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Reactive oxygen species in cell wall metabolism and development in plants

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ABSTRACT

Although reactive oxygen species (ROS) are highly toxic substances that are produced during aerobic respiration and photosynthesis, many studies have demonstrated that ROS, such as superoxide anion radical ($O_2^{\cdot-}$) and hydrogen peroxide (H_2O_2), are produced in the plant cell wall in a highly regulated manner. These molecules are important signalling messengers playing key roles in controlling a broad range of physiological processes, such as cellular growth and development, as well as adaptation to environmental changes. Given the toxicity of ROS, especially of hydroxyl radical (·OH), the enzymatic ROS production needs to be tightly regulated both spatially and temporally. Respiratory burst oxidase homologues (Rboh) have been identified as ROS-producing NADPH oxidases, which act as key signalling nodes integrating multiple signal transduction pathways in plants. Also other enzyme systems, such as class III peroxidases, amine oxidases, quinone reductases and oxalate oxidases contribute to apoplastic ROS production, some especially in certain plant taxa. Here we discuss the interrelationship among different enzymes producing ROS in the plant cell wall, as well as the physiological roles of the ROS produced.

1. Introduction

Reactive oxygen species (ROS: superoxide ($O_2^{\cdot-}$), hydrogen peroxide (H_2O_2), hydroxyl radical (·OH), singlet oxygen ($^1O_2$)) were earlier considered as detrimental side products of several cellular processes such as aerobic respiration and photosynthesis. Research has, however, shown that ROS have important physiological roles in plant development. Certain ROS can be used as an oxidant, for example, in cell wall cross-linking (H_2O_2; Fry, 2004; Passardi et al., 2004; Novo-Uzal et al., 2013), as a powerful cell wall-loosening agent (·OH; Kuchitsu et al., 1995; Fry, 1998; Schopfer et al., 2001; Müller et al., 2009b), or as a signalling molecule controlling various biological processes (H_2O_2 and $O_2^{\cdot-}$; e.g. Miller et al., 2009; Petrov and van Breusegem, 2012; Wrzaczek et al., 2013; Baxter et al., 2014) (Fig. 1). ROS are produced by reduction of O_2 in several stresses (both abiotic and biotic), after wounding, as well as during normal development (reviewed by Suzuki et al., 2011). In addition to intracellular ROS that are produced in several organelles (e.g. chloroplasts, peroxisomes, mitochondria), several plant cell wall- and plasma membrane-located sources have been detected (Table 1; Fig. 1). The existence of several enzymes that deliberately produce ROS into the cell wall shows the importance of spatially and temporally regulated ROS production for development and for defence (Cona et al., 2006).

In addition to the tightly regulated production, the ROS levels are controlled by scavenging enzymes such as class III peroxidases and antioxidant compounds. Due to toxicity of ROS, cells are equipped with numerous scavengers in almost every compartment. Therefore it is very difficult to accurately determine the ROS concentrations inside the cells or in the apoplast *in planta*. It is easier to determine the ROS levels in the culture medium of suspension-cultured cells. When ROS-producing enzymes are activated, the concentration of H_2O_2, a relatively stable ROS species, in the culture medium increases up to micromolar range (e.g. Gómez Ros et al., 2006; Kärkönen et al., 2009). The situation in native cell wall, however, differs from that in cultured cells, as

Abbreviations: DPI, diphenylene iodonium chloride; CuAO, copper-containing amine oxidase; GLP, germin-like protein; KCN, potassium cyanide; MAMP, microbe-associated molecular pattern; Nox, NADPH oxidase; PAMP, pathogen-associated molecular pattern; PAO, polyamine oxidase; PCD, programmed cell death; Rboh, respiratory burst oxidase homologue; ROS, reactive oxygen species; SOD, superoxide dismutase; TE, tracheary element.

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the volume of the culture medium, which can be considered as a continuum of the apoplastic fluid, is much larger than that inside the cell wall. In addition, the ROS concentrations are not homogenous in the cell wall of a single cell. For example, during tip-localised growth of a pollen tube or a root hair, or during pathogen infection or wounding, highly local, transient peaks of ROS are presumably formed in the cell wall, allowing tightly-regulated reactions to occur at the site of ROS production. ROS are thought to diffuse as H_2O_2 back into the cell via an aquaporin-mediated way (Bienert et al., 2007; Dynowski et al., 2008), where it acts as a cytosolic regulator (e.g. Swanson and Gilroy, 2010; Wrzaczek et al., 2013). In addition to extraprotoplasmic generation of ROS, it is also possible that some apoplastic ROS originates from intracellular sources (e.g. O'Brien et al., 2012b). Below we describe the main enzymatic sources for apoplastic ROS, their prevalence in different plant groups, and the physiological significance of cell wall-located ROS in plant development focusing in events of cell wall loosening and cell wall stiffening.

2. Apoplastic ROS production

Plants as well as other eukaryotes possess a variety of enzymes that produce apoplastic ROS, which are then used for signal transduction as well as in cell wall metabolism (Fig. 1). ROS-producing enzymes in plants include NADPH oxidases, amine oxidases, quinone reductases, lipoxygenases, class III peroxidases and oxalate oxidases.

2.1. NADPH oxidases (Nox)

Homologs of the catalytic subunit of NADPH oxidases (Nox) including phagocytic gp91^{phox} are found in most eukaryotic species (Sumimoto, 2008). In animals, ROS produced by Nox are essential to brain physiology, the immune system, vasculature, the digestive tract, and hormone synthesis (Brown and Griendling, 2009). Plant Nox are encoded by *respiratory burst oxidase homologue* (*Rboh*) genes found in a broad range of plant species (Bedard and Krause, 2007; Marino et al., 2012). They have been shown to play key roles in numerous physiological processes, such as root hair and pollen tube tip growth, stomatal closure, and various stress responses (reviewed in Kurusu et al., 2013a). Rbohs contain six conserved transmembrane helices, and cytosolic flavin adenine dinucleotide (FAD)- and reduced nicotinamide adenine dinucleotide phosphate (NADPH)-binding domains in their C-terminal regions, as well as two N-terminal Ca^{2+}-binding (EF-hand) motifs (Torres and Dangl, 2005). NADPH acts as a cytosolic electron donor

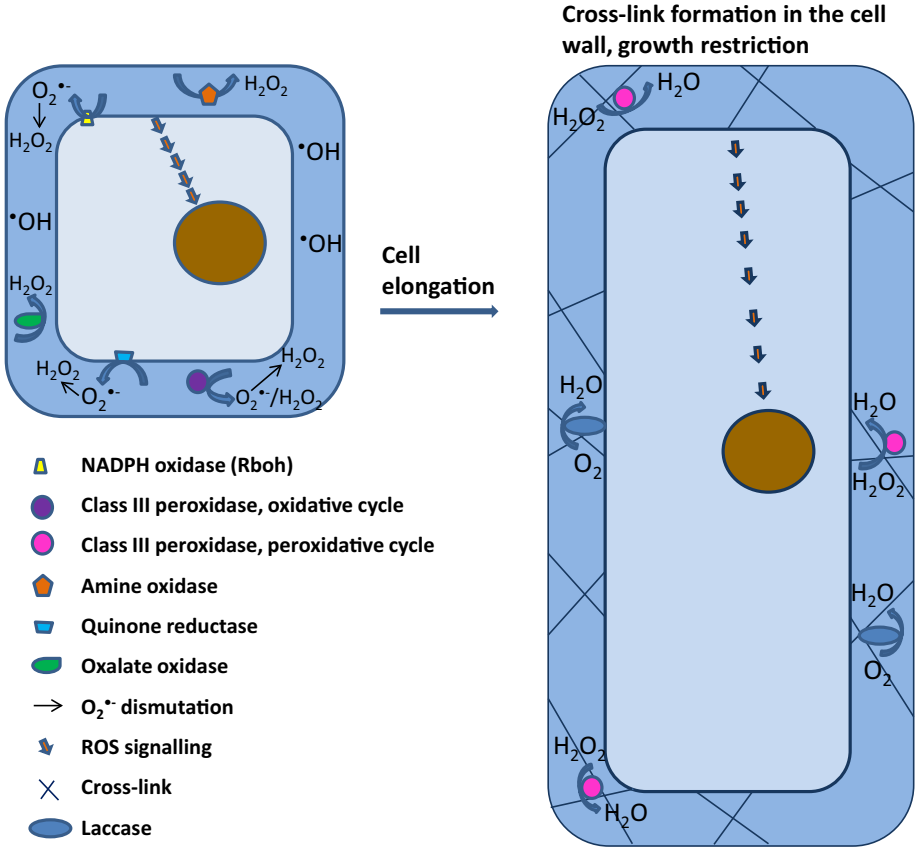

Fig. 1. Schematic representation of the enzymes at the plasma membrane and in the cell wall that are able to form reactive oxygen species (ROS: superoxide anion radical (O_2^-), hydrogen peroxide (H_2O_2), hydroxyl radical ($^{\cdot}OH$)) into the apoplast. O_2^- is dismutated to H_2O_2 either enzymatically catalyzed by superoxide dismutase, or non-enzymatically in the acidic pH that is typical in the cell wall. ROS play important roles both in cell wall loosening during cell elongation and cross-link formation involved in cell growth restriction. $^{\cdot}OH$ is considered as a cell wall-loosening agent formed from H_2O_2 either non-enzymatically by Fenton reaction involving a transition metal such as Fe^{2+} or Cu^+, or enzymatically by peroxidases (not depicted). Di- and oligoferulate bridges, bonds between tyrosine residues abundant in cell wall structural proteins, lignin formation, or cross-linkages between ferulates and lignin are possible cross-links involved in cell growth restriction. For the cross-link formation, oxidative enzymes (peroxidase in a *peroxidative cycle* using H_2O_2 as an oxidant, or laccase using O_2 as an oxidant) catalyze the oxidation of the phenolic residues after which they make a cross-link. In addition to cell wall modifications, ROS are important signalling components in various biological processes. The left cell shows the enzymes producing ROS, and the right cell shows the enzymes consuming ROS during cell wall cross-linking. Note that all enzymes and the cross-link types mentioned may not be present in the same cell, or in all species. In case of quinone reductases, further studies are needed to find out whether enough quinones are present in the plasma membranes to be able to mediate electron transport from the cytoplasmic reductant to apoplastic molecular oxygen.

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