Plant Peroxidases: Biomarkers of Environmental Stresses and Signaling in Plants

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Abstract

Plants faced several biotic and abiotic stresses during its life span. For maintaining the normal growth, plant produces the reactive oxygen species (ROS), which help in the tolerance of such stress. Fluctuation of the redox reaction in plants increases the production of ROS, which further adversely effects the plant physiological processes. Antioxidants governed and maintain the pathway as well as release of ROS. Till today, it became an interesting and challenging topic to understand the plant response to ROS. ROS is responsible for reversible and irreversible modifications of proteins, which act in various signaling pathways. Oxidative post-translational modifications (OX-PTM) cause structural modifications in target proteins and create oxidative damage. Initially, ROS were identified as a toxic by-product of aerobic metabolism. Now, it is clear that ROS play a key role in signal transductions of plants and controlled the process of growth and development. Biotic and abiotic environmental stimulus triggered the generation of ROS. The main site of ROS production in plants is chloroplast, peroxisome, and mitochondria. Apart from these cell walls, cell membrane, endoplasmic reticulum, and apoplast are also secondary site of ROS production. Degradation of biomolecules such as pigments, proteins, lipids, carbohydrates,

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and nucleic acid are the forms of cell damage, which ultimately cause plant cellular death. This chapter discusses the types, mechanism, and response of plant against these peroxides.

Keywords

Reactive oxygen species · Antioxidants · Stress responses · Oxidative post-translational modifications

7.1 Introduction

Peroxidase is heme-containing monomeric glycoproteins and a family of isoenzyme present in all plants. They utilize either H_2O_2 or O_2 to oxidize a wide diversity of molecules. These important enzymes are utilized in enzyme diagnostic assays, immunoassays, and industrial enzymatic reactions. In the molecular breeding of plants, peroxidase genes and their promoters can be used. To explore the physiological and molecular functions of peroxidase genes in plants, transgenic techniques have been utilizing (Jouili et al. 2011).

7.1.1 Plant Peroxidases

Guaiacol is a substrate that was used as the first colored reaction of biological material, as explained by Schönbein (1855). By semi-century later, to explain an enzyme extracted from roots of horseradish, horseradish peroxidase (HRP), the term peroxidase was used for the first time. In cell cultures of many plant species, bean (Arnison and Boll 1975), spinach (Sticher et al. 1981), tobacco (Pickering et al. 1973), and soybean (Griffing and Fowke 1985) peroxidases were observed, which are omnipresent in all living organisms (Hiraga et al. 2001).

7.1.1.1 Classes of Plant Peroxidases

Peroxidases are present in plants, animals, and microorganisms. Based on peroxidase catalytic properties and structure, they are divided into three super families (Welinder 1992, Table 7.1). In animals, fungi yeast, plants, and bacteria, the second peroxidase superfamily includes catalases (EC 1.11.1.6) (Hiraga et al. 2001). The plant peroxidase superfamily can be classified further into three classes on the basis of differences in primary structure (Welinder 1992, classes I, II, and III in Table 7.1). In plants, bacteria, and yeast such as microbial cytochrome c peroxidase, Class I plant peroxidases contain the intracellular enzyme such as (EC 1.11.1.5), ascorbate peroxidase (EC 1.11.1.11), and bacterial catalase-peroxidase (EC 1.11.1.6). Class II plant peroxidases are extracellular peroxidases from fungi, containing Mn^{2+}- dependent peroxidase (EC 1.11.1.13) and lignin peroxidase (EC 1.11.1.14). Class III plant peroxidases (EC 1.11.1.7), which were originally explained as peroxidases and which are the main concern of this article, are plant enzymes that are released outside

Table 7.1 Classification of peroxidases

Super family	Class	Member	EC number	Origin
Plant peroxidase		Glutathione peroxidase	1.11.1.9	Plant
		Catalase	1.11.1.6	Plant, fungus and yeast
	I	Cytochrome *c* peroxidase	1.11.1.5	Yeast and bacterium
		Catalase-peroxidase	1.11.1.6	Bacterium and fungus
		Ascorbate peroxidase	1.11.1.11	Plant
	II	Manganese-dependent peroxidase	1.11.1.13	Fungus
		Ligninase	1.11.1.14	Fungus
	III	Peroxidase	1.11.17	Plant

the cells or move into vacuoles. POX contains horseradish peroxidase, which is a commercially accessible enzyme that is often conjugated to an antibody for chromogenic identification (Hiraga et al. 2001).

These three classes of the plant peroxidase superfamily of enzymes are different in their catalytic properties and structures. Residues in their C-terminal of Class II peroxidases have an extra 40–60 amino acid in contrast to peroxidases in other classes (Welinder 1992). Groups of all classes of the plant peroxidase superfamily have ten simple α-helices. However, three specific helices are present in class III, but peroxidases enzymes of Classes I and II contain one fixed helix (Hiraga et al. 2001). Reductants (cytochrome c and ascorbic acid, respectively) represent strong specificity against Cytochrome c peroxidase and ascorbate Peroxidase. From small molecules to macromolecules, POXs oxidize many substances. However, there is low sequence similarity between the three classes, five independently positioned amino acids that are very significant for catalysis and structure as well as the helical folding of the whole polypeptide. They are strictly preserving among peroxidases in all three classes (Hiraga et al. 2001).

7.1.1.2 Functions

Plant peroxidases act as huge functional enzymes that could identify in plants, from shoot up to senescence. The different types of peroxidases and their origin are given in Table 7.1. The enzyme peroxidase and native ferric peroxidase are transferred into the compound I (comp) during the standard peroxidative cycle by catalyzing the reduction of H_2O_2. Another compound I and II catalyze in continue dehydrogenation reactions of a broad range of electron donor molecules such as phenolic compounds, auxin, or secondary metabolites lignin precursors. Widely speaking, ferriprotoporphyrin is the active part of peroxidases. Indeed, the ferrous heme (Fe IV=O) group contains compound I, which undergoes two continuous steps by AH2 to transform itself into a compound II (CompII). A native form of the enzyme included a ferric heme (Fe III). The reaction is shown to the generation of phenoxy radicals that combine spontaneously to form lignin polymers when the oxidized

substrate is a phenolic compound (Chen and Schopfer 1999). If somehow, the phenolic substrate is restored by NADH or related reduced compounds. The resulting radicals (NAD) start a nonenzymatic oxidative cycle in which O_2 can decrease to O_2-, as O_2- can respond with another NADH molecule to give H_2O_2 and NAD. Peroxidases are known as NADH oxidase (Mäder 1980) and use NADH as the electron donor. They have been recommended to play a crucial role in the production of H_2O_2, which is required for lignification.

7.1.1.3 Subcellular Localization

The enzyme peroxidases Class III are commonly present in the apoplast and vacuoles (Andrews et al. 2002). They have excreted enzymes given by genes that encode a signal peptide. It is mediated by the entry of the developing peroxidase peptide into the endoplasmic reticulum. Therefore, they were present in the Golgi apparatus, the endoplasmic reticulum, and transport vesicles (Mäder 1980). The activity of the nuclei, mitochondria, and plasma membrane was identified by peroxidase. However, it seems that isoperoxidases with an acidic isoelectric point are present in cell walls (Passardi et al. 2004), while normal isoperoxidase is present either in the vacuole or in cell walls. Indeed, they have shown that cationic peroxidases could be discovered from the cell wall.

7.1.1.4 Multigene Family

The number of genes has increased widely from the appearance of the first Class III peroxidases, just before the advent of terrestrial plants, to the emergence of angiosperms (Passardi et al. 2004). The plant adaptation to terrestrial life can be connected with the multifunctional of peroxidases or characterized by the availability of oxygen at high proportions. Therefore, the evolution of a multigene family looks to be associated with the increasing difficulties of plant structure and the diverseness of their biotopes and pathogens (Hiraga et al. 2001).

7.2 Production, Scavenging, and Signaling of ROS

During entire life cycle of plants, there are many environmental conditions such as temperature, humidity, salinity, pathogen attack, herbivores attack, and mechanical stress, which are major challenges for them. A reserve signaling pathway is developed by plants which are nonparalleled in its complexity in living species for resistance of all this type of challenges. There are reprogramming of gene expression and metabolism in plants due to response of stress stimulus through signaling of hormones of plants, receptors of cell surface, photoreceptor, and plastids due to lights (Kami et al. 2010; Jaillais and Chory 2010; Vanstraelen and Benková 2012). A class of reactive forms of molecular oxygen plays a vital role in this signal integration and decision-making, collectively known as reactive oxygen species (Kangasjärvi et al. 2012). Due to many stimuli, either environmental or other cell organelles like peroxisomes mitochondria and chloroplast are generated ROS, and this is a hallmark of response against stress. The causes of generation of ROSs and

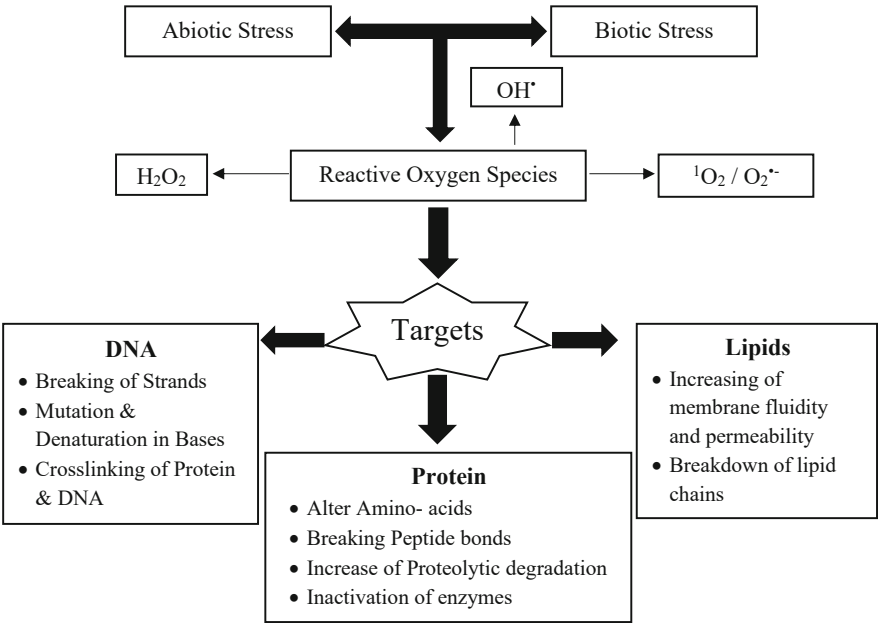

Fig. 7.1 Causes of ROS and their effect on plants

their ultimate effect are described in Fig. 7.1. The production of ROS mostly occurs in apoplast, peroxisome, chloroplast, and sometimes in endoplasmic reticulum, nucleus, and mitochondria (Shapiguzov et al. 2012).

7.2.1 Plastids (Chloroplasts) Responses to ROS

The ROS is being continuously generated in the chloroplasts as the energy is being transfer to O_2 due to partial reduction of oxygen. When cytochrome C oxidase interacts with O_2 generates water. Sometimes, $O^{\cdot -}{}_2$ is liberated due to the reaction of O_2 and discrete ETC constituents, and this is first produced ROS. After undergoing further reactions, superoxide radical ($O^{\cdot -}{}_2$) can also produce member of other ROS family. Singlet oxygen is produced by the reaction of O_2 and triplet state of chlorophyll in the antenna. It is an unusual member of ROS family, which is not produced by electron transfer to O_2 (Das and Roychoudhury 2014).

$^1O_2$ is generated by PSII via two ways (Das and Roychoudhury 2014). Firstly, when environmental stress disturbs the delicate balance between energy utilization and light harvesting, followed by triplet Chl (^{3}Chl*), which are formed and react with dioxygen ($^3O_2$), singlet oxygen ($^1O_2$) is liberated (Karuppanapandian et al. 2011). Secondly, due to over reduction of ETC, $^1O_2$ is produced by the light harvesting complex (LHC) at the PSII (Asada 2006). Due to accumulation of $^1O_2$ in the chloroplast, peroxidation of membrane lipid mainly PUFA (polyunsaturated

fatty acid) takes place and damages the proteins of PSII at P680 reaction center. It can also cause the death of cells (Triantaphylides et al. 2008). It is important to control and scavenge the ROS in the chloroplast for survival of plants under stress conditions (Tseng et al. 2007).

7.2.2 Mitochondrial Responses to ROS

The mitochondria is the main production site of $O^{\cdot -}_2$ and H_2O_2 like injurious ROS (Navrot et al. 2007). Due to engaging in photorespiration, having rich environment of carbohydrate and O_2, plant mitochondria is different from animal mitochondria (Rhoads et al. 2006). Complex I and Complex III play lead role in the generation of ROS; hence, mitochondria is a crucial culprit because it stores energized electron to reduced O_2 and form ROS (Noctor et al. 2007). In Complex I (NADH dehydrogenase) at its flavoprotein region, O_2 directly decreases into $O^{\cdot -}_2$. Due to shortage of NAD^+-linked substrates, a reverse electron flow occurs from Complex III to Complex I followed by the production of ROS that increased at Complex I (Das and Roychoudhury 2014). For the prevention of the oxidative stress in mitochondria, there are two types of vital enzymes named mitochondrial alternative oxidase (AOX) and mitochondrial SOD (Mn-SOD) (Das and Roychoudhury 2014). The main function of AOX is to maintaining the lower state of the UQ pool and reduced the production of ROS (Ho et al. 2008).

7.2.3 Peroxisomal Responses to ROS

Single-membrane-bound spherical micro-bodies, peroxisomes, and their integral oxidative metabolism are responsible for the responses against ROS. In matrix, hypoxanthine and xanthine are metabolized into uric acid by xanthine oxidase (E.C.1.17.3.2), and $O^{\cdot -}_2$ is liberated as a by-product. In peroxisomal membrane, NADPH-dependent electron transport chain having the component of Cyt b and NADH, which utilized O_2 as the electron acceptor and cytosolic $O^{\cdot -}_2$ is generated (Das and Roychoudhury 2014). There are three transmembrane proteins of peroxisomes, which cause the production of ROS, having molecular mass of 18 kDa, 29 kDa, and 132 kDa.

The electron donor of 18 and 132 kDa peroxisomal membrane polypeptide is NADH and NADPH that also act as electron donor for 29 kDa PMP to lower cytochrome c. During low water availability, stomata remain closed; in these stressful abnormal situations, the ratio of CO_2 to O_2 reduced and caused the occurrence of the increase of photorespiration followed by the formation of glycolate (Das and Roychoudhury 2014). With the help of glycolate oxidase, glycolate oxidized and gave rise to H_2O_2, and during photorespiration, it is a chief generator of H_2O_2 (Noctor et al. 2002). In peroxisomes, there are some other metabolic pathways that produced ROS such as β-oxidation of fatty acids and flavin oxidase pathway (Das and Roychoudhury 2014).

7.2.4 Apoplastic Responses to ROS

Apoplast is a notable site for H_2O_2 production due to the combination of abscisic acid(ABA) and stress signals during the time of stressful environmental (Hu et al. 2006). NADPH oxidase is expressed by *AtRbohD* and *AtRbohF* for the purpose of generation of apoplastic ROS, which is vital for stomatal closure via ABA induction (Kwak et al. 2003). In apoplast, there are some other enzymes that generate ROS like pH-dependent peroxidases, some polyamine oxidases, cell wall linked oxidases, etc., which are responsible for the production of H_2O_2 (Das and Roychoudhury 2014).

7.2.5 ROS Transport Through Cellular Membranes

The plasma membrane is surrounded with whole plant cell below the cell walls and plays a key role for the interaction with changeable environmental conditions and helped in the survival of the cells. The NADPH-dependent oxidases are remarkable due to the presence of different homologs in various adverse conditions and their gene expression, which are situated in the plasma membrane (Apel and Hirt 2004). NADPH oxidase transferred electron from cytosolic NADPH to O_2 and gives $O^{\cdot -}{}_2$ by the help of SOD (Das and Roychoudhury 2014).

7.2.6 Cell Walls Responses to ROS

The cell wall becomes active source of H_2O_2, $OH^{\cdot}$, $O^{\cdot -}{}_2$, and O_2 by hydroperoxidation of polyunsaturated fatty acids with the help of lipoxygenase (LOX) situated in cell walls during stressful conditions. Polyamines or diamines are utilized by diamine oxidase, which is located in the cell wall for the production of ROS (Das and Roychoudhury 2014). For reinforce of the cell wall with lignin during attack of pathogen, the lignin precursors are cross-linking with the help of H_2O_2-mediated pathways (Higuchi 2006).

7.2.7 Endoplasmic Reticulum Responses to ROS

The NADPH-mediated electron transport is situated in the ER including $CytP_{450}$, produced $O^{\cdot -}{}_2$ (Mittler 2002). A free radical intermediate (Cyt P_{450} R^-) are produced by the interaction of $CytP_{450}$ with RH, an organic substrate. Sometimes, this oxygenated complex decompose to Cyt P_{450}-Rh and liberated $O^{\cdot -}{}_2$ in the form of a by-product (Das and Roychoudhury 2014).

7.3 ROS-Sensing Mechanisms via Oxidative Post-Translational Modifications of Cysteine Residues

The oxidative post-translational modification (Ox-PTM) of Cys residues is a necessary mechanism that controls protein structure and functions. Cysteine (Cys) side chain's special properties allow various Ox-PTMs, which potentially results in diverse regulatory effects (Tripathy and Oelmüller 2012). The side chain of a Cys residue consists of a terminal thiol (−SH) functional group. At the core of the thiol, the sulfur atom is rich in electron, and its d-orbitals permit for the multiple oxidation states (Waszczak et al. 2015). The accessibility of different oxidation states permits the formation of a diverse range of Ox-PTMs containing sulfenylation (SOH), sulfhydration (SSH), S-nitrosylation, S-glutathionylation (SSG), disulfide bonds (RS-SR), sulfinic acid (SO_2H), and sulfonic acid (SO_3H).

Most Cys Ox-PTMs are stimulated by diffusible small molecules and are reversible. Via antioxidant defense system, they can decrease back to a free thiol (SH) or be transformed to other Ox-PTMs depending on the cell's redox-state (Waszczak et al. 2015). Many factors are involved in the reactivity of the individual Cys residue, its surrounding environment, and the composition of the local redox environment leads to the formation of a single Ox-PTM. A summary of the variety of different Ox-PTMs and the redox-chemistry is associated with their formation. Mainly, Cys Ox-PTMs are persuaded by reactive oxygen or nitrogen species molecules (ROS/RNS) that react with the free thiol on a Cys side chain (Waszczak et al. 2015).

Plants have evolved different strategies to keep ROS levels under a tight control that is governed by nonenzymatic and enzymatic ROS-producing and ROS-scavenging systems (Mittler et al. 2011).

Ascorbate (Asc) and glutathione (GSH) are the prime nonenzymatic cellular redox systems, with tocopherol and diverse alkaloid, carotenoid, and flavonoid metabolites often listed but consistently debated as physiologically relevant antioxidants (Hernández et al. 2009). Lower glutathione pool (high GSH/GSSG ratio) regulation is pivotal for cellular redox homeostasis, since GSH is used to regenerate oxidized ascorbate in the glutathione–ascorbate cycle (Del Río 2011). Asc and GSH work hand in hand with ascorbate peroxidases (Nakano and Asada 1981) and glutathione peroxidases (Mills 1957), respectively, which together with catalases, peroxiredoxins (Prxs), and superoxide dismutases establish the main enzymatic classes involved in ROS scavenging (Mittler et al. 2004). Glutathione is fully protonated at physiological pH because of its relatively high pK_a (Van Laer et al. 2013), and thereby its reactivity toward disulfides and ROS is rather limited (Waszczak et al. 2015).

The chemical properties of the sulfur atom (i.e., broad range of oxidation states) make Met and Cys residues the crucial sites of oxidation within proteins (Davies 2005). The −2 oxidation state of the sulfur atom is represented by the thiol group (R-SH) in Cys Ox-PTMs, which is the fully decreased form. Not all Cys residues in a protein are prone to ROS-mediated modifications, and the reactivity of distinct thiol-proteins toward ROS differs according to their physiological function and local redox environment (Waszczak et al. 2015). Between discrete Cys residues, the

reactivity is strongly correlated with their pK_a, i.e., the potential to form the anionic form of the sulfur, called thiolate (R-S$^-$), which is much more reactive than the thiol.

The protonated thiol will be the dominant species, if the pK_a of the sulfur atom is higher than the pH of the solution. However, the majority of the thiols will be present as a thiolate (Cys prone to oxidation), if the pK_a is lower than the pH (Waszczak et al. 2015). The existence of dipoles or proximal charged residues as well as the hydrogen bonding between thiolates/thiols and neighboring residues can stabilize the cysteine thiolates (Harris and Turner 2002). Hydrogen bonding has a great credit on the pK_a of reactive Cys residues. Generally, the lower the pK_a is, the more hydrogen bonds a Cys-sulfur receives, and the more the thiolate form is stabilized (Roos et al. 2013).

The nucleophilicity of the Cys is also a vital factor in its reactivity; sometimes, a lower stabilization of the thiolate in Cys residues enhances its nucleophilicity, while a highly stabilized thiolate requires a great amount of energy to gain the transition state (Ferrer-Sueta et al. 2011). The steric accessibility of Cys residues within the three-dimensional structure of the protein is another important factor that controls the reactivity of Cys residues (Marino and Gladyshev 2010). The first step involves the reversible oxidation of reactive Cys residues to sulfinic acid (R-SOH) in ROS-dependent signaling. This modification is highly unstable and leads to further modifications, unless stabilized within its protein environment (Claiborne et al. 1993).

An extreme concentration of oxidant can result in further oxidation to sulfinic acid (R-SO_2H) and thereafter to irreversible sulfonic acid (Roos and Messens 2011). An ATP-dependent sulfiredoxin enzyme (Srx) catalyzed the reversion of the R-SO_2H modification that can reduce R-SO_2H to R-SOH in *Arabidopsis* (Rey et al. 2007). However, so far, R-SO_2H reduction is rather exceptional with the only two known substrates of *AtSrx*: mitochondrial *PrxIIF* (Iglesias-Baena et al. 2011) and the chloroplast 2-Cys Prx (Iglesias-Baena et al. 2010). On the other hand, R-SOH can react with free protein thiols to form intra- or intermolecular disulfide bonds (R-S-S-R/R-S-S-R′) or is modified by low-molecular-weight thiols (like GSH in plants), induced to Cys *S*- glutathionylation. Initially, *S*-glutathionylation events were regarded to serve as a protective mechanism on active-site Cys residues, preventing overoxidation and subsequent permanent protein damage (Waszczak et al. 2015). Only recently, the role of *S*-glutathionylation in redox signaling was recognized (Zaffagnini et al. 2012).

The reduction of deglutathionylation and disulfide bonds is controlled by thioredoxins (Trxs) and glutaredoxins (Grxs), respectively. Plants are equipped with a much more complex Trx/Grx network, compared with prokaryotes and animals. Fifty Grx/Grx-like and 44 Trx/Trx-like proteins are encoded by the *Arabidopsis* genome (Meyer et al. 2012). Trxs use multiple sources of reducing equivalents to perform the reduction of intra-/intermolecular disulfide bonds, depending on the subcellular localization (Waszczak et al. 2015). Light reactions reduce ferredoxin (Fdx) in chloroplasts, which in turn reduces ferredoxin–thioredoxin reductase (FTR), which eventually regenerates the Trx sulfhydryl groups (Schürmann and Buchanan 2008). Another origin of decreasing equivalents, common in the Trx and Grx systems, is NADPH, which after oxidation to $NADP^+$ is

reduced by Fdx: $NADP^+$ reductase within the chloroplast stroma, also during the oxidative pentose phosphate pathway.

7.4 Intracellular Interactions Between Redox Signaling and Organelle ROS

Cytoplasmic NADPH is a core for redox signaling pathway for the detoxification of ROS. NADPH supplied electrons to ROS generating enzymes like NADPH oxidase and also maintained disulfide or thiol status. For the changes in the gene expression level in nucleus, all the signaling either from apoplast or cell organelles must have to pass through cytoplasm. Khandelwal et al. (2008) provided an example for the information of ROS where redox state of any cell is combined with other regulators. In last decades, the genetic approaches significantly contribute for understanding the mechanism of it. This is also helpful in the field of genetic engineering of crop plants (Tripathy and Oelmüller 2012).

7.4.1 Chloroplast-Mitochondrion Cross talk, Signaling, and PAP

Mitochondria are the end products of an endosymbiotic event, like chloroplasts, and have a portion of ancestral genome (Woodson and Chory 2008). It is a crucial signaling from mitochondria-to-nucleus in retrograde manner for coordination of the expression of nuclear genes encoding mitochondrial proteins with the expression of the mitochondrial genome (Rhoads 2011). The core function of chloroplast and mitochondria is to capture and utilize the energy in the metabolic exchanges. Apart from these functions, they are also coupled with cellular redox status (Bobik and Burch-Smith 2015). To regulate gene expression of mitochondria, the regulated translocation of proteins would mediate chloroplast signaling. Direct contact between mitochondria and chloroplasts would be made such translocation much easier, and by physical interaction, there may be direct communication (Bobik and Burch-Smith 2015). Mitochondria, peroxisomes, and chloroplasts have frequently been observed in close association in leaves, consistent with metabolic exchange among these organelles. Chloroplast-peroxisome association are established and followed by mitochondria recruited and formed triorganellar unit (Oikawa et al. 2015). These techniques are becoming less time-consuming and easier (McDonald 2014), and we can used these approaches for biology of plant cell (Bobik et al. 2014). This will be an energetic approach for interrogation of ultrastructure of plant cell body when coupled with fluorescence microscopy, as exemplified by recent work from Caplan et al. (2015).

7.4.2 During Stress, the Apoplastic and Organelle ROS Interactions

By the presence of plasmodesmata which is a specialized channel present in the cell wall between two adjacent cells, communication between plant cells is enhanced. Plasmodesmata are discovered 100 years ago, but the structure and regulation of plasmodesmata are not well understood till now (Bobik and Burch-Smith 2015). Recent advancement in plant biology and genetics helped very much to understanding their unknown fact and function. Plasmodesmata gives a way for the metabolite exchange and also water, ions, and product of photosynthesis; beside these also information coded by nucleic acids, proteins like transcription factor and hormones are essential for proper development of plants (Jackson 2015). Firstly, maize *sucrose export defective1* (Russin et al. 1996) mutant was reported (Bobik and Burch-Smith 2015). From sites of photosynthesis, because of callose accumulation at plasmodesmata of bundle sheath and vascular parenchyma locations, the export of photosynthate is decreased by *sxd* 1 mutants (Botha et al. 2000).

Photosynthesis is not inhibited by sxd1 mutants, while accumulation of starch and sugar occur in source cells (Provencher et al. 2001). The first clue is that chloroplast redox state may affect plasmodesmata provided by the *sxd1* mutant. However, mutants were un-differentiable from wild-type plants under optimal growth conditions; however they are much more sensitive to stress of photooxidative stage (Porfirova et al. 2002). With metabolism of tocopherol defects, cautiously examination of *Arabidopsis* mutants should take place for plasmodesmata-related changes in intercellular trafficking (Bobik and Burch-Smith 2015). Identification of the *gfp* arrested trafficking (*gat*) mutants can be done by a genetic screening with altered plasmodesmal function for *Arabidopsis thaliana* mutants (Benitez-Alfonso et al. 2009). The *gfp* is synthesized in the companion cells of the *Arabidopsis* mutant; in wild type, tissue phloem moves through plasmodesmata, while this is not seen in mutants, which means that intercellular trafficking is reduced by *gat* mutants. After about ten days of development become cease, the *gat1, 2, 4*, and *5* mutations are all seedling lethal (Bobik and Burch-Smith 2015). A thioredoxin-m3 (TRX-m3) is localized in plastid, and *gat1* roots is encoded by *GAT1* gene, which accumulate ROS in more amount than wild-type roots.

GAT1 overexpression leads to the reciprocal phenotype of increased intercellular transport. Hence, GAT1 probably functions in redox homeostasis like SXD1/VTE1, including the perturbation of plastid and chloroplasts redox state that leads to altered plasmodesmata. Also, in the *gat1* mutant, altered metabolic flux may change the redox state of TRX-m3 and eventually leads to plasmodesmata function (Benitez-Alfonso et al. 2009). A separate screen is managed by the lab of Zambryski for mutants of *Arabidopsis* with changing intercellular trafficking mediated by plasmodesmata (Burch-Smith and Zambryski 2012). Numerous *increased size exclusion limit (ise)* mutants were identified with the help of screening of the embryonically lethal mutant. *ISE1* and *ISE2* have been cloned and mapped (Kobayashi et al. 2007). Additionally, *ise1* and *ise2* embryos also consist of increased numbers of plasmodesmata with multiple branches to increased plasmodesmal trafficking (Burch-Smith and Zambryski 2010). Hence, due to

defective chloroplasts, there are overlapping plasmodesmatal phenotypes of the *ise1* and *ise2* mutants (Bobik and Burch-Smith 2015).

7.4.3 ROS in Stomatal Closure and Plant Immunity

For the regulation of the closure of stomata, reactive oxygen species (ROS) acts as an important signal (Murata et al. 2015). Organisms, which are aerobic in nature, possess ROS (H_2O_2, $HO^{\cdot}$, $O^{\cdot -}{}_2$ and $^1O_2$) as metabolites. Firstly for the regulation of stomatal closure, ROS is generated in apoplast of guard cells, and after this, sensing and signaling cause activation of anion channels (Sierla et al. 2016). NADPH oxidase of plasma membrane, which is also known as respiratory burst oxidase homologs [RBOHs], is considered ROS production in apoplast of plants and is known for stress-induced response developmental control (Sierla et al. 2013). NADPH oxidases are present all over and are evolutionarily conserved in nature (Sierla et al. 2016).

Molecules transported to intercellular space with the help of microcapillary, which are inserted to stroma nanoinfusion (Guzel Deger et al. 2015). Rapid stomatal closure is facilitated by nanoinfusion of flg22 and ABA (Guzel Deger et al. 2015). There is further a detailed study that is required for the role of RBOH generated ROS in the closure of stomata (Sierla et al. 2016). In the apoplast, amine oxidases and peroxidases helped in the production of ROS, aside from RBOHs (Sierla et al. 2016).

In guard cells, apoplastic signaling of ROS create complexity by both peroxidases and amine oxidases (Wang et al. 2012). Further studies are required for vital role of enzymes, their molecular identity, and functions, which generate ROS in stomatal movement (Sierla et al. 2016). Stomatal closure is done by accumulation of ROS in chloroplast, further ABA treatment, ozone, extracellular Ca^{2+} (Wang et al. 2012), and also by some other external stimulus. These discoveries demonstrate the chief role of ROS accumulation in chloroplast for stomatal movement (Sierla et al. 2013).

ROS accumulation gets in the guard cell vicinity of chloroplast by the help of ABA due to which in adjacent cells ROS signaling is increased (Zhang et al. 2001). An NADPH oxidase inhibitor diphenyleneiodonium is inhibiting the accumulation of ROS in chloroplast partially but not completely (Sierla et al. 2016). The late ROS peak was noticeably reduced in the double mutant of *atrbohD and atrbohF;* the late ROS peak is decreased, which demonstrates that the ROS derived by RBOH is engaged in initiating cytoplasmic or chloroplastic accumulation during treatment of O_3 (Joo et al. 2005; Vahisalu et al. 2010). These data depict a relation between the production of ROS by chloroplast and apoplast and describe a signaling in guard cell of chloroplast (Noctor et al. 2016).

7.5 ROS in Plant Development

Plants throughout their life cycle are subjected to different environmental stresses. In managing normal plant growth and improving their stress tolerance, reactive oxygen species (ROS) play crucial roles (Huang et al. 2019a). Having aerobic conditions for any organism, there is a chance to utilize oxygen as an electron acceptor and trapping their reacting quality for signaling and metabolism (Foyer and Noctor 2016). From seed germination to plant senescence, ROS are either produced or removed, due to which plants control their development to their adaptation in different environments (Huang et al. 2019a).

7.5.1 The Maintenance of Plant Vegetative Apical Meristems Engaged by ROS

ROS homeostasis shapes plant vegetative apex development indicated by emerging evidence. $O_2^{\cdot -}$ is required for cell divisions; it is mainly accumulated in the *Arabidopsis thaliana* in meristematic tissue of the root, and accumulation site of H_2O_2 is mainly the elongation zone, which is the confirmation of cell differentiation (Tsukagoshi et al. 2010). These two, i.e., meristematic zone and elongation zone, are called ROS microenvironment, and they are very crucial for distribution of transition zone. Cell of transition zone can be divided due to having gradient of ROS. Level of $O^{\cdot -}{}_2$ is decreased, and the level of H_2O_2 starts to increase the cells being elongating and stop dividing (Dunand et al. 2007). The balance of ROS is very essential for the transition zone. And this balance is provided by a transcription factor UPB1 (UPBEAT1). H_2O_2 itself also affects *the* expression of *UPB1*, and this system of regulation contained a feedback loop, which plays a role in both for ROS homeostasis and for root growth showed by further studies (Tsukagoshi et al. 2010). Additionally, distal stem cell (DSC) and the quiescent center (QC) are needed for root apical meristem (RAM) size maintenance (Huang et al. 2019b). The root stem cell niche (SCN) identity is affected by *Arabidopsis thaliana P-loop NTPase1* (*APP1)* via its control of local ROS homeostasis. Reduction in ROS levels accompanied disruption of *APP1*, which is an ultimate reason for increase in the rate of cell division at the point of quiescent center and root DSC differentiation (Yu et al. 2016). Plant root primary growth is regulated by ROS combined with hormones and some other signal molecules. ROS and auxin signaling acted antagonistically for the purpose of balancing root meristem growth in the RAM (Tognetti et al. 2017). For controlling the regulation of cellular ROS pathway, autophagy is a necessary mechanism and assisting the degradation of the oxidatively damaged peroxisomes is proposed by the findings. Brassinosteroids (BRs) also regulate root tip stem cell activity through ROS, which is shown in current studies (Huang et al. 2019b).

Due to binding of BR to its receptor kinase BRI1 (BRASSINOSTEROID INSENSITIVE1), the levels of H_2O_2 in cell are increased and the enhanced level of peroxide to altered the vital transcription factors in signaling of BR. The oxidative modification is responsible for increased transcriptional activity of BZR1; root

meristem development is enhanced by increasing its interaction with ARF6 (AUXIN RESPONSE FACTOR6) and PIF4 (PHYTOCHROME INTERACTING FACTOR4) (Tian et al. 2018). There are limited details about the relationship between cytokinin and ROS in the apex growth regulations. Hormonal network and the ROS are interconnected and not to be considered as independent mechanism; they together activate physiological and stress adaptation response. In the *Arabidopsis* RAM, glutathione reductase (GR) plays a key role for the regulation of the levels of reduced glutathione in the *Arabidopsis* RAM (Huang et al. 2019a).

Oxidized glutathione enormous accumulation in *GR2* (*glutathione reductase2*) mutants leads to root apical cells entering the oxidized state and eventually results in abnormal growth. After applying glutathione exogenously, the normal phenotype is restored partially (Yu et al. 2013). For different *Arabidopsis* ecotype, a novel thioredoxin DCC1 has signify the shoot regeneration ability (Kka et al. 2018). Bust of *DCC1* activated the formation of mitochondrial ROS. Shoot regeneration further regulates by the process. Simultaneously, in the *DCC1*gene sequence, for the purpose of bud regeneration in different ecotype of *Arabidopsis*, there are about six different SNPs (single-nucleotide polymorphism) found, and the level of ROS is different in ecotypes harboring different SNPs (Zhang et al. 2018). ROS homeostasis acts crucially in various processes apical meristem maintenance, shoot initiation, etc. (Huang et al. 2019a).

7.5.2 Organ Morphogenesis Triggers by ROS in Plants

In all plant tissue, metabolically active ROS is found as a signaling component (Ishibashi et al. 2015). In rice, OsLEA5, the late embryogenesis protein, which is present, abundantly interacted with transcription factor ZFP and regulated APX *OsAPX1* gene expression for ABA-inhibited germination coregulation (Huang et al. 2018). A biosynthetic activity of phenylalanine of AROGENATE DEHYDRATASE3 (ADT3) plays a crucial role in cotyledon development and coordinating ROS homeostasis in etiolated seedlings of *Arabidopsis*. From heterotrophy to autotrophy, a crucial role is played by Phe at the time of the transition phase of seedlings by protecting the cells from damage of ROS (Para et al. 2016).

For the development of crown roots in case of rice, ROS also play an essential role. WOX11 is a transcription factor needed for crown root development, which is a WUSCHEL-related homeobox gene (Jiang et al. 2017). Under flooding conditions, ethylene is accumulated in crown roots of rice, and this is helped in the generation of ROS. With the help of other signals, ROS increased elongation of crown cells, and this leads to death of epidermal cells (Steffens et al. 2012). Salicylic acid prohibited the expression of genes related to the scavenging of ROS. In case of mutant *ABNORMAL INFLORESCENCE MERISTEM,* crown root synthesis is inhibited due to the decreased level of ROS, which helped in the synthesis of salicylic acid. Root development is again restart after using H_2O_2 externally (Xu et al. 2017).

7.6 Catalases of Plants Targeted on Nitric Oxide and Hydrogen Sulfide

The catalase system is the oldest known and first discovered antioxidant enzyme because it may be a main member of cell metabolism in maximum of the aerobic beings (Góth 2018). For example, it's been proved that human catalase displays 245 single-nucleotide polymorphisms, which are involved in diverse physiological and pathological situations, including hypertension, DM, insulin resistance, dyslipidemia, asthma, bone metabolism, or vitiligo (Kodydková et al. 2014). Besides these genetic factors, CAT activity could also be suffering from age, physical activity, and differences due to the season and certain chemical compounds (Palma et al. 2020). Additionally, catalase was found to manage lipid metabolism in liver without compromising the general oxidative damage of cells (Pérez-Estrada et al. 2019), and therefore, the modulation of its expression in cancer cells seems to be a technique to be potentiated for chemotherapy purposes (Palma et al. 2020).

7.7 Metabolomic-Guided Elucidation od Abiotic Stress Tolerance by Plants

Plants are unable to flee from unfavorable environmental conditions, e.g., biotic and abiotic stresses; thus, their responses are manifested through physiological and metabolomic changes (Maritim et al. 2015). Salt and water stresses are the main abiotic environmental conditions that reduce plant growth and end in significant yield losses (Llanes et al. 2018). Although plants have a good spectrum of mechanisms to adapt to adverse environmental conditions, the present understanding of mechanisms related to the power of plants to take care of their growth under abiotic stresses are poorly understood. All chemical species having molecular weight less than 1800 Da is known as metabolome, and their study is metabolomics (Hall 2018).

Therefore, the metabolites are the top products of cellular functions, and their levels are often considered because the plant responses to environmental or genetic manipulation (Llanes et al. 2018). In plants, metabolomic studies aim to spot and quantify the set of primary and secondary metabolites involved in biological processes. Plant primary metabolites are implicated within the normal plant growth, development, and reproduction, whereas the secondary metabolites are crucial to plant survival under unfavorable conditions by maintaining a fine-tuning with the environment (Llanes et al. 2018). Secondary metabolites vary from species to species, place to place, and even season to season, but essentially primary metabolites are highly conserved in their structures and abundances across the *Plantae* (Scossa et al. 2016).

The diversity of plant metabolites and their complicated regulatory mechanism highlights the necessity to investigate the biochemical nature of these compounds. Plant metabolome reported so far consists of roughly 30,000 endogenous metabolites that mainly comprise carbohydrates, amino acids, organic acids, and

lipids (Llanes et al. 2018). Also, small molecules like plant hormones and signaling molecules are vital for plant growth and development. Plant metabolomic research depends largely on its methodologies and instrumentation to comprehensively identify, quantify, and localize every metabolite.

Thus, several strategies for the analysis of metabolites are being developed rapidly (Hegeman 2010): (1) metabolite profiling, identification and quantification of variety of predefined metabolites, which are related to a specific metabolic pathway(s); (2) metabolic fingerprinting, global screening of samples to discriminate among samples of different biological status or origin; (3) metabolite target analysis, qualitative and quantitative analysis of one or a couple of metabolites associated with a selected metabolic reaction; and (4) metabonomics, analysis of tissues and biological fluids for changes in endogenous metabolite contents resulting from disease or therapeutic treatments (Llanes et al. 2018).

Plant metabolism is notably perturbed under abiotic stress conditions. In the last years, metabolomics has been employed for the identification of putative metabolites responsible for phenotypes tolerant/sensitive to several environmental stressors. In general, the metabolic changes that are observed in plants subjected to worry may have different causes; thus, they differ in their significance and are expected to differently correlate with tolerance/sensitivity phenotypes. The main goal of studying metabolic changes during stress responses is to identify metabolites that allow the reestablishment of homeostasis and normal metabolic fluxes and to detect the accumulation of groups of compounds involved in mediating the strain tolerance (Llanes et al. 2018).

A set of primary metabolites (osmolytes and osmoprotectants) and secondary metabolites (defense metabolites) accumulate to strengthen plant stress tolerance. Among them, primary metabolites are the foremost important metabolites suffering from stress, usually as a result of impairment in CO_2 assimilation (Llanes et al. 2018). Although an increased accumulation of osmolytes by plants exposed to abiotic stresses has been reported, not all plant species synthesize all types of osmolytes; some species synthesize and accumulate very low quantities of a number of these compounds, whereas some others don't do so in the least (Llanes et al. 2018).

7.8 Conclusions

Reactive oxygen species (ROS) can synthesize intracellular and extracellular locations. ROS can cause extensive damage to the integrity of the cell that causes death. To overcome such a situation, plants can be equipped with a wider range of defense measures including the morphological change in plants and metabolic and genetic level changes for the adaptation of nonfavorable environmental conditions. ROS has short half-life and high reactivity, which is very important for our understanding about the formation of ROS. Interaction between ROS and calcium signaling during multiple environmental stresses is still unanswered. Recent works reported many sources for the production and removal of ROS, different types of

enzymes, and antioxidant molecules for the signaling to ROS. But still, there are many points, which are not disclosed about ROS, like how various ROS cause signaling in spite of having very short half-life and susceptible nature to many chemicals. Also, production of various ROS and their interaction with each other cannot be clearly understood. Further, we need some more work in order to understand complete mechanism and hope for the best.

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