Role of Phenolic Compounds in Plant-Defensive Mechanisms

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Abstract

Phenolics are ubiquitous secondary metabolites found in plant. They are aromatic compounds synthesized by phenylpropanoid pathway. Phenolics have been in the focus of many findings on plant-defenses mechanisms to pathogens, including bacteria, fungi, and viruses, and major abiotic stresses like drought, salinity, and UV. Phenolic compound exhibits antimicrobial and antioxidant properties which helps plant to evade pathogenic infections as well as protect the major tissues from toxic effect of reactive oxygen species. Rapid upregulation of genes in the phenylpropanoid pathway and the accumulation of phenolics can be observed in response to environmental stress. Phenolic compounds also play an important role in protecting the plant from insect herbivory. Phenolic compounds are diverse and classified based on the number of carbons. Structural diversity of the phenolic compound defines its functional properties and distribution in different plant species. Beside defensive mechanisms, phenolic compounds are also important in cross-talk or plant-microbe interaction and communications. Structural diversity of flavonoids from the leguminous plant is important in species-specific symbiotic relationships.

Keywords

Phenolics · Ubiquitous · Drought · Salinity · Antioxidant · Stress

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R. Lone et al. (eds.), *Plant Phenolics in Sustainable Agriculture*,
https://doi.org/10.1007/978-981-15-4890-1_22

22.1 Introduction

Phenols are compounds with one or more hydroxyl groups attached directly to an aromatic ring. They are similar to alcohols of aliphatic structure where hydroxyl group is attached to a chain of carbon. However, hydrogen of the phenolic hydroxyl is influenced by the presence of an aromatic ring, and they are labile, which makes phenols as weak acids. The term phenolic covers a diverse group of chemical compounds. On the basis of structure, phenolic compounds comprise an aromatic ring, bearing one or more hydroxyl substituent's which range from simple phenolic molecules to highly polymerized compounds (Balasundram et al. 2006). Harborne and Simmonds (1964) classified phenolic compounds into different groups based on the number of carbons in the molecule (Table 22.1) (Harborne and Simmonds 1964).

Table 22.1 Classification of phenolic compounds

No. of carbon atoms	Structure	No. of phenolic cycles	Class	Examples
6	C_6	1	Simple phenols, benzoquinones	Catechol, hydroquinone, 2,6-dimethoxybenzoquinone
7	C_6–C_1	1	Phenolic acids, phenolic aldehydes	Gallic, salicylic acids
8	C_6–C_2	1	Acetophenones, tyrosine derivatives, phenylacetic acids	3-Acetyl-6-methoxybenzaldehyde, tyrosol, p-hydroxyphenylacetic acid, homogentisic acid
9	C_6–C_3	1	Hydroxycinnamic acids, phenylpropenes, coumarins, isocoumarins, chromones	Caffeic, ferulic acids, myristicin, eugenol, umbelliferone, aesculetin, bergenin, eugenin
10	C_6–C_4	1	Naphthoquinones	Juglone, plumbagin
13	C_6–C_1–C_6	2	Xanthonoids	Mangiferin
14	C_6–C_2–C_6	2	Stilbenoids, anthraquinones	Resveratrol, emodin
15	C_6–C_3–C_6	2	Chalconoids, flavonoids, isoflavonoids, neoflavonoids	Quercetin, cyanidin, genistein
16	C_6–C_4–C_6	2	Halogenated algal phenolic compounds	Kaviol A, colpol
18	$(C_6$–$C_3)_2$	2	Lignans, neolignans	Pinoresinol, eusiderin
30	$(C_6$–C_3–$C_6)_2$	4	Biflavonoids	Amentoflavone
Many	$(C_6$–$C_3)_n$, $(C_6)_n$, $(C_6$–C_3–$C_6)_n$	$n > 12$	Lignins, catechol melanins, flavolans, polyphenolic proteins, polyphenols	Raspberry ellagitannin, tannic acid

Phenolic compounds are secondary metabolites, universally present in plants. They are the derivatives of pentose phosphate, shikimate, and phenylpropanoid pathways (Balasundram et al. 2006; Cheynier 2012). They are present in plant seeds, leaves, bark, and flowers. More than 8000 phenolic structures are currently known. They can range from simple molecules of low-molecular-weight (phenolic acids, flavonoids, phenylpropanoids) to highly polymerized compounds (lignins, melanins, lignans, tannins). With at least 4000 identified molecules, flavonoids represent the most common and widely distributed subgroups comprising flavones, isoflavones, and 2,3-dihydro derivatives of flavone (Cheynier 2012). Besides flavonoids, lignans are one of the most distinctive groups of phenylpropanoids. They are known to possess a variety of biological activities including antibacterial, antifungal, antiviral, anti-inflammatory, anti-cancerous, and antioxidant effects (Pereira et al. 2016). Phenolic compounds also relate to the human health benefits which derived from consuming high levels of fruits and vegetables. The beneficial effects derived from phenolics have been attributed to their antioxidant activity. Phenolic compounds act as a natural source of antioxidants (Parr and Bolwell 2000).

The term polyphenol is often used as an alternative of phenolic compounds; however, it should be restricted to molecules bearing at least two or more phenolic rings in their structure (Quideau et al. 2011). Polyphenols or polyhydroxyphenols are organic chemicals with multiple phenols as structural units. It was first defined by Bate-Smith (1962) as "water soluble phenolic compounds having molecular weights between 500–3,000 Da." They have special properties such as the ability to precipitate alkaloids, gelatin, and other proteins from solution (Cheynier 2012). These compounds are one of the most widely occurring groups of extracted phytochemicals and are of considerable morphological and physiological importance in plants. Phenolics play a major role in growth and reproduction, and also it provides protection against pathogens and predators (Balasundram et al. 2006). It also contributes toward the color and sensory characteristics of vegetables and fruits (Balasundram et al. 2006). Some phenolic compounds are widely distributed, while others are specific to certain families of plant or found only in certain plant organs at certain developmental stages. Structural diversity of phenolic compound defines its functional attributes and its specific distribution. For example, anthocyanin is the pigment of most red and blue plant organs. They are found in flowers and in mature fruits and play an important role in attracting pollinators and helping in pollination. Presence of anthocyanin in young leaves protect them from photodamage and help in normal growth. A red anthocyanin coating of leaves also protects the young leaves from insect herbivory (Karageorgou and Manetas 2006). Phenolic compounds like proanthocyanidins (flavan-3-ol oligomers and polymers) and hydrolyzable tannins (i.e., gallotannins and ellagitannins, based on multiple esters of gallic) participate in plant defense against herbivores, fungi, and viruses. They are mostly found in early developmental stages of plant based on their functional properties (Cheynier 2012). Flavonoids have been identified to guard the tissue against UV radiation. The depletion of ozone layer over the last three decades has created UV radiation stress

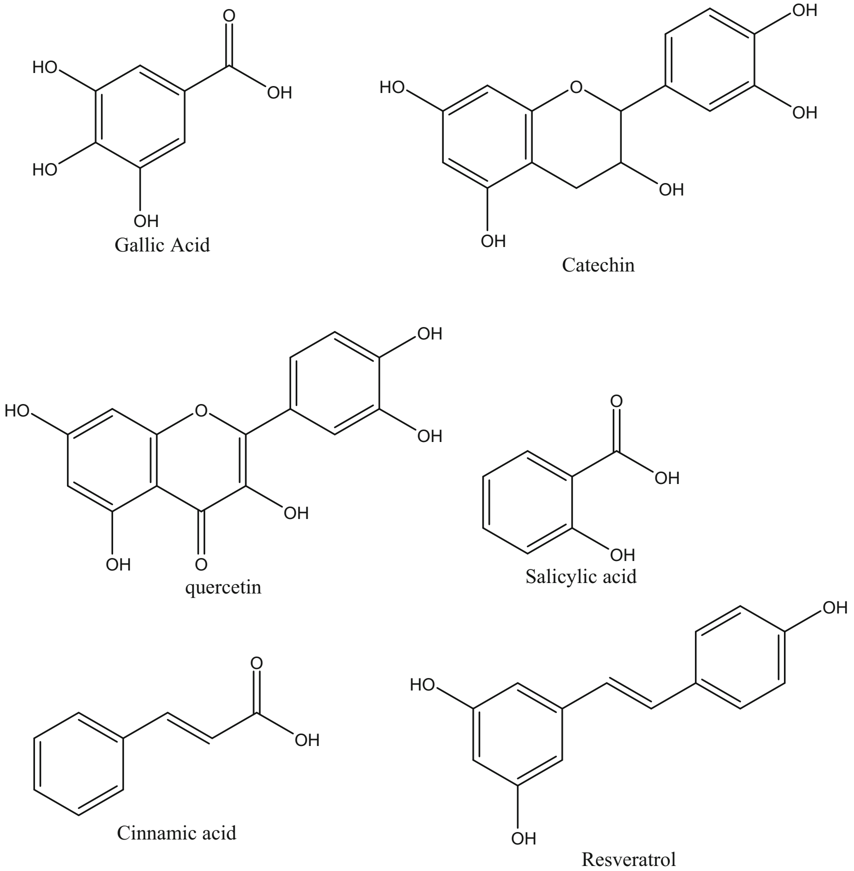

Fig. 22.1 Structure of some of the common plant phenolic compounds

on plant. Flavonoids were identified to reduce the reactive oxidative species generated over the UV-B stress (Agati and Tattini 2010) (Fig. 22.1).

22.2 Functional Properties of Phenolic Compounds

Phenolic compounds are mainly synthesized from cinnamic acid, which is formed from phenylalanine by the action of phenylalanine ammonia-lyase (PAL) through phenylpropanoid pathway (Heleno et al. 2015). The importance of this pathway can be supported by the fact that, in normal growth conditions, 20% of carbon fixed by plants flows through this pathway (Michalak 2006a, b). Phenolic compounds have various functions in plants. An enhancement of phenylpropanoid metabolism and accumulation of phenolic compounds can be observed under different environmental stress conditions (Bergmann et al. 1994; Król et al. 2014; Caliskan et al. 2017). The combination of isoflavones and some other flavonoids is induced when plants are infected, wounded, under low temperatures, low nutrient conditions, and UV, metal stress condition (Mierziak et al. 2014; Schulz et al. 2016). Plants accumulate UV-absorbing flavonoids and additional phenolic compounds mainly in vacuoles of epidermal cells, to avoid the penetration of UV-B into the deeper tissues of the plant (Rodríguez-Calzada et al. 2019). The initiation of phenolic compound biosynthesis was observed in wheat in response to nickel toxicity and in maize in response to aluminum. *Phaseolus vulgaris* exposed to cadmium accumulate soluble and insoluble phenolics. *Phyllanthus tenellus* leaves contain more phenolics than control plants after being sprayed with copper sulfate (Michalak 2006a, b). Phenolic compounds have also an important role in pathogenic resistance as bioactive or antimicrobial compounds. In response to microbial attack, induce defense mechanism synthesizes broad-spectrum antibacterial compounds which initiate site-specific hypersensitive response to protect the spread of infection and future attack (Mandal et al. 2010).

Besides the stress response metabolites, phenolic acid has also an important role in plant-microbe interaction. Legume plants release phenolic acids as root exudates during germination and seedling growth stage. *Rhizobium* community of rhizosphere respond to the phenolic acid (flavonoids) and undergo metabolic changes, which initiate the nodulation process in legumes. The structural and functional diversity of phenolics secreted by legumes provides a competitive advantage for nodulation by selective rhizobial strains (Blum et al. 2000; Mandal et al. 2010). A current study also suggested that root exudates contribute to plant pathogenic resistance via secretion of antimicrobial compounds. These findings point to the importance of plant root exudates which are mainly phenolic compounds as belowground signaling molecules, particularly in defense responses (Lanoue et al. 2010). The study showed that under *Fusarium* attack, the barley root system secrets t-cinnamic acid which has antimicrobial activity. The secretion of de novo biosynthesized t-cinnamic acid induced within 2 days and shows dynamic plant-defense mechanisms at root level (Lanoue et al. 2010).

Plants grow and live in very complex and varying ecosystems. Because plants lack the mobility to escape from pathogens or herbivores attack, they have developed constitutive and inducible defenses mechanisms that are triggered by spatio-temporally dynamic signaling mechanisms. These defenses counteract pathogens directly via the production of toxins or defense plant structures. Root exudates play an important role in induced plant-defense mechanisms. The roots of *Ocimum basilicum* secrete rosmarinic acid when challenged by the pathogenic fungus *Pythium ultimum* (Bais et al. 2002). Stimulation of iridoid glycosides in root exudates of *Plantago lanceolata* in the presence of nematodes acts as nematicides (Wurst et al. 2010) (Fig. 22.2 and Table 22.2).

Several simple and complex phenolic compounds also act as allelochemicals, phytoalexin, phytoanticipins, and nematicides. Phenolic compounds like terpenoids, hydroquinones, hydroxybenzoates, hydroxycinnamates, and hydroxynaphthoquinones are known for allelochemical activity for competitive plants and weeds (Weir et al. 2004; Jilani et al. 2008). Compounds like cajanin, medicarpin, coumestrol, and

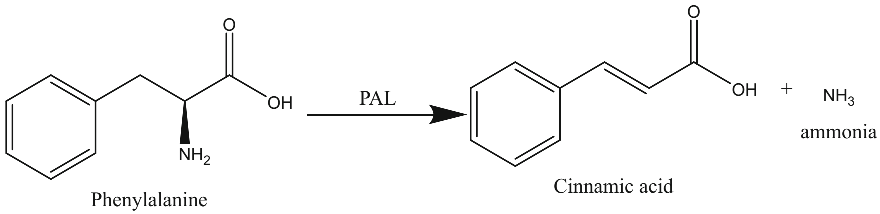

Fig. 22.2 Enzymatic conversion of phenylalanine to cinnamic acid. [Phenylalanine ammonia-lyase (PAL)]

limonoids can act as nematicides in plant-defense mechanisms. Plants respond to pathogen attack by accumulating phytoalexins, such as hydroxycoumarins and hydroxycinnamate conjugates (Karou et al. 2005). The synthesis, release, and accumulation of phenolics in particular salicylic acid (SA) are central to many defense strategies against pathogenic invaders (Boller and He 2009; Bhattacharya et al. 2010). De novo synthesis of SA occurs followed by infection or stress response. Accumulation of SA is a key molecule of systemic-acquired resistance. The volatile derivative, viz., salicylic acid methyl ester, has the ability to induce protection in other parts of the plant and to neighboring plants (Horvath and Chua 1994; Heil 1999; Bhattacharya et al. 2010).

22.3 Phenolics and Derivatives

22.3.1 Flavonoids

Flavonoids are the largest group of secondary metabolites, which are derivatives of simple phenols. Structurally they have a 15-carbon skeleton, consisting of two aromatic rings connected by three carbon bridge (C6–C3–C6) (Kulbat 2016). Structural and functional differentiation of flavonoids depends on its substituents (Martens et al. 2010). Flavonoids can be basically classified into three classes based on structural skeleton, viz., *flavonoids* or *bioflavonoids*, *isoflavonoids* derived from 3-phenylchromen-4-one (3-phenyl-1,4-benzopyrone), and *neoflavonoids*, derived from 4-phenylcoumarine (4-phenyl-1,2-benzopyrone) (Fig. 22.3). Flavonoids can be further subgrouped into anthocyanidins, anthoxanthins, chalcones, flavones, flavonols, flavandiols, flavans, proanthocyanidins, and tannins (Falcone Ferreyra et al. 2012).

In higher plants, flavonoids are involved in floral pigmentation, symbiotic relationships with prokaryotes, protection from pathogenic infection, insect herbivory, UV filtration, and antioxidant activity. Characteristics of unique color of plants like yellow are due to quercetin, or shades of blue color are due to malvidin (Mol et al. 1998). The flavonoids secreted by leguminous plant roots act as a messenger for the initiation of rhizobial infection stage toward the symbiotic relationships. Plants accumulate flavonoids in vacuoles of epithelial cells to protect tissues against

Table 22.2 Function of some of the naturally occurring phenolic compounds. (Bhattacharya et al. 2010)

Phenolic compounds	Function
Coniferyl alcohol, sinapinic acid, cinnamic acid	*vir* gene inducers, determinants of scent and attractants of pollinators and symbiotic microbes in plants, etc.
Hydroxybenzoate, hydroxycinnamates, 5-hydroxyanthraquinones	Allelochemicals for plant competition
Umbelliferone, *p*-hydroxybenzoic acid, vanillyl alcohol, isoflavones	Chemoattractant in *Rhizobium*
Sinapinic acid, syringic acid, ethylsyringamide, propylsyringamide, carbethoxyethylensyringamide, parahydroxybenzoate, ferulic acid	*vir* gene inducers in *Agrobacterium*
Vanillyl alcohol, bromo acetosyringone	Inhibitors of *vir* gene induction in *Agrobacterium*
Acetosyringone, α-hydroxyacetosyringone, *p*-hydroxybenzoate	Chemoattractant in *Agrobacterium* and *Rhizobium* and *vir* gene inducers in *Agrobacterium*
Salicylic acid	Quorum quencher in *Agrobacterium*
Hydroquinone	Allelochemical for plant competition
Coumarins, xanthones, anthocyanidins	Determinants of color and attractants of pollinators in plants
Caffeic acid	*vir* gene inducer in *Agrobacterium*
3,4-Dihydroxybenzoic acid	Chemoattractant in *Agrobacterium* and *Rhizobium*
Protocatechuic acid, β-resorcylic acid, protocatechuate, *p*-resorcylate, catechol	*vir* gene inducer in *Agrobacterium*
Chlorogenic acid	Precursor for lignin and suberin synthesis in plants
Lignin, tannins, and suberins	Structural components of plant cells
Catechins	Plant defense
Flavonoids, flavonols, flavones, genistein, daidzein, *O*-acetyldaidzein, 6-*O*-malonylgenistin, 6-*O*-malonyl daidzin, glycitin, 6-*O*-malonylglycitin	*nod* gene inducers in *Rhizobium*
Apigenin, naringenin, luteolin	Chemoattractant in *Agrobacterium* and *Rhizobium* and *nod* gene inducers in *Rhizobium*
Gallate, gallic acid, pyrogallic acid, syringic acid, kaempferol	*vir* gene inducers in *Agrobacterium*
Flavanones, quercetin	*nod* gene inducers in *Rhizobium*
Isoflavonoids	Chemoattractant and *nod* gene inducers in *Rhizobium*
Cajanin, medicarpin, glyceoline, rotenone, coumestrol, phaseolin, phaseolin, limonoids, tannins, flavonoids	Phytoalexins, phytoanticipins, and nematicides in plant defense

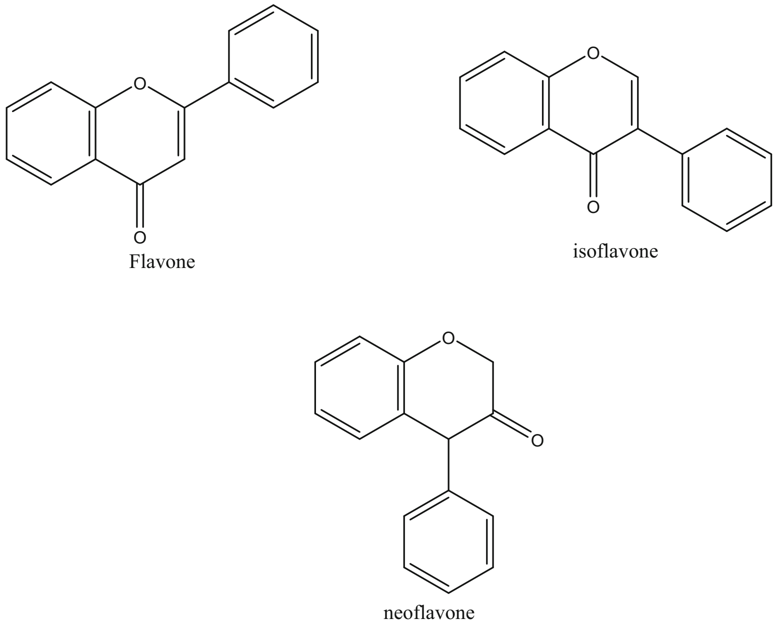

Fig. 22.3 Flavonoids classes

UV stress. Flavonoids can absorb radiation of high energy (maximum absorbance at 250–270 nm and 335–360 nm) (Winkel-Shirley 2002; Liang et al. 2006). Flavonoids also protect the plants from metal toxicity by metal – chelation. Metal – flavonoids chelates displays superoxide dismutase activity (A. 2006).

22.3.2 Coumarins

Coumarin acid is another important product of shikimic acid pathway, which is produced by hydroxylation of cinnamic acid or deamination of tyrosine by tyrosine ammonia – lyase (TAL) enzyme. It has a basic structure of $C_9H_6O_2$. Coumarins exhibit toxicity against herbivores. Bitter-taste coumarin also discourages animals from eating plants containing large amount of these compounds (Kulbat 2016) (Fig. 22.4).

22.3.3 Tannins

Tannins are polyphenolic compound that protects plants from herbivory. There are three classes of tannins: hydrolyzable polymer synthesized from gallic acid, phlorotannins, and condensed tannins and phlobatannins (Haslam 1966; Mueller-Harvey 2001). Tannins are generally found in high concentration in the bark and

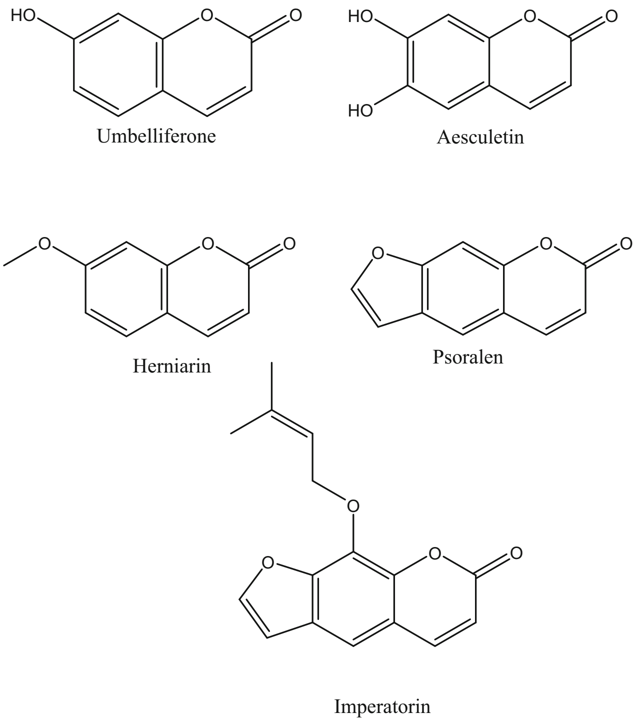

Fig. 22.4 Some naturally occurring coumarin derivatives

leaves of trees. Unpleasant, bitter taste and ability to denature protein makes tannin an exceptional compound to provide plant protection against insects (Kulbat 2016).

22.3.4 Salicylic Acid

Pathogenic infection initiates the accumulation of pathogenesis-related (PR) protein at a distant location from the infection site to enhance the state of resistance. Along with the PR protein, accumulation of salicylic acid (SA) and hydrogen peroxides also occurs at the site of infection as a systemic-acquired resistance, which is mediated by different signaling molecules. SA acid is one of the major signaling molecule for initiation of systemic-acquired resistance (SAR) (Fig. 22.5). It has been found that the exogenous supply of SA can induce SAR and provide resistance to infected plants.

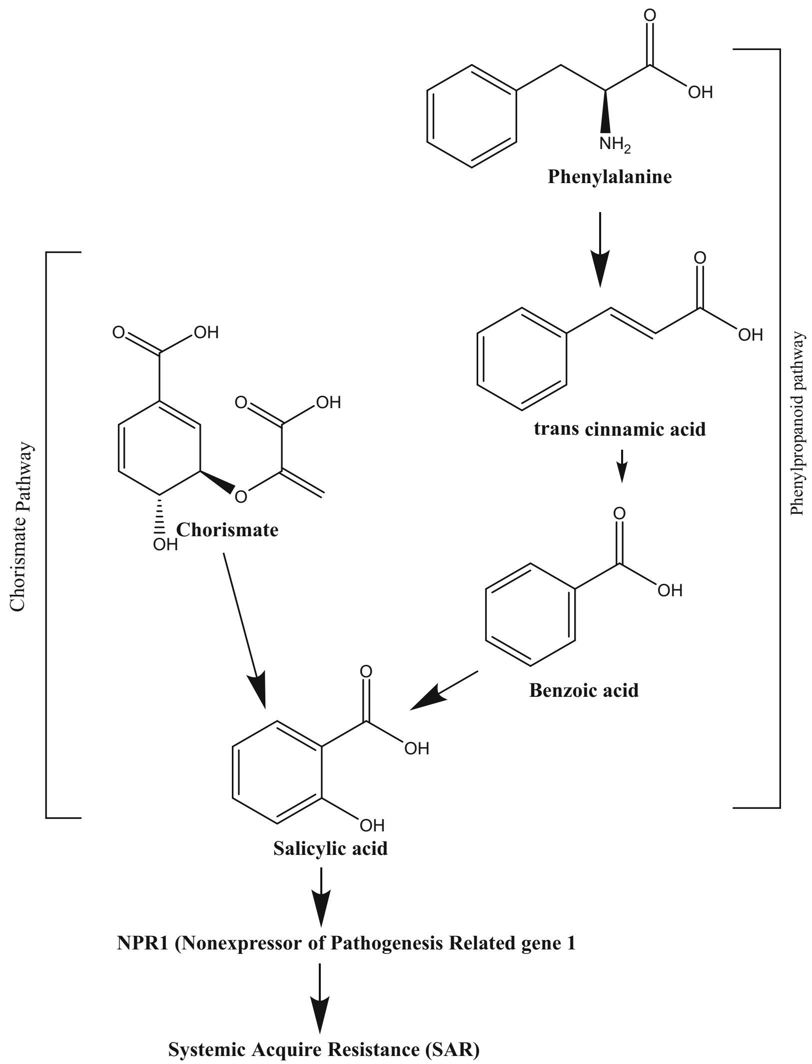

Fig. 22.5 Biosynthesis pathway of salicylic acid

22.3.5 Lignin

Lignin is a polyphenolic compound synthesized by polypropanoid pathway. Lignin is structural materials of some vascular plants and some algae. Lignin is important in the formation of cell walls. Synthesis of lignin can be de novo and specifically in response to pathogenic attack. In cultivar variety of wheat which are resistant to *Puccinia recondite* f. sp. *tritici*, fungal pathogen-causing leaf rust shows more accumulation of lignin compared to susceptible varieties (Southerton and Deverall

1990). A similar reaction can be observed in wheat in response to *Fusarium graminearum* infections which cause *Fusarium* head blight. Several researchers showed the importance of lignin biosynthesis in response to pathogenic attack. Inhibition of the enzyme PAL and cinnamyl alcohol dehydrogenase which are important in lignin biosynthesis showed reduced resistance to stem rust (*Puccinia graminis* Pers f. sp. *triti* Erics. & E. Henn.) (Moldenhauer et al. 2006). Coordinated expression of lignin biosynthesis is required against pathogenic infections.

22.3.6 Phytoalexin

Stress response initiates formation of two different types of compounds. In one response, the plant can form compounds which are off-target and work from considerable distance from the infection site. In other response, plant forms compounds which specifically act at the site of infection. In general, the stress metabolites or the compounds formed under stress and infections are referred to as phytoalexin. Phytoalexin shows specific toxicity against pathogens. Most of the phytoalexins belong to flavonoids and isoflavonoids group and exhibit antimicrobial and antioxidant activity (Vermerris and Nicholson 2006). Phytoalexins can break-down cell wall, disrupt metabolism, and prevent growth of the pathogenic microorganisms. The importance of phytoalexin can be gleaned from the fact mutants for phytoalexin exhibit more pathogenic colonization compared to wild types, and susceptibility of plant tissues increases when phytoalexin biosynthesis is inhibited (Glazebrook and Ausubel 1994). Synthesis of phytoalexins is important for defensive mechanisms against fungal and other microorganisms.

- Trans-resveratrol is a phytoalexin which can inhibit the growth of *Botrytis cinerea* (Timperio et al. 2012).
- Grapevine secretes delta viniferin against the infection of *Plasmopara viticola* (Favaron et al. 2017).
- Danielone, a phytoalexin found in papaya fruit, shows antifungal activity against *Colletotrichum gloeosporioides* (Echeverri et al. 1997).
- Chlorogenic acid present in the periderm of potato tubers is toxic to the *Streptomyces scabies*, which causes potato scab (Villegas and Kojima 1985) (Fig. 22.6).

22.4 Phenolic Compounds in Abiotic Stress

Environmental condition governing the agricultural lands is often inadequate for crop production. Abiotic stress including drought, salinity, and water scarcity causes huge economic and yield losses every year around the world. Climate change and improper land use have also aggravated the land degradation. Drought and salinity are still major abiotic stress for many agricultural lands. Research showed that

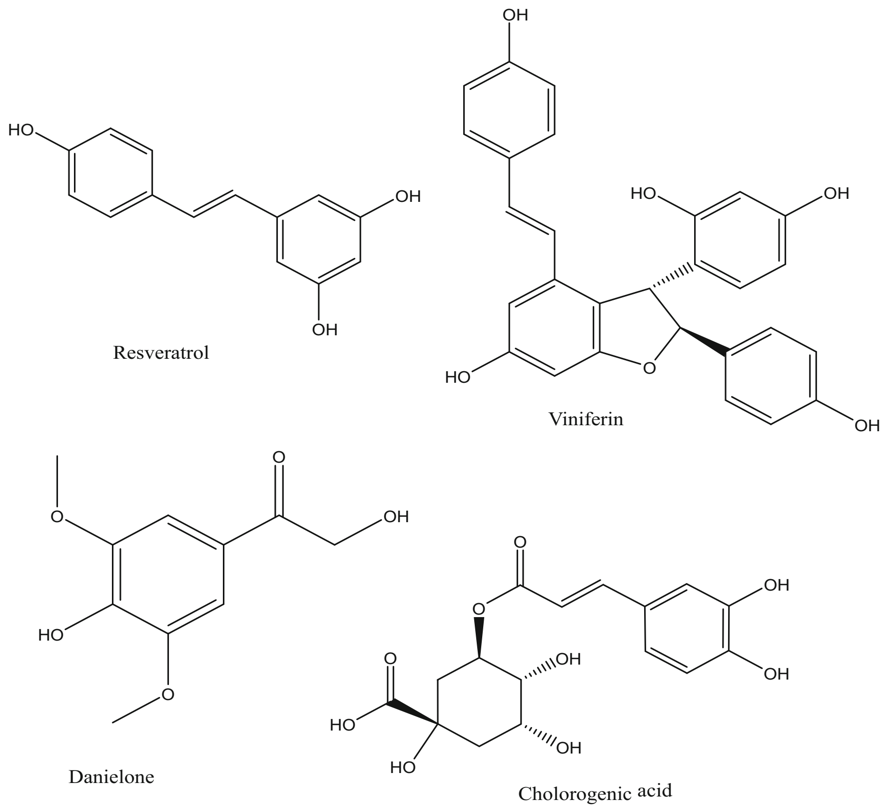

Fig. 22.6 Structure of few of the phytoalexin

increased abiotic stresses like drought, salinity, low/high temperature, and nutrient deprivation are associated with oxidative stress and production of reactive oxygen species (ROS) (Schulz et al. 2016; Caliskan et al. 2017). Reactive oxygen species are superoxide anion (O_2^-), hydrogen peroxide (H_2O_2), and hydroxyl radical (HO) which are formed in cells during partial reduction of oxygen species. Plant has evolved different antioxidant mechanisms to mitigate the cytotoxic effect of ROS. Plant can use enzymatic and non-enzymatic components for antioxidant activity. In enzymatic components, superoxide dismutase, ascorbate peroxidase, and glutathione reductase are most important. In non-enzymatic antioxidant mechanisms, a polyphenolic compound like phenolic acids, flavonoids, proanthocyanidins, and anthocyanins play an important role to balance the ROS effect. Evidence suggest the accumulation of antioxidant metabolites in major cellular tissues like mesophyll cells, chloroplast, and mitochondria which can suffer major damage from ROS (Martinez et al. 2016).

22.5 Phenolic Compounds in Insect Herbivory

A complex interaction can be observed between the insect pest and phenolics. A positive correlation has been recorded for the insect herbivory of spotted spider mites (*Tetrancychus urticae*) and constitutive concentration of catechol phenolics in strawberry leaves (Luczynski et al. 1990). Gossypol, a phenolic pigment of cotton, has a deterrent effect on numerous insect pest and is toxic to *Heliothis virescens* (tobacco bollworm) and *Heliothis zea* (bollworm) (Maxwell et al. 1965). Catechol can control the mite's population. It binds to mite's digestive system and inactivates them (Rehman et al. 2012). Another example is tannin; Feeny reported the tannin can control the larvae of the oak month (*Opheropthera brumata*) (Feeny 1970). Wheat cultivars containing phenolics are much less attractive to *Rhopalosiphum padi* (cereal aphid) (Fürstenberg-Hägg et al. 2013).

22.6 Conclusions

Phenolic compounds play an important role in plant growth and development, particularly in defense mechanisms. Most of the phenolic compounds have potent antioxidant properties, neutralizing the effects of oxidative stress. Some of them exhibit ability to chelate heavy metal ions. Importantly, phenolic phytoalexins exhibit antibiotic and antifungal activity. Coumarins and tannins repel herbivores, whereas phenylpropanoids are starting molecules for the synthesis of lignin and suberin, in order to strengthen cell walls. Flavonoids act as a chemoattractant and initiate the symbiotic relationship between Rhizobium and leguminous plant.

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