Singlet Oxygen in Plants

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In а recent review published in Int. J. Mol. Sci. (https://doi.org/10.3390/ijms21093237 (https://doi.org/10.3390/ijms21093237)), we summarize the current understanding of the sites and mechanisms of production of singlet oxygen $({}^{1}O_{2})$ in the plant body, and of emerging physiological roles of ${}^{1}O_{2}$ production in plants. We consider well-characterized mechanisms of ¹O₂ generation in chloroplast grana cores and novel data on ¹O₂ formation at grana margins. We discuss signal functions of ${}^{1}O_{2}$ in acclimation to excess light, in chloroplast quality control and in the initiation of programmed cell death (PCD), as well as the less clear roles of stress-related ${}^{1}O_{2}$ production in roots. We argue that infiltration of ¹O₂-specific membrane-impermeable fluorescent probes in the apoplast provides a useful comparative approach to estimate levels of ¹O₂ formation in chloroplasts. We present a preliminary overview of cellular mechanisms and signaling pathways leading to ¹O₂-triggered PCD in plants.

Keywords: singlet oxygen ; plant acclimation to excess light ; programmed cell death

1. Introduction

During photosynthesis, specifically in the course of water oxidation, molecular oxygen in its ground triplet state $({}^{3}O_{2})$ is generated which is released into the atmosphere. Oxygen can be converted to reactive oxygen species (ROS) either via acquisition of electrons or via acquisition of energy. The latter pathway results in the formation of singlet oxygen $({}^{1}O_{2})$ which represents the first excited electronic state of molecular oxygen. ${}^{1}O_{2}$ is much more reactive than ${}^{3}O_{2}$ and readily oxidizes different biological molecules; therefore, it can be toxic [1].

2. Development

In plants, the main source of ${}^{1}O_{2}$ is photosystem II (PS II) in chloroplasts ^{[2][3]}. PSII reaction centers are the sites of formation of long-lived excited triplet states (${}^{3}Chl^{*}$) of the P680 chlorophyll "special pair". The triplet states of chlorophylls can transfer their excitation energy to oxygen leading to the formation of ${}^{1}O_{2}$ [4]. ${}^{1}O_{2}$ production essentially increases under high light conditions. Under such conditions, irreversible damage of PS II can occur. It was shown that ${}^{1}O_{2}$ can inhibit the repair of the proteins of the PS II reaction center ^[5] which leads to down-regulation of photosynthesis, a phenomenon referred as photoinhibition ^{[6][2]}. Notably, the main sites of ${}^{1}O_{2}$ generation under high light conditions are the cores of chloroplast grana.

Apart from the P680 "special pair" chlorophyll, other compounds can act as photosensitizers and cause ${}^{1}O_{2}$ generation. In particular, in chloroplasts, the chlorophyll precursors chlorophyllide and protochlorophyllide can function as photosensitizers [3][8][9]. These molecules, however, occur very rarely as free compounds; yet, free chlorophylls, chlorophyllides and protochlorophyllides might occur at grana margins where they participate in the assembly of newly synthesized, as well as in the disassembly of damaged, PSII complexes. Therefore, grana margins are sites of ${}^{1}O_{2}$ generation indicative of accumulation of free chlorophylls or free chlorophyll precursors. Another, recently suggested, source of ${}^{1}O_{2}$ generation at grana margins are incomplete PS II complexes lacking an oxygen evolving complex (OEC) [10]. In such PSII complexes, the long-lived ion-radical pair P₆₈₀^{*+}TyrZ^{*} (where TyrZ is the tyrosine residue which transfers the electrons from the OEC to P₆₈₀^{*+}) might form in the light, leading to the generation of lipid and protein hydroperoxides [10]. These tetrahydroperoxides can produce ${}^{1}O_{2}$ while decomposing [11].

Minor sources of ${}^{1}O_{2}$ production in plants can be triplet carbonyls of lipids and proteins which are able to transfer energy to triplet oxygen ${}^{[10]}$. Some enzymatic reactions like those mediated by heme proteins and lipoxygenases were shown to lead to ${}^{1}O_{2}$ generation ${}^{[12]}$. Important sources of ${}^{1}O_{2}$ production are phytoalexins which function as defense compounds. In particular, phenalenone-like phytoalexins are photosensitizers playing a key role in ${}^{1}O_{2}$ generation during protection against pathogens ${}^{[13]}$. Noteworthily, ${}^{1}O_{2}$ can be produced not only in leaves, but also in roots of plants ${}^{[14][15]}$.

Although the lifetime of ${}^{1}O_{2}$ is very short (ca. 10^{-6} s), it can diffuse from the site of its generation over a distance of approximately 155 nm ${}^{[16]}$, and permeate through membranes. Thus, ${}^{1}O_{2}$ readily oxidizes neighboring molecules: its most common targets are proteins ${}^{[17]}$ but ${}^{1}O_{2}$ also attacks DNA and lipids ${}^{[4][18][20]}$. Products of lipid peroxidation can act as signal molecules eventually causing cell death ${}^{[19]}$. Plants have evolved a variety of mechanisms of defense from ${}^{1}O_{2}$. On the large scale, the most important ${}^{1}O_{2}$ quenchers are carotenoids ${}^{[8]}$. Apart from physical quenching of ${}^{1}O_{2}$ (i.e. energy dissipation as heat), the b-carotene in the reaction centers of PSII can act as a chemical quencher by being oxidized by ${}^{1}O_{2}$. This reaction leads to the formation of volatile signaling molecules such as the endoperoxide of b-carotene, b-cyclocitral, a specific signature of ${}^{1}O_{2}$ production at grana cores in chloroplasts.

 ${}^{1}O_{2}$ is a prominent signal in chloroplast-to-nucleus signaling pathways. The main signaling roles of ${}^{1}O_{2}$ revealed thus far are part of plants' acclimation to high light and the induction of PCD, respectively ${}^{[21]}$. Two ${}^{1}O_{2}$ -mediated signaling pathways have been studied in two *Arabidopsis thaliana* mutants specifically producing high levels of ${}^{1}O_{2}$ either at grana margins (*flu*) or at grana cores (*ch*1) in chloroplasts. It was shown that after transfer from the darkness to light, *flu* plants accumulate free protochlorophyllide which acts as a strong photosensitizer resulting in ${}^{1}O_{2}$ production at grana margins ${}^{[19][22][23]}$. *ch*1 mutants are unable to synthesize chlorophyll *b*, which leads to decreased functional activity of PS II and a disturbance of lateral diffusion in thylakoid membrane ${}^{[24][25][26]}$, resulting in an essential increase of ${}^{1}O_{2}$ production at grana cores ${}^{[24]}$. In *flu*, nuclear-encoded chloroplast proteins, EXECUTER1 (EX1) and EX2 are specifically activated by ${}^{1}O_{2}$, and lead to activation of PCD ${}^{[23]}$. In *ch*1, a serine-threonine kinase OXIDATIVE SIGNAL INDUCIBLE1 (OXI1) plays the key role in ${}^{1}O_{2}$ -dependent PCD, while EX1/2 do not seem to be involved ${}^{[24]}$. Recently, a novel signaling pathway mediated by the SAFEGUARD1 (SAFE1) chloroplast protein was proposed, where SAFE1 physically protects grana margins from damage and at the same time might trigger an EX1/2 independent PCD ${}^{[29]}$.

Phytohormones jasmonic acid (JA) and salicylic acid (SA) play an important role in the transduction of ${}^{1}O_{2}$ signals leading to PCD during both EX1- and OXI1-mediated pathways. JA causes PCD in both *flu* and *ch*1 mutants. Moreover, in *ch*1 mutants, the levels of JA and other jasmonates "define" whether PCD or acclimation to ${}^{1}O_{2}$ will occur ^[30]. In *ch*1 mutants, the acclimation response to excess light and to high levels of ${}^{1}O_{2}$ production specifically involves signaling by b-cyclocitral ^[30]. In summary, two major retrograde-to-nucleus signaling pathways mediated by ${}^{1}O_{2}$ allow plants to distinguish between its production at grana cores and at grana margins, respectively; while the former can result either in acclimation or in induction of PCD, the latter specifically activates PCD. Another recently discovered ${}^{1}O_{2}$ signaling pathway is related to chloroplast quality control ^[31].

To date, our understanding of mechanisms of ${}^{1}O_{2}$ -mediated PCD remains incomplete. In particular, it is known that ${}^{1}O_{2}$ can trigger PCD in roots but the components of signal transduction pathways have not been studied sufficiently. Undoubtedly, chloroplasts play a key role in ${}^{1}O_{2}$ -mediated PCD in leaves but PCD involves other cell compartments as well. For instance, photosensitizers such as red-chlorophyll-catabolite can be transported from chloroplasts to mitochondria and thereby induce ${}^{1}O_{2}$ -mediated PCD in mutants lacking the ACCELERATED CELL DEATH2 protein [32] [33]. A recently revealed important player in ${}^{1}O_{2}$ -mediated PCD is the endoplasmic reticulum (ER)-mediated unfolded protein response (UPR) [33]. Furthermore, it was shown that ${}^{1}O_{2}$ produced in the vacuole and at the plasma membrane can be involved in vacuole-mediated PCD [34].

A variety of methods detecting ${}^{1}O_{2}$ has been developed. The most selective is electron paramagnetic resonance (EPR) spectroscopy which enables the identification of ${}^{1}O_{2}$ based on spectral characteristics of "trapping" molecules that form radicals after interaction with ${}^{1}O_{2}$ [${}^{35|[36]}$. This technique, however, has a serious limitation in that it cannot be applied to plants in vivo due to its high sensitivity to reductants, especially to those produced in illuminated thylakoids, and to the high water contents in plant tissues. Therefore, specific fluorescent probes changing their properties after reaction with ${}^{1}O_{2}$ have been developed [${}^{37|[38]}$. ${}^{1}O_{2}$ generation in chloroplasts can be studied with the use of fluorescing spin probe DanePy; ${}^{1}O_{2}$ quenches its fluorescence in a quantitative manner. Another available, highly selective probe is Singlet Oxygen Sensor Green (SOSG) [${}^{39|}$. The use of this probe is quite convenient, as SOSG solutions can be introduced into leaves by vacuum-infiltration [${}^{40|[41]}$]. Finally, ${}^{1}O_{2}$ can be detected by in vivo imaging of plants for the detection of autoluminescence which arises due to spontaneous photon emission during decomposition of lipid hydroperoxides and endoperoxides produced by ${}^{1}O_{2}$ -caused lipid oxidation [42,43].

Altogether, ¹O₂ is highly significant for plants. Its detection and signal transduction in plants can lead to opposite strategies such as stress acclimation or induction of PCD. For this reason, elucidation of the mechanisms of its perception and signal transduction is required. Moreover, it is important to extend the knowledge obtained using *Arabidopsis* to other plant species including crops.

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