared to UV-B and UV-C. However, it has also been reported that UVR8 could be involved in the induction responses of phenolic compounds by UV-A (Neugart and Schreiner 2018). In accordance to Morales et al. (2013), UVR8 participates in the induction of phenolic acids. However, it also affected the induction of kaempferol in *Arabidopsis* leaves. Likewise, in another study in *Arabidopsis*, it has been observed that cryptochromes regulate the accumulation of phenolic compounds in response to blue light and UV-A, while UVR8 participates in the accumulation of flavonoids in low doses of UV-A (Brelsford et al. 2019). Also, UV-A is related to the response of enzymes such as PAL and CHS, in addition to anthocyanin pigment 1 (PAP1) and dihydroflavonol-4-reductase (DFR) (Verdaguer et al. 2017).

19.4 Related Enzymes to the Biosynthesis of Phenolic Compounds

Enzymes are catalysts, which means that they can accelerate chemical reactions without being part of the products or consumed in the process. They can be classified as transferases, hydrolases, lyases, ligases, isomerases, and oxidoreductases. Previously it was thought that all enzymes are proteins. However, it is now known that some RNA molecules have catalytic activity, known as ribozymes. Enzymes catalyze specific chemical reactions and act on substrates. The union between the enzymes and the substrate is known as the enzyme-substrate complex, and at the end of the reaction, the products are obtained (Blanco and Blanco 2017). In plants there is a wide diversity of enzymes involved in the synthesis of phenolic compounds, either in the formation of the main compounds or in the biosynthesis of specific phenolic compounds. Therefore, some enzymes have been studied depending on the response of plants to exposure to ultraviolet light. A review of the main enzymes related to the increase in the content of phenolic compounds derived from the application of ultraviolet light will be presented below.

19.4.1 Phenylalanine Ammonia-Lyase (PAL)

Phenylalanine ammonia-lyase (PAL EC 4.3.1.5) is the key enzyme in the metabolism of phenylpropanoids. PAL catalyzes the non-oxidative deamination of L-phenylalanine to obtain trans-cinnamic acid and a free ammonium ion; this is considered the first step in the phenylpropanoid pathway and where products of the primary metabolism are diverted for the initiation of secondary metabolism (Kumar et al. 2019; Hyun et al. 2011). PAL has shown an increase in its activity as part of the defense mechanism of plants against different types of biotic and abiotic stress, including stress generated by ultraviolet light (Zhang and Liu 2015).

For example, an increase in PAL activity has been observed in lotus root when treated with two different doses of UV-C (30 and 60 min of exposure); the increase in enzyme activity was not observed within the first days of storage. However, there were significant increases compared to the control on days 3, 7, 11, and 15 of storage (Li et al. 2020). Likewise, an increase in PAL activity has been observed when treating tomato (*Solanum lycopersicum* L.) with UV-A in cotyledons and hypocotyls; PAL activity reached its maximum level at 6 and 12 h, respectively, but activity decreased at 24 h. An increase in the expression of SIPAL5 genes was observed in tomato fruits after 3 and 24 h. However, it was not related to an increase in the expected anthocyanin content (Guo and Wang 2010).

In another study, asparagus was subjected to white, red, blue light (3 h, 30 μmol m^{-2} s^{-1}), and UV-C (8 min, 1 kJ m^{-2}), and a greater increase in PAL activity was observed in UV-C treatment. However, the highest content of anthocyanins was presented by white light (Huyskens-Keil et al. 2020). Similar results have been observed in a medicinal plant called *Ixeris dentata* Nakai (3 weeks after being transplanted), which was subjected to UV-A and UV-B light. UV-A treatment was carried out continuously 24 h for 1 week, observing a 30% increase in PAL activity after days 1 and 3. However, there were no significant differences on days 5 and 7 after treatment. UV-B treatment consisted of 4 h d^{-1} with a gradual increase from 1 to 7 h day^{-1} over 6 days; it showed an increase of 230 and 120% of PAL after 2 days of treatment, respectively. This increase was related to the content of phenolic compounds, flavonoid content, and antioxidant activity (Lee et al. 2013).

Also, similar behavior has been reported in *Vigna mungo* L. when increasing PAL activity after being irradiated with UV-B (10, 20, 30, and 40 min) after 4 days. However, a decrease was observed of activity at control levels after 8 days. Additionally, an increase in the content of total phenolic compounds, flavonoids, and anthocyanins was reported (Shaukat et al. 2013). Likewise, in strawberries treated with UV-C, an increase of 18% in PAL activity was observed (de Oliveira et al. 2016). In another study carried out on pears, doses of 5 kJ m^{-2} of UV-C were used in order to maintain the quality of the fruit. It was observed that the doses were effective in inhibiting the growth of *Monilinia fructícola*, in addition to significantly increasing the activity PAL after 48 h up to 176% compared to control (Li et al. 2010). With the same approach of maintaining quality and delaying senescence in oyster mushroom (*Pleurotus ostreatus*), 4.0 kJ m^{-2} doses of UV-C were used, obtaining an improvement in total quality (loss of electrolytes, color, soluble solids, among others) and a significant increase in PAL compared to the control during the 15 days of storage (Wang et al. 2017).

19.4.2 Other Enzymes

Flavonoids participate in different functions such as pathogen protection, signaling, auxin transport, pollinator attractants, and protection against UV Light (Falcone Ferreyra et al. 2012). Therefore, the activation of enzymes related to its biosynthesis in response to UV has been the subject of interest in various investigations. Among them, chalcone synthase (CHS EC 2.3.1.74) is considered the key enzyme, since it participates in the first step of flavonoid biosynthesis. It catalyzes the condensation of 3 units of malonyl-CoA acetate with 4-coumaroyl-CoA to obtain naringenin chalcone, from where a great diversity of flavonoids such as flavonols, flavones, and anthocyanins are derived (Dao et al. 2011; Tian et al. 2011). After this, chalcone isomerase (CHI) catalyzes the stereospecific isomerization of chalcone in flavanone (Morita et al. 2014). Then, flavanone-3-hydroxylase (F3H) catalyzes the biosynthesis of dihydroflavonols, which through the enzyme flavonol synthase (FLS) can become flavonols with the introduction of double bonds between C-2 and C-3 (Sun et al. 2019). Meanwhile, flavone synthase (FNS) catalyzes the conversion of flavanones to flavones (Ferreyra et al. 2015).

Other important enzymes are those that are involved in the anthocyanin biosynthesis. For instance, dihydroflavonol-4-reductase (DFR) participates in the reduction of dihydroflavonols to leucoanthocyanidins, and anthocyanidin synthase (ANS) converts colorless leucoanthocyanidins to colored anthocyanidins (Li et al. 2017; Wang et al. 2011).

There are several studies that have shown the increase in the activity of enzymes related to flavonoid biosynthesis. Pinto et al. (2016) studied the postharvest effect of applying UV-C (65.6 J m^{-2}) on conventional and organic grapes; they observed a significant increase in transcription levels of mRNA encoding CSH in both organic and conventional grapes. Similarly, *Brassica rapa* was subjected to 15 W m^{-2} UV-A; after 24 h, a significant increase was observed both in the content of anthocyanins and in the expression of three genes (*BrCHS1*, *BrCHS4*, and *BrCHS5*) that express for CHS and other genes related to anthocyanin biosynthesis such as F3H, DFR, and ANS (Zhou et al. 2013).

Liu et al. (2018) treated tomato fruits with 4 KJ m^{-2} UV-C and observed changes in enzyme activity during 35 days of storage and found that PAL and C4H (cinnamic acid 4-hydroxylase) activity was significantly higher than control throughout storage time. On the other hand, the enzymes 4CL (4-coumaric-CoA ligase) and CHS increased their activity significantly until day 28 of storage but decreased on day 35 to control levels. In the case of CHI, it showed a significant increase until day 21. Besides, the expression for FLS and F3H enzymes was significant after 14 days of storage; this increase in enzyme activity corresponded to the increase in phenolic compounds.

In another study carried out on grapes, UV-B and UV-C treatments in doses of 3.6 kJ m^{-2} were compared. A significant increase in the content of phenolic compounds, flavonoids, anthocyanins, and flavanols was observed compared to the control. After 7 days of storage, this increase was related to the increase in the expression for the enzymes PAL, CHS, F3H, LAR (leucoanthocyanidin reductase), ANS, and STS (stilbene synthase). This overexpression was significant compared to the control during on days 7, 14, 21, and 28 of storage for both treatments; however, the best response corresponded to grapes treated with UV-C (Sheng et al. 2018).

Similarly, Xi et al. (2015) studied the effect of UV-C light on grape leaves, which were treated with 10 min of exposure (6 W m^{-2}) at a distance of 40 cm. The leaves were analyzed for 48 h and observed a significant increase in the resveratrol content from 0.97 μg μ^{-1} to 467.62 μg μ^{-1} of f.w. This increase was related to the increase in expression for PAL and STS. The authors suggest that in this case, the biosynthesis pathway was aimed at stilbenes since STS catalyzes the condensation of 3-malonyl-CoA and 4-coumaroyl-CoA to form resveratrol and CHS that compete for the same substrate and did not show changes. In another study carried out on grape plants treated with UV-C for 10 min at a distance of 15 cm, a similar behavior was observed when an increase in STS activity and expression was found after UV-C treatments, with a peak maximum in the content of resveratrol and STS after 16 and 24 h (Wang et al. 2010).

In addition to the above, the increase in response to UV light of tyrosine ammonia-lyase (TAL) has also been reported. This enzyme catalyzes the reaction of L-tyrosine to p-coumaric acid (Ganapathy et al. 2016). For example, Shaukat et al. (2013) reported a significant increase in TAL compared to the control for 8 days in *Vigna mungo* in all UV-B treatments (10, 20, 30, and 40 min). Li et al. (2014b) carried out treated strawberries with abscisic acid and UV-C radiation (4.1 kJ m^{-2}) and found an increase in PAL and TAL compared to the control. However, this increase was not maintained during storage days. It has also been reported that UV-A dose (5.5 W m^{-2}) has been effective in increasing anthocyanins in hypocotyls of soybean sprout; this was related to the expression of genes from the anthocyanin biosynthesis pathway such as DFR, ANS, and UFGT (flavonoid 3-O-glucosyltransferase) (Su et al. 2017).

19.5 Effect of UV Stress on Phenolic Compounds in Plants

In response to different types of stress, plants synthesize different secondary metabolites as a defense mechanism. Abiotic stress produced by UV radiation has been extensively studied because the damage that this stress can cause to DNA, proteins, and the cell membrane has been demonstrated, causing deregulation in the photosynthetic process. However, UV radiation may have beneficial effects by increasing the content of secondary metabolites, such as phenolic acids, flavonoids, tannins, stilbenes, lignins, and coumarins (Madani et al. 2019).

19.5.1 Phenolic Acids

The phenolic acids, as other secondary metabolites, are widely available in the plant kingdom. Phenolic acids are a subdivision of phenolic compounds, classified as non-flavonoid polyphenols, which are responsible for many plant characteristics such as color, bitterness, acerbic taste, flavor, odor, and antioxidant properties. Also, they are related to protection against, insects, viruses, bacteria, and UV light, even to allelopathic action of plants (Khadem and Marles 2010; Khanam et al. 2012; Heleno et al. 2015).

Phenolic acids have a particular carboxyl group attached or linked to a benzene ring. They are synthesized from the shikimate pathway from L-phenylalanine or

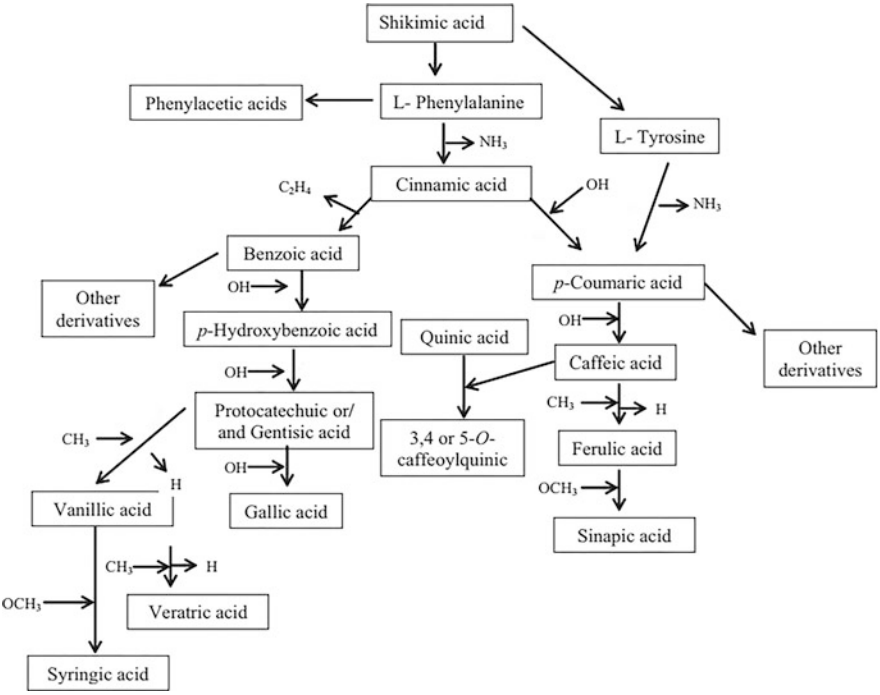


Fig. 19.1 General representation of the phenolic acid biosynthesis derived from the shikimic acid pathway (Heleno et al. 2015)

L-tyrosine by deamination, hydroxylation, and methylation reactions (Fig. 19.1). First, deamination of the phenylalanine or the tyrosine occurs, giving cinnamic or p-coumaric acids, respectively. Then, the degradation of the side chain of cinnamic acid leads to benzoic acid. Finally, cinnamic, *p*-coumaric, and benzoic acid aromatic rings are then hydroxylated and methylated to form its derivatives (Khadem and Marles 2010; Heleno et al. 2015).

Depending on their structure, phenolic acids can be distinguished in two classes: benzoic acid derivatives and cinnamic acid derivatives (Khadem and Marles 2010) (Fig. 19.2).

As we mention above, phenolic acids provide antioxidant properties to the plants, mostly as a defense mechanism to several hazards. However, there is scientific evidence that the antioxidant capacity also provides health-promoting properties to the human body, and is considered a major factor in determining the quality and value of crops (Wang and Frei 2011; Jacobo-Velázquez and Cisneros-Zevallos 2012; Heleno et al. 2015).

For this reason, the increase in the content of phenolic acids in fruits, vegetables, and horticultural crops has been sought, with genetic engineering being the most widely used tool to increase the improved concentrations of desirable compounds; however, genetically modified plants are not yet accepted by society and could even

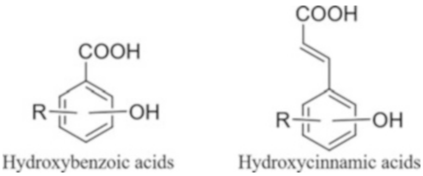


Fig. 19.2 Classes of phenolic acids. (Adapted from Khadem and Marles 2010)

Table 19.2 Effect of UV light on the phenolic acid concentration of different crops

Crop species	UV light	Phenolic acids	Effect	References
Lettuce (*Lactuca sativa* L.)	UV-A	Gallic acid, chicoric acid, and chlorogenic acid	Increase	Li and Kubota (2009); Oh et al. (2009)
Sweet basil (*Ocimum basilicum* L.)	UV-B	Gallic acid, cinnamic acid, and ferulic acid	Increase	Ghasemzadeh et al. (2016)
Apple (*Malus domestica* Borkh)	UV-B	Chlorogenic acid	Increase	Lancaster et al. (2000)
Satsuma mandarin (*C. unshiu* Marc. cv. Owari)	UV-C	Caffeic acid, *p*-coumaric acid, ferulic acid, and sinapic acid	Non-effect	Shen et al. (2013)
Tomato (*Solanum lycopersicum* L.)	UV-solar simulation	Caffeic acid, p-coumaric acid, and ferulic acid	Increase	Luthria et al. (2006)

be considered as potential biological hazards that create an ecological imbalance (Jacobo-Velázquez and Cisneros-Zevallos 2012). Due to this, postharvest abiotic stresses become alternative technologies for the accumulation of phenolic acids, since a general trend related to it was observed. If a chronic exposure to stress occurs, this affects the chemical composition of crops, and thus the quality of agricultural products. Abiotic stress is defined as a growth condition, in which one or more stress factors (drought, heat, salinity, tropospheric ozone, and UV radiation) are elevated relative to a non-stress treatment (Wang and Frei 2011; Jacobo-Velázquez and Cisneros-Zevallos 2012).

Among these stress conditions, we focus on UV radiation, since many studies related to UV stress found, in most cases, an increase in phenolic compound concentration in various crops (Wang and Frei 2011). Table 19.2 shows some examples of UV light effects on phenolic acids.

19.5.2 Coumarins

Coumarins comprise a very large class of compounds found all over the plant kingdom. Coumarins are derived from shikimic acid, via cinnamic acid, by ortho-hydroxylation of *p*-coumaric, caffeic, and ferulic acid; they are classified as a member of the benzopyrone family, which possess a characteristic benzene ring joined to a pyrone ring (Fig. 19.3).

Coumarins are divided into four main subtypes: simple coumarins, furanocoumarins, pyranocoumarins, and pyrone-substituted coumarins. Coumarins can occur in nature as aglycones or glycosides, most probably present as a trans-O-glycoside. Most coumarins are present in higher plants, distributed throughout all parts of the plant, mostly in the fruits, followed by the roots, stems, and leaves (Jain and Himanshu 2012; Yin et al. 2014; Matos et al. 2015).

The function of coumarins in plants is not entirely clear, but they participate as plant growth regulators, bacteriostats, and fungistats, and are even suggested as waste products (Venugopala et al. 2013). The commercial applications of coumarins are wide, mainly in organic chemistry and medical chemistry; they are also used in the formulation of cosmetic products and food additives (Matos et al. 2015). Coumarins exhibit a wide range of pharmacological activities, which include antidiabetic, antiviral, antimicrobial, anticancer, antioxidant, antiparasitic, antihelminthic, antiproliferative, anticonvulsant, anti-inflammatory, and antihypertensive activities (Venugopala et al. 2013; Venkata Sairam et al. 2016; Mohammed et al. 2019).

Environmental conditions and seasonal changes such as light levels and soil nutrients, including nitrogen, phosphorus, and potassium, affect the accumulation of coumarins. In the case of light, the furanocoumarins are photoactive, which absorb wavelengths at 330 nm in the UV-A region. It has been observed that furanocoumarin concentration may increase up to 50% after UV radiation, probably as a mechanism by which the plants avoid the harmful effects of exposure to UV light (Zangerl and Berenbaum 1987; Kuhlmann and Müller 2011; Jain and Himanshu 2012).

The activity of the furanocoumarins depends on their photoactivation by UV; for example, the UV exposure also increases the phototoxicity of furanocoumarin. Xanthotoxin and bergapten are particularly photoactive, and they are toxic to insects. It has been observed that their concentration increases with the increase in the intensity of UV light. It is worth to mention that UV light appears to have a bigger effect on these two furanocoumarins. The furanocoumarin phototoxicity is not limited to insects. They also exert toxicity on the parasitoid larvae. In this sense, it has been demonstrated that UV effects on plant metabolites can extend up to the third trophic level (Berenbaum and Zangerl 1987; Zangerl and Berenbaum 1987; Kuhlmann and Müller 2011).

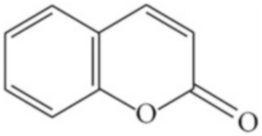


Fig. 19.3 Chemical structure of a coumarin (Venugopala et al. 2013)

19.5.3 Stilbenes

Stilbenes are a subdivision of phenolic compounds characterized by the presence of two benzene rings linked via an isopropylene moiety that forms a compact ring structure separated by a double bond. Stilbenes are synthesized by the phenylpropanoid pathway, involving the action of key enzymes such as PAL, C4H, 4CL, and STS (Fig. 19.4). Most plant stilbenes are derivatives of the basic unit *trans*-resveratrol (3,5,4′-trihydroxy-trans-stilbene) (Gambini et al. 2013; Kasiotis et al. 2013; Xu et al. 2015).

Stilbenes are secondary metabolites considered as phytoalexins. They are involved in constitutive and inducible plant defense responses against plant fungal pathogens, nematodes, and herbivores. Besides, stilbenes exert potent and diverse biological activities and medicinal properties, being the most extensively studied resveratrol and its derivatives, such as pterostilbene, oxyresveratrol, and viniferins (Fig. 19.5). Therefore, the induction of the production of stilbenes, as well as other secondary metabolites, is desirable to increase the nutraceutical properties, in addition to its function in the control of crop diseases (Jeandet et al. 2010; Vannozzi et al. 2012; Kasiotis et al. 2013; Freitas et al. 2015; Dubrovina and Kiselev 2017).

Stilbenes, like other secondary metabolites, can be induced by environmental and stress conditions, such as pathogen attack; biotic or chemical elicitation including methyl jasmonate, polysaccharide, hydrogen peroxide, and cyclodextrin; and ultraviolet exposition. In particular, UV-C treatments, pre- or postharvest, increase the *trans*-resveratrol amount (Wang et al. 2010; Guerrero et al. 2010; Xu et al. 2015).

Wine, therefore, grapes are recognized by the health benefits, being the most significant sources of stilbenes in the human diet, hence the most studied. Stilbenes occur mainly in the skin of grape berries. Subsequently, they pass from grape to wine during alcoholic fermentation; however, resveratrol has also been detected in the stem, axillary bud, shoot tip, petiole, root, and the leaf of grape plants (Guerrero et al. 2010; Wang et al. 2010).

Scientific evidence has shown that resveratrol accumulation after UV-C exposure is organ-specific and variety-dependent; for example, Wang et al. (2010) found that the maximum content of resveratrol was presented in the stem phloems, followed by axillary buds, roots, stem xylems, shoot tips, and petioles. The minimum was found in leaves (254 nm, 3 W cm^{-2} for 10 min at 15 cm distance). Meanwhile, Guerrero et al. (2010) tested three varieties of *Vitis vinifera sylvestris*, seven of *Vitis vinifera sativa*, and two direct hybrid producers, and reported differences in the resveratrol and total stilbene concentration after UV-C treatment depending on the variety and campaign but not on the subspecies. They also demonstrated that the varieties with a high stilbene concentration on the day of harvesting have better biosynthetic mechanisms in order to respond to stress as postharvest UV-C treatment.

It is worth to mention that combination of UV-C with other technologies could reach better results compared with the same treatments applied alone. Freitas et al. (2015) used UV-C (2.82 ± 0.44 mW cm^{-2} for 2 min at 60 cm distance) combined with chitosan coating followed by incubation for 24 h at 20 °C before refrigerated storage. They observed the increase of the resveratrol content, maintained sensory

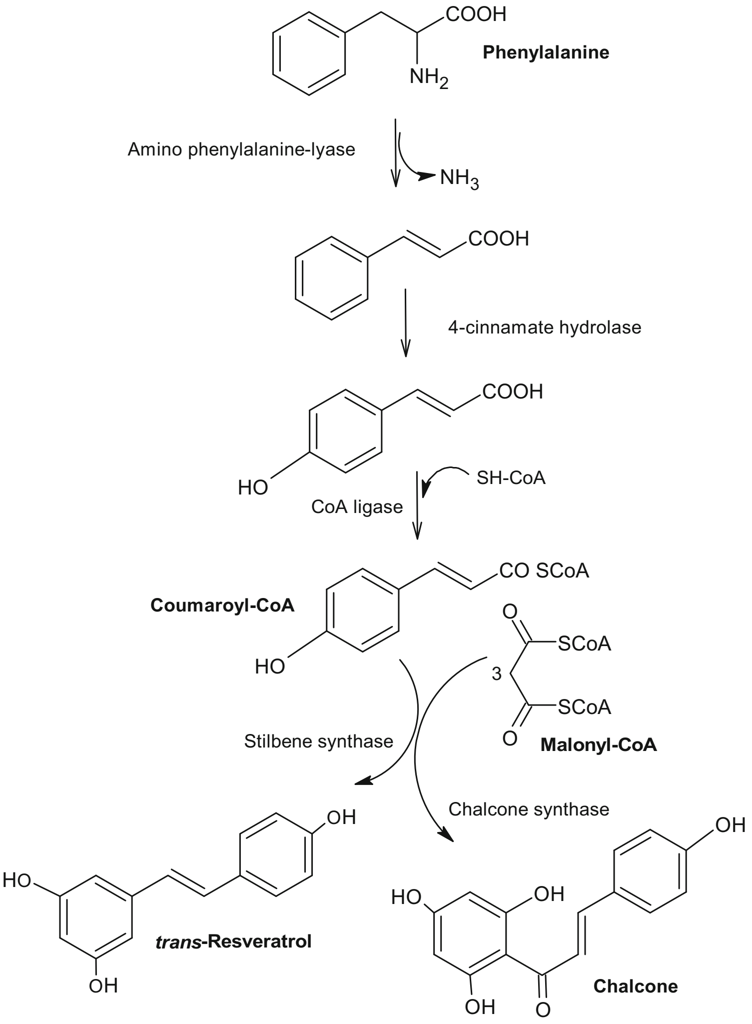
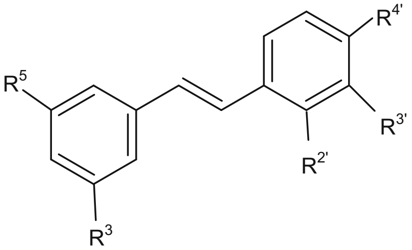


Fig. 19.4 Biosynthesis of *trans*-resveratrol (Gambini et al. 2013)

Fig. 19.5 Chemical structures of common plant stilbenes (Dubrovina and Kiselev 2017)



quality, and reduced fungal decay of red table grapes variety Crimson when compared to control grapes. Likewise, Xu et al. (2015) treated *Vitis vinifera* L. cv. Cabernet Sauvignon cell suspension cultures, with UV-C (254 nm, 10 W cm^{-2} for 10–30 min at 8 cm distance) in combination with methyl jasmonate or salicylic acid. In both cases, the combination of treatments improved the stilbene production, compared by themselves; however, UV-C and methyl jasmonate showed a synergistic effect.

19.5.4 Flavonoids

Flavonoids are the most abundant phenolic compounds in nature. More than 5000 flavonoids have been identified, and are ubiquitous in plants, more commonly found in leaves and the skin of fruits as they act as UV light-absorbing pigments. Their basic structure is depicted in Fig. 19.6. It consists of a C6-C3-C6 carbon skeleton, where the two C6 units are named as ring A and ring B, and the C3 is the ring C. Flavonoids are commonly divided into six groups: flavones, flavanones, flavonols, flavan-3-ols, anthocyanidins, and isoflavones. The biosynthesis of flavonoids is similar to stilbenes. They are derived from a phenylpropanoid unit by sequential decarboxylative addition of three molecules of malonyl-CoA, in a reaction catalyzed by the CHS enzyme, where the formation of chalcones results. Finally, different enzymes give rise to the different types of flavonoids (Demkura and Ballaré 2012; Reis Giada 2013; Santana-Gálvez and Jacobo-Velázquez 2018).

Exposure of plants to different types of UV radiation has enabled the defense mechanisms of plants to be activated, producing secondary metabolites such as flavonoids. For instance, under plant exposure to UV-B, flavonoids can act as natural filters because they absorb at 280–320 nm wavelength; therefore, they act as natural UV-B filters. An increased flavonoid synthesis has been reported in different plants treated with UV light radiation (Li et al. 2019). *Conocarpus lancifolius* (Engl), exposed to different levels of UV-B (1.8, 3.6, 7.2 kJ m^{-2}) for 6 h/day during 30 days, showed a 91.5% increase in flavonoids (Redha et al. 2013). In another study, broccoli florets submitted to different UV-B radiation doses (2.2, 8.8 and 16.4 kJ m^{-2} day^{-1}) in a glasshouse showed an enhancement in the concentration of total flavonoid compounds. Furthermore, the greatest total flavonoid increase (0.40 mg GAE g dry $matter^{-1}$) was shown with the UV-B radiation treatment of 16.4 kJ m^{-2} day^{-1} (Topcu et al. 2018). Also, increases in total glucosinolates were

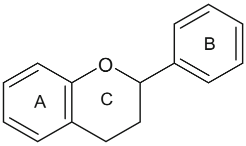


Fig. 19.6 Chemical structure of flavonoids (15 carbon atoms arranged in 2 phenyl rings (ring A and ring B), linked through a heterocyclic pyran ring (ring C).

associated with the increment in flavonoid content since they share the same signaling pathway (Topcu et al. 2018).

Ruiz et al. (2016) evaluated the short-time exposure to UV-B radiation on the peel of mature lemons (*Citrus limon*). UV-B radiation was applied at 2200 J m^{-2} for 3 min during 30 days, applied at a distance of 50 cm above the lemons. On day 2 of treatment, the results showed an increase in flavanones-dihydroflavonols and flavonols of 29 and 214%, respectively, compared with the control. In another study, *Centella asiatica* L. Urban was grown in two sun simulators and treated with UV-B radiation at 0.3 W m^{-2}. In this study, flavonoids were measured in situ with a multiparametric portable optical sensor, and the results showed a rise in flavonoid content in all treatment groups. Also, a high fluorescence-based flavonol index was observed in the UV-B-radiated plants. This index is related to the concentration of ortho-dihydroxy B-ring-substituted flavonols, which are known to possess an excellent ability to scavenge light-induced reactive oxygen species (Müller et al. 2013).

On the other hand, it has been observed that the synthesis of flavonoids varies among species submitted to the same UV light conditions. For instance, UV-B radiation (from 1.2 to 7.2 kJ m^{-2}) caused different responses in *Vigna aconitifolia* and *Vigna mungo*, having a better accumulation in the former one. Moreover, a decline in the accumulation of total flavonoids after UV-B at 2.4 kJ m^{-2} was observed (Dwivedi et al. 2015).

In another study, rutin, a common flavonoid in buckwheat, was enhanced with UV-B treatment. Buckwheat (*Fagopyrum esculentum* Moench) sprouts treated with different radiation intensities of UV-B (410, 550, and 890 W m^{-2}) and UV-A (250 W m^{-2}) radiation showed the highest rutin content (1000 mg/100 g dry $weight^{-1}$) with UV-B radiation of 890 W m^{-2}. Also, the rutin concentration was 1.6 times higher than the control. Furthermore, a positive correlation between rutin concentration and DPPH radical scavenging activity was observed. However, irradiation longer than 24 h is detrimental to the growth of buckwheat sprouts (Tsurunaga et al. 2013).

Some studies have evaluated a pre-treatment to reduce the harmful effect of UV radiation. In this context, titanium dioxide nanoparticles (25 and 50 mg L^{-1}) were applied to *Crocus sativus* L. before the UV treatment. UV-B (18.3 KJ m^{-2}) was applied for 30 and 45 min, at 40 cm from the top of the plant. Interestingly, the titanium dioxide nanoparticles' pre-treatment showed a great effect on flavonoid content, more than UV-B alone. Also, the maximum content of total flavonoids was enhanced with titanium dioxide nanoparticle pre-treatment (25 mg L^{-1}) and 30 min of UV-B exposure. However, the total anthocyanin content was reduced with the same treatment (Moradi Rikabad et al. 2019).

Leaves of *Ginkgo biloba* L. treated with UV-B (82.90 $\mu Ws \cdot cm^{-2}$) at a 20 cm of distance showed an increase in the total flavonoid concentration at 240 min with 10.3 mg g^{-1} dry weight, where quercetin (1.35 mg g^{-1} dry weight), kaempferol (2.28 mg g^{-1} dry weight), and isorhamnetin (0.49 mg g^{-1} dry weight) were the main components. Nonetheless, a decline after 360 min was shown in total flavonoid content (Sun et al. 2010). Furthermore, quercetin and kaempferol glycoside synthesis are greatly influenced by UV-B radiation, as demonstrated in *Arabidopsis thaliana* seeds with a dose of UV-B of 5.5 kJ m^{-2} (Demkura and Ballaré 2012).

In a study in the field, samples every 3 months during 1 year of *Buxus sempervirens* L. leaves, six flavonoids were detected: quercetin-3-arabinoside, quercetin aglycon, kaempferol-3-glucoside, luteolin derivative and two glycosylated flavonols with rhamnose (isorhamnetinedirhamnoside and isorhamnetinerhamnoside), and two gallotannins (digalloylglucose and pentagalloylglucose) (Bernal et al. 2013). Also, UV-B treatment enhanced quercetin-3-glucuronide, quercetin-3-arabinoglucoside, kaempferol-3-glucuronide, chlorogenic acid, and neochlorogenic acid in *Populus tremula* (Randriamanana et al. 2015).

Grapevine cv. Tempranillo, exposed to UV-B radiation (5.98 and 9.66 kJ m^{-2} day^{-1}) with different levels of ripeness, fruit set (FS) to ripeness or from the onset of veraison to ripeness (OV), showed the presence of 14 anthocyanins and 12 flavonols. The highest anthocyanin content was reached with 5.98 kJ m^{-2} day^{-1}; however, there was no significant difference with the control (no radiation). On the other hand, total flavonols reached its maximum concentration with UV-B at 9.66 kJ m^{-2} day^{-1} for FS and with 5.98 kJ m^{-2} day^{-1} for OV being significantly different from the control. A significant correlation between UV-B and the accumulation of some individual flavonols was observed. For instance, isorhamnetin-3-O-glucoside and quercetin-3-O-glucuronide, followed by kaempferol-3-O-glucoside and kaempferol-3-O-galactoside, were the most highly correlated flavonols (Martínez-Lüscher et al. 2014). *Tilia platyphyllos* leaves showed both quantitative and qualitative differences between leaves exposed to the sun and leaves on the shadow, showing higher flavonoid contents in sun leaves, and a higher kaempferol ratio (Majer et al. 2014).

In another study, broccoli heads grown under three different doses UV-B radiation, 27 min (for 2.2 kJ m^{-2}), 64 min (8.8 kJ m^{-2}), and 120 min (16.4 kJ m^{-2}), fixed at 15 cm of distance above the upper parts of plants, showed a decreased total carotenoid, the chlorophyll a and chlorophyll b content but increased the ascorbic acid, total phenolic, and total flavonoids. The total flavonoid content with UV-B treatment at 16.4 kJ m^{-2} was 0.27 mg CE g^{-1} dry matter and decreased to 0.24 mg CE g^{-1} DM after 60 days of storage. The authors suggest that preharvest UV-B radiation during the vegetative period might be a promising tool for increasing the antioxidant components of broccolis (Topcu et al. 2015).

Another experiment in UV-A and UV-C has been shown an important effect in flavonoid content. UV-A treatment (5.5 W m^{-2}) showed an enhancement in the total flavonoid and anthocyanin content in immature radish microgreens (*Raphanus sativus* L. cv. Yanghua). Also, cyanidin-3-rutinoside-5-glucoside, cyanidin-3-glucoside, petunidin-3,5-O-diglucoside, and cyanidin were detected (Zhang et al. 2019).

A postharvest of UV-C light (4 kJ m^{-2}) was applied to Shiitake (*Lentinus edodes*) mushrooms. The results showed that after 9 days of storage, the total flavonoid contents increased and continued to increase in the following days (Jiang et al. 2010). In another study, short-term UV-B (4.2 kJ m^{-2} day^{-1}) and UV-C (5.2 kJ m^{-2} day^{-1}) radiation pre-treatments in a greenhouse before transplantation into the field were applied to *Artemisia annua*. The results showed an enhanced biosynthesis of secondary metabolites such as artemisinin and flavonoids compared to nonirradiated plants (Rai et al. 2011). In another study, flax (*Linum usitatissimum* L.) treated with UV-C radiation (3.6 kJ m^{-2}) increased by 2.94-fold (98.9 mg L^{-1}) the total flavonoid content, compared to the control (Anjum et al. 2017).

Flavonoids and other secondary metabolites are enhanced by abiotic stress, such as UV radiation. However, some limitations must be addressed in order to have a better understanding on the flavonoid induction, specifically, standardized the measurement of flavonoids as some studies measured them in situ, or by spectrophotometric methods, without proper identification. Additionally, the content of phytochemicals might change according to the way of planting (in the field or greenhouse), the pre-treatment, altitude, temperature, and the duration of the study. Also, more studies should be addressed in order to minimize the harmful effects of UV radiation on the plant tissues and yield. Finally, more information about the effects of UV-C radiations on the mechanism responsible for the stimulation of the plant's secondary metabolism is needed.

19.5.5 Tannins

Tannins are phenolics with high molecular weight from 500 to 20,000 Da and are classified into two groups: (1) condensed tannins (CT) also named as proanthocyanidins or non-hydrolyzable tannins and (2) hydrolyzable tannins (HT). CT are polymers of the flavonoids: flavan-3-ols or flavan-3,4-diols. On the other hand, HT are polymers having a center of glucose or polyhydric alcohol esterified with phenolic acids, specifically ellagic acid (ellagitannins) or gallic acid (gallotannins). HT can be hydrolyzed with hot water, enzymes, acids, or bases. Other less common types of tannins are complex tannins and phlorotannins (Reis Giada 2013).

Some authors have reported the enhancement of tannin content in plants with UV-B radiation. *Heteropogon contortus* BL-1, commonly known as Pili grass, was treated with either ambient or elevated UV-B radiation (ambient +7.2 kJ m^{-2} day^{-1}), during 3 h daily until the end of the experiment (110 days after germination). The highest tannin concentration was shown on day 40 after germination (Hamid et al. 2019). In another study, *Populus tremula*, in UV-B conditions simulating a 20% decrease in stratospheric ozone, enhanced the total condensed tannins (Randriamanana et al. 2015). Birches (*Betula pendula* Roth.) were exposed to ambient and elevated UV-B radiation (were treated with 4.12 and 7.95 kJ m^{-2} day^{-1}, and enhanced CO_2 concentration, this treatment showed a high content of soluble tannins as well as flavonoids) (Lavola et al. 2013).

19.6 Conclusion

Although the stress by irradiation of UV light can induce negative effects such as DNA damage and affect the development of plants, there are positive responses such as induction in the biosynthesis of phenolic compounds by the effect of the different types of UV. This response is evident, mainly in the activation of the flavonoid pathway, where the activation of the different enzymes is key. In addition, it has been shown that several studies show the increase of the different phenolic compounds in response to UV-A, UV-B, and UV-C light, which largely depend on the dose and exposure time used. In addition to the above, UV treatments have been used as postharvest treatments as antimicrobials. However, the increase in the content of phenolic compounds is of great interest in the industry due to its bioactive properties.

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Role of Nanotechnology in Phenolic Compound Dynamics

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Shazia Iqbal, Umair Riaz, Javaid Akhtar, Humera Aziz, and Ghulam Sarwar

Abstract

Nanotechnology has become a promising technique in almost every field of today's life. Nanoparticles, which range in size from 1 to 100 μm, are usually prepared by a conventional chemical and physical process that contains toxic by-products for the environment as well as health. To overcome this issue, phenolic compound-based nanoparticles are now attaining more attention especially in the fields of agriculture and medicine. This chapter summarizes the production of phenolic compounds in response to reactive oxygen species and application of nanoparticles, the role of phenolic compounds in making nanoparticles, and mechanism involved in nanoparticle-mediated phenolic compounds.

Keywords

Nanotechnology · Phytochemical-based nanoparticles · Phenolic compounds · Plant's secondary metabolism

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Abbreviations

Ag	Silver
Au	Gold
CaC_2	Calcium carbide
CeO	Cerium oxide
CuO	Copper oxide
Fe	Iron
Fe_3O_4	Iron oxide
FeO	Iron oxide
GAE	Gallic acid equivalent
mg/mL	Milligram/milliliter
NaC	N-acetyl cysteine
NiO	Nickel oxide
Pd	Palladium
PVA	Polyvinyl alcohol
Si	Silicon
TiO_2	Titanium dioxide
ZnO	Zinc oxide
$ZnSO_4$	Zinc sulfate
µg/mL	Microgram/milliliter
µm	Micrometer
µM	Micromole

20.1 Introduction

Postmodern society is now seen as a technologized society, in which technical innovations, from the traditional industry to communications, will solve the key solutions to human problems. In this respect, nanotechnology has since the beginning been seen as leaving the existing microfabrication sector, semi-conductive physics, expanded surface science to store energy, molecular biology, and organic chemistry applications, in handling of at the atomic matter molecular as well as supramolecular scales. Nanotechnology is able to develop new nanoscale materials along with a broad variety of applications in emerging areas, such as biomaterials, nanomedicine, or nanoelectronics. Throughout this regard, nanoscale micronutrients that have led to disease suppression in crop and relation among plant diseases and nutritional status have been studied; nanotechnologies have been called upon to play a role in the production of food, food safety, and security globally in the last few years. The widespread use of nanotechnology is a concern of the toxicity and economy of the new materials involved. The problem is associated with weak accidental release regulation, atmospheric deposition, and deliberate disposal as plague-repairing agents in the atmosphere, including the use of nanomaterial soil modifications (manurers, sludge) or waters. Apart from its toxicological risk, nanotechnology is regarded a way to use natural agricultural resources, e.g., water, nutrients, and chemicals effectively during farming. Nanotechnology provides the potential benefits of growing crop yields as well as the opportunity to optimize the benefits of natural farming tools, by using successful products as pesticides to handle pesticides and to regulate the quality of the soil and the health of plants, i.e., by resolving an environmental pollution problem. A large number of patents have been issued in this context over the last decade, and numerous commercial items using nanomaterials, e.g., nanopesticides, nanofertilizers, or nanosensors, have been used in agricultural practices.

In a general factor, the most critical challenge of higher farm yields is the world society marked by an ever-increasing population level. The goal is to reduce the applied volume of plan safety products, improving nutrient use efficiency, and ultimately improve produce by optimizing different fertilizer management.

Various nanomaterials used as additives have large surfaces and are therefore ideal for sorption processes that reduce losses by reducing runoffs and reducing kinetic releases. Specially formed nanoparticles can prevent photodegradation against active ingredients or increase plant absorption. The features of nanomaterials contribute to the inclusion in plant protection products of harmful organic solvents through their increased sensitivity, and can minimize the rate of applications (Predoi et al. 2020).

As previously mentioned, certain nanomaterials with specific properties can be potentially harmful despite these positive impacts. In agriculture, particularly plant protection as well as nanomaterial fertilization may pose risks by deliberate nanomaterial input to environment. In this context, residues of nanomaterials in soil and crops may upsurge human and environmental exposure due to the nanomaterial bioaccumulation in the environment as well as in the food chains (Gogos et al. 2012). The increasing nanomaterial-containing product demand on a growth of food market indicated the urgent need for a regulatory process. At the beginning of the twenty-first century, plant protection and fertilization was the most common agriculture application for nanotechnology. Higher plants can establish satisfactory mechanisms in harsh conditions in the atmosphere and the soil. To help plant growth, nanomaterials with physicochemical features to enhance plant metabolism are one of the latest methods (Giraldo et al. 2014). In this view, nanotechnology fertilization can improve production of plants supplying the requested micronutrients and by controlling plant growth. Nanomaterials may enter herbic cells and carry chemical compounds as well as DNA within cells (Talebi 2018) which expand the possibility of specific gene manipulation in plant biotechnology (Predoi et al. 2020).

As nontoxic methods for synthesizing metal nanoparticles (Iravani et al. 2014; Thakkar et al. 2010; Mohanpuria et al. 2008), biological synthesis techniques using microorganism or plants were implemented. Such strategies can lead to undesirable immunogenic reactions (Thomas et al. 2003). However, these methods result in nanoparticles that are not homogeneous (Iravani et al. 2014). Gold and silver particulate nanomaterials used as medical treatment and medicinal compounds have been studied widely (Giljohann et al. 2010; Prabhu and Poulose 2012). A safe synthesis approach has been implemented to generate desirable metal nanoparticles with appropriate structural characteristics using phytochemicals as reducing agents or as stabilizers.

Plant-related compounds are graded as primary and secondary metabolites based on their metabolization. The main components of amino acids, nucleic acids, carbohydrates, proteins, chlorophyll, and other essential metabolites are phytochemicals (Hahn 1998). Plant extracts are still important materials used for synthesizing metal nanoparticles. Phytochemicals are small, simple, and environmentally safe structures that are extremely effective in the synthesis of metallic nanoparticles. This chapter deals with the synthesis of natural phenolic acid and the role of nanomatter in phenolic compound elicitation (Amini and Akbari 2019).

20.2 Phenolic Acids

Phenolic compounds are a group of small molecules categorized by their structures with at least one phenol unit (Gan et al. 2019). They are secondary metabolites synthesized by plants through phenylpropanoid and shikimic acid pathways (Rosa et al. 2019). Plants produce secondary metabolites along with primary metabolites (Malik et al. 2020). Phenolic compounds protect plants from photosynthesizing and anthropogenic emission exposure against reactive oxygen species (Dumay et al. 2004). Based on chemical structures, phenolic compounds may be classified as phenolic acids, tannins, flavonoids, curcuminoids, coumarins, quinones, lignans, and stilbenes (Gan et al. 2019).

Phenolics and their derivatives because of their strong antioxidant ability and with one carboxylic group as a functional group at least were commonly used in the drug industry (Lam et al. 2001). Phenolic compounds are linked to illness prevention; also, the positive impact of phenolic compounds has been attributed mostly to their antioxidant activity (Cabanillas-Bojórquez et al. 2020). Many phenolic acids are present in polyphenols and many other compounds (Lam et al. 2001). They are synthetic and structural. Along with the number of aromatic ring hydroxylation sites, two major groups of natural phenolic acids are derivatives of cinnamic acids and benzoic acids (Balasundram et al. 2006).

20.3 Phenol Nanomaterial Scavenging of Reactive Oxygen Species

Overproduction of reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2), hydroxyl radical (OH^-), and superoxide (O_2^-) occurs in plant cells when they are exposed to engineered nanomaterials. This is another conceivable method for growing the secondary metabolites. Because of numerous abiotic and biotic effects, the fast and additional generation of H_2O_2 regulates antioxidant defense systems both enzymatic and nonenzymatic in plants which is known as an H_2O_2

oxidative burst (Low and Merida 1996). The redox status of the plant cells is changed because of H_2O_2 generation. This change functionally triggers a signal molecule for activation of secondary metabolite biosynthesis pathways (Jabs et al. 1997). The development of antioxidants such as carotenoids, antioxidant enzymes, and phenols, by plants, has developed various protection mechanisms to reduce oxidative damage caused by reactive oxygen species (García-López et al. 2018). In the reactive oxygen species detoxification pathways, phenolic compounds play a prominent role (Mahendra et al. 2008). The efficiency of phenolic compounds for the inactivation of reactive oxygen species primarily depends on the chemical structure of phenolic compounds. The simplest phenolic compound, phenol, comprises only one hydroxy group and one benzene ring. Flavonoids and lignins contain many functional groups attached to a single molecule of multiple benzene rings. The number, type, and functional group arrangement regulate the antioxidant activity (Pereira et al. 2009). Phenolic compounds with more hydroxy groups have more ability to reactive oxygen species scavenge (Caputo et al. 2015: Nagajyothi et al. 2015). The molecular species of active oxygen can be directly removed by phenolic compounds primarily by its redox behavior. Phenolic compounds can also eliminate reactive oxygen species by acting as electron donors in structures of organs. They absorb or neutralize the free radicals, eliminate single and threefold oxygen, or can cause the decomposition of peroxides (Bhumi et al. 2014). That is why phenols and flavonoids have the highest concentration in fruits from plants subjected to ZnO nanoparticle treatments (García-López et al. 2019).

Following increased H_2O_2 levels resulting from the application of high multi-walled carbon nanotube rates, the levels of different forms of secondary metabolites including phenolics, caffeic acid, flavonoids, and rosmarinic acid have increased (Ghorbanpour and Hadian 2015). With growing hydrogen peroxide concentration in Morinda elliptical cell suspension culture, a regulation in the biosynthesis of the secondary metabolite was observed (Chong et al. 2005). Similarly, from Ag-engineered nanomaterial treatment, enhancement of artemisinin biosynthesis is reported that suggestively correlated reactive oxygen species overproduction (Zhang et al. 2013).

Maghemite (γ-Fe_2O_3) nanoparticles made by oxidation and coprecipitation were used to yield γ-Fe_2O_3@Hep by coating with heparin (Hep), and then with chitosan that was changed with different phenolic compounds. Different phenolic compounds used include phloroglucinol (CS-P), gallic acid (CS-G), and hydroquinone (CS-H), to yield γ-Fe_2O_3@Hep-CS-P, γ-Fe_2O_3@Hep-CS-G, and γ-Fe_2O_3@Hep-CS-H particles, respectively. A 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay was used to analyze the antioxidant properties of the nanoparticles. The phenolic modification meaningfully decreased intracellular reactive oxygen species levels to 35–56%, compared to the control (Świętek et al. 2019).

20.4 Nanoparticle Synthesis Through Phenolic Compounds

For the green synthesis of metal oxide (metallic) nanoparticles, plant-driven phenolic acids were used. Phenolic acids are essential in the process of nanoparticle synthesis as both reducing and stabilizing agents. Numerous studies were performed to progress in successful green synthesis technique development for nanoparticles. This is reproducible using phenolic acids (Amini and Akbari 2019). For the synthesization of nanomaterials, several active plant chemicals were added. Between these, the use of flavonoids and phenolic acids in nanomedicine is commonly considered. Most phenolic acids for metal nanoparticle synthesis have also been used as reducers or stabilizers (Kadoma and Fujisawa 2008; Zhang et al. 2007). For light-triggered metal nanoparticles using cinnamic acid, a reducing agent, the carboxylate precursor to metal (I) has been applied (Schliebe et al. 2013).

A researcher in 2006 developed gold particles capsulated with cinnamic acid and reported the reduction and antioxidant activity of phenolic acids in metal nanoparticle synthesis (Wang et al. 2006). Several methods have been used to examine the H-donation potential of phenolic acids (Kadoma and Fujisawa 2008, Zhang et al. 2007). Phenolic acids for synthesizing gold nanoparticles, including ferulic acid, propyl gallate, vanillic acid, caffeic acid, and protocatechuic acid, were also studied (Scampicchio et al. 2006). Sinapinic acids, in addition to these compounds, were also investigated as possible mediators for metal nanoparticle synthesis. This enables the 4-nitrophenol reduction to 4-aminophenol to be catalyzed by the nanoparticles formed by phenolic acid. Gold (iii) may be reduced from gold nanoparticles by all of the investigated phytochemicals. However, the future biomedical use of synthesized gold nanoparticles remains to be investigated (Lerma-García et al. 2014).

In recent years, several other phenolic acids have been used to synthesize metal nanoparticles. Among phenolic acids, gallic acid is commonly utilized in the synthesis of various metallic or metal oxide nanoparticles. Gallic acid is an antiviral, antibacterial, and anticancer natural antioxidant (Kang et al. 2008; Kratz et al. 2008; Chuang et al. 2010). To synthesize silver, gold, and selenium nanoparticles, gallic acid has been used as a reducer or stabilizer (Table 20.1). In addition, gallic acid-synthesized functionalized ZnO nanoparticles provided antibacterial action (Lee et al. 2017). Various research groups have tested the antifungal and antibacterial activities of silver nanoparticles synthesized with gallic acid (GA@Ag nanoparticles) (Martinez-Gutierrez et al. 2010). Not only did GA@Ag nanoparticles inhibit *S. aura*, *E. coli*, *C. aura*, and *C. albicans* development but also act against cancer cells as selective cytotoxicity (Li et al. 2015). For gallic acid- and quercetin-synthesized nanoparticles of silver selenium alloy, similar properties have been reported (Mittal et al. 2014) These properties as nanoparticles synthesized with gallic acid were selenium-ruthenium alloy (Zhou et al. 2016). Polymeric nanoparticles coated with gallic acid were applied in therapy of anxiety as therapeutic agents (Nagpal et al. 2013a) and amnesia (Nagpal et al. 2013b). Such results can also be repeated with gallic acid-coated metal nanoparticles.

Pyrogallol is a decarboxylated derivative of gallic acid. For the synthesis of silver nanoparticles, pyrogallol was added. A chain structure is delivered via hydrogen

Table 20.1 Changes induced by nanomaterial in plant's secondary metabolism

Nanomaterial	Changes induced in plant's secondary metabolism	References
Ag	Increased ROS enzyme activity and/or phenolic content, increased α-terpinyl acetate content, and decreased thymol content and essential oil constituents (formate, citronellol, geraniol, iso-menthone cirtonellyl, E-caryophyllene, and linalool, enhanced artemisinin content (a sesquiterpene lactone). Decreased total saponin and anthocyanin contents	Corral-Diaz et al. (2014); Yasur and Rani (2013); Zhang et al. (2013); Mittler (2002); Ghorbanpour (2015)
CeO_2	Antioxidant capacity of tubers increased in plants treated with 250 mg/kg, CAT, SOD, GSH, POD, CAT, GPOX, SOD, APX, DHAR, and GR activity increased	Zhang et al. (2017); Majumdar et al. (2014); Ma et al. (2016)
Cu	Phenolic compound upregulation to improve antioxidant-mediated defense the system, increased uptake of macro- and micronutrients	Zhao et al. (2016)
$C_{60}(OH)_{20}$	Enhanced antidiabetic contents (insulin and charantin) and anticancer (lycopene and cucurbitacin-B) phytomedicines	Ghanati and Bakhtiarian (2014)
MWCNTs	Induction of flavonoids, phenolics, caffeic acid, and rosmarinic acid	Ghorbanpour and Hadian (2015)
TiO_2	CAT concentration was increased and APX was decreased in high concentration, enhanced total alkaloid yield, increased total phenolic, monoterpene content (p-cymene, camphene, camphor, 1,8-cineol, and cis-thujene), flavonoids and essential oils	Servin et al. (2013); Ghorbanpour and Hatami (2015); Ghorbanpour (2015)
ZnO and CuO	Increased total phenolic compounds, glycyrrhizin content, anthocyanins, and flavonoids	Oloumi et al. (2015)
NiO	CAT, SOD, and GSH showed higher antioxidant enzymes activities	Faisal et al. (2013)

bonds of the pyrogallolic silver nanoparticles, resulting in a novel plasma resonance peak for the wavelength region of near-infrared. A simple synthesizing technique using pyrogallol as a stabilizing agent for silver nanoparticles was also studied (Jiang and Yu 2010). The propyl gallate which is propanol and gallic acid ester is another gallic intermediate used for synthesizing silver (Ping and Yong-Nian 2013) and gold (Scampicchio et al. 2006) nanoparticles. Wang et al. reported similar activity in cinnamic acid-coated gold nanoparticles (Wang et al. 2006).

The iron chelation characteristics of phenolic acids refer to iron nanoparticle preparation. The collaboration between iron and caffeic acid will lead to the development of colloidal metastable nanoparticles (Nilsson et al. 2008). Synthesis of Fe_3O_4 nanoparticles has also been based on salicylic acid as shells. Some advantages have been shown for salicylic acid-coated magnetic nanoparticles, for instance, good biocompatibility, low vascular embolism, and good bioavailability (Mihaiescu et al. 2013). In positron emission tomography, imaging-guided photothermic therapy was used for the 64 Cu-labeled polymeric iron-gallic acid nanoparticles (Jin et al. 2017).

20.5 Mechanisms Involved in Phenol-Mediated Synthesis of Nanoparticles

All the hydroxyl as well as carbonyl group of polyphenols plays a significant role collectively in manufactured nanoparticle. The polyphenolic synthesis mechanism follows nanoparticle synthesis. Those hydroxyl groups in polyphenol compounds that are adjacent to each other from a five-member chelation make ring arrangement accompanied by chelated dihydroxy oxidation of quinone groups. The synthesis of gold nanoparticles occurs after a collision of neighboring Au^0 atoms with polyphenolic compounds like quinones and is stabilized. Reduction of quinones occurs as it goes from Au^{3+} to Au^0 because of their high oxidation-reduction potential (Dash and Bag 2014). The reduction of Au^{3+}/Ag^+ ions is carried out in a two-step process. First is reduction of apiin that is carried out by hydroxyl groups, and then the hydroxyl group oxidation to the carbonyl occurs. Finally, carbonyl groups bond to the metal ion (binding of apiin) and cover the surfaces of the nanoparticles to prevent agglomeration (Kasthuri et al. 2009). The hydroxyl groups found in kaempferol rings, both B and C, engaged in Au nanoparticle production (Raghavan et al. 2015; Halder et al. 2017). Quercetin was observed to chelate in three locations, first the catechol group at positions C3′ and C4′, including carbonyl as well as the hydroxyl groups at locations C5 and C3 (Makarov et al. 2014). Such groups help to chelate various metals in ionic forms through the following steps: metal surface adsorption (Zhang et al. 2016), nanoparticle budding (Bundschuh et al. 2018), aggregation (Hussain et al. 2016), and bioreduction (Saratale et al. 2018).

Dihydromyricetin (DMY)-medicated synthesis by hydroxy-to-carbonyl groups of Au nanoparticles occurred. In addition to oxidation of hydroxyl group leading to hydrogen intramolecular bonding, carbonyl group stretching vibrations shift to lower even numbers (Guo et al. 2014). The potential mechanism for genistein Au nanoparticles was proposed as follows: transferring the genistein electron into Au central areas (Zhang et al. 2016), reducing Au^{3+} to Au^0 by genistein DMY-mediated Au nanoparticle synthesis by hydroxyl oxidation into carbonyl groups (Bundschuh et al. 2018). Furthermore, the Au nanoparticles were produced in a layer of negative ions (Hussain et al. 2016) as stabilizing agents (Stolarczyk et al. 2017). Table 20.2 and Fig. 20.1 show the plausible mechanism for phenol-mediated synthesis of nanoparticles.

Table 20.2 Mechanism involved in the synthesis of nanoparticles by phenolic compounds

Nanomaterial	Mechanism	References
Au	Carbonyl and hydroxyl groups of polyphenol-mediated bioreduction of Au metal ions	Mata et al. (2016); Patra et al. (2015); Guo et al. (2014); Patra and Baek (2015)
	Au metal ion reduction mediated by hydroxyl groups of apiin (phenolic compounds) leads to the eventual development of metal ions bonded carbonyl groups leading to apiin-coated nanoparticles	Kasthuri et al. (2009)
	Reduction of Au metal ions mediated by amide and hydroxyl groups	Yu et al. (2016)
	Reduction of Au^{3+} to Au^0 by electron transfer from genistein, resulting in the creation of Au nanoparticles via stabilization with a coating of negative ions	Stolarczyk et al. (2017)
Ag	Reduction of Ag metal ions mediated by hydroxyl groups of polyphenols/ phenolic compounds	Ghosh et al. (2016); Sumitha et al. (2018); Sheikh et al. (2018); Elemike et al. (2017); Vanaja and Annadurayi (2013); Escárcega-González et al. (2018); Krishnaraj et al. (2010); Elumalai et al. (2016); Otunola et al. (2017); Khandel et al. (2018); Ahmed et al. (2016b)
Pd	Reduction of Pd ions mediated by polyols	Dauthal and Mukhopadhyay (2013)
FeO	Fe metal ion reduction mediated by hydroxyl groups of polyphenols/ phenolic compounds	
c-Si	Si metal ion reduction mediated by hydroxyl groups of polyphenols/ phenolic compounds	Tewari et al. (2016)
Zn	Hydroxyl group caused the reduction of Zn	Halevas et al. (2016)

20.6 Influence of Nanomaterial on Phenol Contents in Plants

Because of their special physical and biological properties, nanoparticles are more common in the fields of biology, medicine, and electronics (Morones et al. 2005). Phenolic compounds are the key components of most plant species' antioxidants, and their redox effects have an important effect on their antioxidant activity. It helps them to reduce free radicals and decrease metallic ions from metal to metallic nanoparticles as reduction agents (Schwarz et al. 2001).

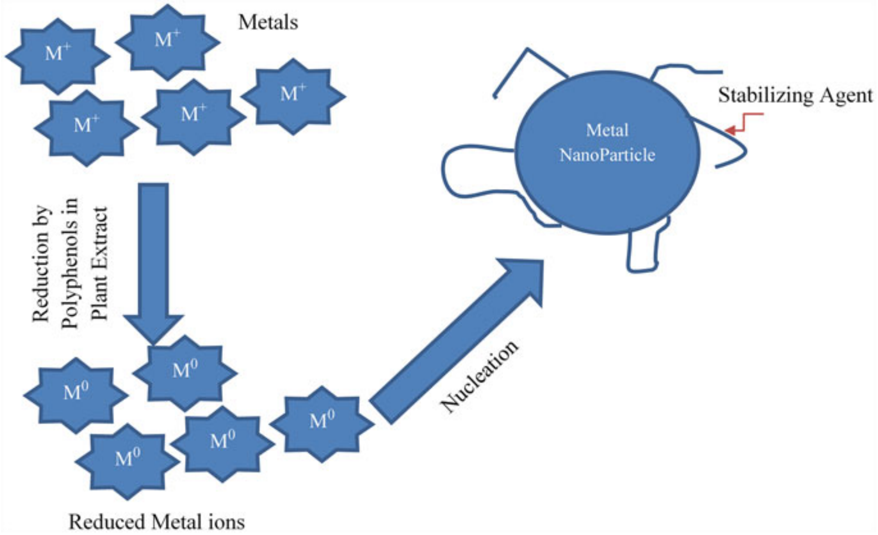

Fig. 20.1 Mechanism for phenol-mediated the synthesis of nanoparticles

This phenolic compound parameter is considered one of the main parameters of nutritional importance for nanofertilizers (Tehranifar et al. 2010). Foliar use of zinc and boron nanofertilizers on pomegranate fruit alters total sugars and total phenolic compounds (Davarpanaha et al. 2016). Air parts of *S. intermedia* are a strong source of phenolic compounds, effective antioxidants, and a strong bioreduction and silver nanoparticle biosynthesis option (Firoozi et al. 2016).

In *Satureja khuzestanica*, which is grown in in vitro, the effects of the multiple wall carbon nanotubes (multi-walled carbon nanotube diameters 5–15 nm) have been studied most recently. Different rates of the multi-walled carbon nanotube (0, 25, 50, 100, 250, and 500 μg/mL) have been used for the Gamborg B-5 (B5) medium. On exposure to all concentrations, the total phenolic content began to improve at lower levels of exposure of multi-walled carbon nanotube. The gross flavonoid and the phenolic content of both phenolic acids (rosmarinic acid and caffeic acid) after 15 days of exposure were valued at 2.6 and 1.9, respectively, compared with regulation. More than that, the exposure of 100 μg/mL multi-walled carbon nanotube substantially improved in comparison with other therapies, with two phenolic acids (Ghorbanpour and Hadian 2015).

Results indicate that ZnO nanoparticles significantly affected phenols and flavonoids (soluble + bound) in fruit by the operation of the foliar test ($p < 0.01$). The soluble component had the highest concentrations of phenols and flavonoids in all analyses of phenolic compounds, and the lowest concentration was found in bonding compounds. In the same concentration (1000 mg L^{-1} and 2000 mg L^{-1}), differences also occur in the accumulation of phenolic compounds induced by ZnO nanoparticles from those formed by $ZnSO_4$ (García-López et al. 2019). This is explained by the high solubility of $ZnSO_4$ and the bioavailability of Zn ions with the use of $ZnSO_4$ over a longer period is not safe when added to the plant's leaves and can be easily (Doolette et al. 2018). It should, therefore, be kept in mind that $ZnSO_4$ foliar application cannot be as stressful as the ions formed by ZnO nanoparticles because the nanoparticles are more transport-friendly and therefore more bioavailable and absorbed, which enables interaction with intracellular structures to stimulate the formation of the reactive oxygen species (Lopez-Moreno et al. 2010; Ghosh et al. 2016). Nevertheless, the phytotoxicity of ZnO nanoparticles could only be clarified by dissolved ions by other authors. Because exposure to plants can affect the properties of nanoparticles (Kouhi et al. 2015; García-Gómez et al. 2018). have shown an increase in nonenzymatic antioxidant molecules such as phenolic compounds and flavonoids induced by the application of the ZnO nanoparticle on *Brassica nigra* shoots and, especially, have been observed as a result due to the accumulation of reactive oxygen species (Zafar et al. 2016). The use of Cu nanoparticles in chitosan-PVA hydrogels at 2.0 mg in pepper jalapeño plants enhanced phenol accumulation in fruit (64.71 mg GAE 100 g^{-1}), which exceeded 5.9% in control and decreased oxidative stress induced by reactive oxygen species (Pinedo-Guerrero et al. 2017).

Silver nanoparticle effects on induction of secondary metabolite profiles were analyzed, and seedlings were treated with silver nitrate in equivalent concentrations to nanoparticles. Significant differences occur in phenolic compound accumulation. Silver nanoparticles and silver ions encouraged the biosynthesis of hydroxycamalexin O-hexoside, hydroxycamalexin malonyl-hexoside, and camalexin. Significant changes have been also recorded for five phenolic compounds in different treatment conditions (Kruszka et al. 2020). TiO_2 nanoparticles doped with AgCl in alkaline conditions resulted in the highest phenolic production (Tsapekos et al. 2018). The influence of TiO_2 nanoparticles on the growth of *Arthrospira platensis*, *Chlorella vulgaris*, and *Haematococcus pluvialis* was investigated. Under stress conditions, to prevent damage to cells, photosynthetic microorganisms produce antioxidant compounds. Titanium dioxide nanoparticles statistically affected phenolic concentrations of two microorganisms (Comotto et al. 2014).

20.7 Nanomaterial Elicitation of Secondary Metabolites

Plants develop many secondary metabolites, including phenolics, alkaloids, and terpenoids known as essential mediators for the interaction of environmental conditions with biotic or abiotic agents. Both types of elicitors induce the biochemical and physiological processes and activate protection mechanisms for target plants (Zhao et al. 2005). An effective technique for developing pharmaceutically active compounds has emerged as elicitor application. In terms of the application of engineered nanomaterials, however, as possible sources of industrial compounds, very little research was undertaken. Here, we will briefly list studies that demonstrate that engineered nanomaterials can function as a producer of defensive chemical products most of them associated with improved secondary metabolite development.

Extracts produced from *E. coli*, supplemented by 100 μg/mL multi-walled carbon nanotube, demonstrated sturdy activity of antioxidant than positive reagent power, and other treatments (Ghorbanpour and Hadian 2015).

There is no good description of the basic biochemical and/or biophysical interactions of engineered nanomaterials to biological interfaces. It was however proposed that carbonated nanomaterials adsorb electrostatic, hydrophobic, and receptor-ligand on cell surfaces (Nel et al. 2009). Carbs also develop on the cell surface, create clusters of filamentous structures, and penetrate the plant cell wall, which leads to metabolic events. Plant cell culture exposure to elicitors leads to a cascade of transmission leading to various genes that encode enzymes tangled in the secondary metabolite procedures of biosynthesis (Ponti et al. 2010).

Modified activities of various enzymes, phenylalanine ammonia-lyases, polyphenol, and peroxidase, may be attributed to changes in secondary metabolite biosynthesis after exposure to a multi-walled carbon nanotube. It was found that an increase in total phenolic contents was positive with PAL activity following exposure to 100 and 250 μg/mL multi-walled carbon nanotubes (Ghorbanpour and Hadian 2015). Furthermore, the growth in PAL activity was stated to be correlated with the manufacture of in vitro total phenolics (Jalalpour et al. 2014). Carbon-based nanomaterials can trigger a molecular pattern and activate several genes in stress signal pathways that are like plant reactions against biotic stresses (Khodakovskay et al. 2011).

The components of phenolics as well as flavonoids are biologically and financially useful metabolites and are produced in terrestrial plants through a pathway of shiki metaphenyl prostanoids-flavonoids. These compounds show the free radical activity of scavenging and protection against oxidative damage, mainly caused by redox properties (Osawa 1994). In an alternative analysis, the TiO_2 nanoparticle effect on a medicinal plant named *Salvia officinalis* was assessed (Ghorbanpour 2015). The plants with specific TiO_2 nanoparticles were applied as foliar applications. TiO_2 nanoparticles substantially improved total phenolics in leaves and improved plant flavonoids after exposure. However, the yield of the extract (percent w/w) between the treatments used did not change significantly. Phenolic compounds and glycyrrhizin (natural sweetener) in the agar growth medium of Hoagland nutrient solution have enhanced the exposure of 1 and 10 μM ZnO and CuO nano parts to *Glycyrrhiza glabra* seedlings (Oloumi et al. 2015). Many other plant phenolics and flavonoid reports have been identified for production when exposed to abiotic elicitors (Cristina and Constantin 2011). Extract yields are somewhat ambiguous (percent w/w) after TiO_2 nanoparticle exposure in *Salvia officinalis* (Shimada et al. 1992). In *Salvia officinalis*, leaf extract (90% methanol) was reported to display strong antioxidant action at 200 mg/L compared to untreated controls and butylated hydroxytoluene, which was exposed to TiO_2 nanoparticles (low IC50) (Ghorbanpour 2015). There is a sturdy connection between flavonoid and phenolic compounds and the ability for antioxidants. Phenolics, therefore, defend the plants against oxidative damage by decreasing the cellular toxicity of reactive oxygen species (Li et al. 2008). Increased dry matter in plants can also impact the link between primary and secondary metabolism, thereby improving secondary metabolite development and accumulation (Harrewijn et al. 2002). As secondary metabolites are essential for the pharmaceutical industry and the food industry, an innovative tool for the elicitation of bioactive compounds and these plant metabolites could be used with potential nanomaterials.

There have been few studies on the co-exposures of engineered nanomaterials and other chemicals concerning plant metabolism according to current literature, and the antagonistic or synergistic connections between the two are unidentified. The effects on bioaccumulation of essentially oily components of geranium (*Pelargonium graveolens*) were reported (Ghorbanpour and Hatami 2015) in various concentrations (20–80 mg/L) of Ag nanoparticles (diameter 5–35 nm) and thidiazuron (thidiazuron: 0–100 μM) and combination of both. The use of Ag nanoparticles and thidiazuron has resulted in major improvements in the quantity and consistency of essential oil. When co-exposed to Ag nanoparticles 80 + thidiazuron 100, the highest content and highest levels of major essential oils were observed in geraniol, and citronellol. Nonetheless, Ag nanoparticles 40 + thidiazuron 75 co-exposure showed a C/G ratio of equal to one, suggesting that Ag nanoparticles and thidiazuron co-exposure to the consistency of essential oils had a good synergistic relationship. Tomentin is important because of the good odor and fragrance of C/G essential oil, which are promoted in various industries for instance pharmaceuticals, foodstuffs, and cosmetics (Bakkali et al. 2008).

An improvement in dose-related H_2O_2 generation using Ag nanoparticles and/or thidiazuron was proposed, which would then show a major part in accumulating secondary metabolites. Essential oil production was associated with carotenoids and chlorophyll in substantially positive proportions. Higher concentrations of chlorophyll, together with an increase in photosynthesis, then increase the concentration of primary (e.g., carbohydrates) metabolites. The metabolism of carbohydrates involves complex biochemical pathways that lead to plant *P. graveolens* to cause secondary metabolism (Swamy and Rao 2009). The authors found that engineered nanomaterials (e.g., Ag nanoparticles) were co-exhibited with appropriate regulators for plant growth (e.g., thidiazuron) (Hatami et al. 2016).

20.8 Possible Mechanisms of Plant's Secondary Metabolism Modulation by Nanomaterial

Nanoparticles are recorded to interfere with various signal pathways, and they can modulate the secondary metabolism of the plant. However, the exact mechanism is unknown by which this modulation may occur. We assume that the initial responses to nanoparticles may involve high reactive oxygen species level, cytoplasmic Ca_2C, and upregulation of mitogen-activated protein kinase (MAPK) cascades. A plasma membrane-bound receptor identification of the Ag nanoparticles caused a burst of Ca_2C and activation of reactive oxygen species in *A. thaliana* (Sosan et al. 2016). Upregulated proteomic analysis of Ag nanoparticle-treated *O. sativa* roots was identified by Ca_2C levels and associated proteins of a signaling pathway (Mirzajani et al. 2014). Ag nanoparticles or ions unconstrained from Ag nanoparticles inhibit the metabolism of cells by binding Ca$_2$C channels, Ca$_2$C receptors, and Ca$_2$C-NaC-ATPase. When a calcium-binding protein or other NP-specific protein is observed, nanoparticles mimic either Ca$_2$C or cytosol signaling molecules (Khan et al. 2017). Phosphorylation of MAPK and downstream transcription instigation lead in general to secondary metabolism transcription reprogramming in plants (Phukan et al. 2016). While there is no clear evidence to prove that MAPK pathways participate in plant nanoparticle interactions, cell-line studies in animals and humans find that analog pathways are involved in signalization from the Ag nanoparticle (Lim et al. 2012). It is suggested that plants may also use MAPK cascade upon exposure to Ag nanoparticles (Kohan-Baghkheirati and Geisler-Lee 2015). Changes induced by some nanomaterial in the plant's secondary metabolism are shown in Table 20.1.

20.9 Phenol-Based Nanomaterial Synthesis: A Safe Approach

Metal nanoparticles (manufactured nanoparticles) are widely used in many fields every day, and so they are deeply concerned about environmental and biological health issues. The key approaches to nanoparticle synthesis are physical and chemical processes that are not only environmentally toxic but also expensive and safety hazardous (Latif et al. 2019). However, keeping in mind the health concerns, nanoparticles synthesized by these dangerous methods are inadequate for the medical field (Hussain et al. 2016). Although traditional methods are sufficient to synthesize large quantities of particulate matter, these techniques are difficult, expensive, inefficient, and trendy in a shorter time with specified shapes and sizes. The nano synthesis of environmentally friendly particles has become increasingly desirable in recent years without the processing of harmful by-products as part of the synthesis process (Saratale et al. 2018; Iravani 2018; Shah et al. 2015). It can be accomplished only if the use of biological-biotechnological tools that are defined as safe and environmentally friendly for nano synthesis as an alternative to traditional physical and chemical methods is adopted environmentally friendly synthesis procedures (Sathishkumar et al. 2018; Santhoshkumar et al. 2017). This green and sustainable approach has been used as an alternative to traditional hazardous solutions in recent years. It proved to be a cost-effective and nontoxic process that consumes less time and energy, is safe, and is environmentally friendly to synthesize manufactured nanoparticles by different biological measures (Latif et al. 2019). For the biological synthesis of nanoparticles, there are three main factors: the solvent medium choice, the choice of an environmentally friendly and safe decreasing agent, and a nontoxic substance choice as a capping agent to stabilize the synthesized nanoparticles (Shah et al. 2015). In this way, plant extracts or materials extracted from trees have been formed into nanoparticles of synthetic methods. During nanoparticle synthesis, the compounds in the extracts serve as reducing and stabilizing agents (Iravani 2011). As such, the key precursors to the formation and stability of nanoparticles were the phenolic compounds found in the extracts (Devatha et al. 2016). Because of several features, nanoparticles synthesized by green technology are very superior to those generated by conventional processes.

Green technology, for example, hires inexpensive industrial materials, reduces energy consumption, and produces environmentally friendly goods and by-products. The more biological systems are required for nanoparticle synthesis, the more nano-biotechnology is beneficial than other traditional methods (Ahmed et al. 2016a; Fakruddin et al. 2012).

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