**Review**

**Distribution and Role of Oct-1-en-3-ol in Marine Algae**

Igor Jerković 1,*, Sanja Radman 1 and Stela Jokić 2

1 Department of Organic Chemistry, Faculty of Chemistry and Technology, University of Split, Rudera Boškovića 35, 21000 Split, Croatia; sradman@ktf-split.hr
2 Department of Process Engineering, Faculty of Food Technology, Josip Juraj Strossmayer University of Osijek, Franje Kuhača 18, 31000 Osijek, Croatia; sjokic@ktf-split.hr

* Correspondence: igor@ktf-split.hr; Tel.: +385-21-329-461

**Abstract:** Oct-1-en-3-ol has been studied among oxylipins as a global metabolome that induce the defense of marine algae. The present short review summarized the research of oct-1-en-3-ol as the stress response molecule in marine algae including different aspects: (i) its biosynthesis from fatty acids; (ii) its distribution in marine algae; (iii) a direct effect of oct-1-en-3-ol on microorganisms infecting the thalli; (iv) an indirect communication molecule for alga-alga signaling; and (v) as an inducer that initiates the defense response of algae.

**Keywords:** oct-1-en-3-ol; biosynthesis; indirect communication molecule; Pyropia haitanensis; Macrocytis pyrifera

1. **Introduction**

Marine algae produce and emit a large variety of volatile organic compounds (VOCs) [1] including fatty acid derivatives (oxylipins) as the dominant VOCs in some algae in order to develop their chemical defenses to fight pathogens and damage [2–4]. The external chemical signals are more important for algae than for terrestrial plants since the algae lack vascular connections and internal signaling molecules [5]. Volatile oxylipins act as airborne signals that respond to external challenges [6] and mediate inter-plant communication and enable the protection against pathogenic bacteria and fungi [7,8]. Aliphatic short-chain VOCs are more likely to function as communication signals since their slow dispersal in seawater allows the development of higher concentration plumes that could be carried as intact parcels [9,10]. Marine VOCs are small, low-molecular compounds with low to moderate hydrophilicity and high vapor pressure, and can cross cell membranes to be released freely into the environment. They have been reviewed regarding their ecological function in aquatic systems [11], as well as for their emission and roles in algae [12]. The production and role of algal volatile halogenated compounds was reviewed separately [13]. The role of algae and cyanobacteria in the production and release of odorants in water was also summarized [14]. The review published by Rinnan et al. [15] reported the plant and algal VOCs production and emission in extreme environments (temperature, water availability, salinity or other environmental factors). The algal intraspecific chemical communication was also reviewed [16].

Oct-1-en-3-ol has been studied, among oxylipins, as a global metabolome that induces the defense of marine algae [17]. It was initially found in fungi [18], but later also in other terrestrial plants such as Arabidopsis thaliana [18]. Oct-1-en-3-ol was found in the marine red alga Pyropia haitanensis [4] as a cellular self-stimulating oxylipin messenger that inhibits the growth of associated bacteria and reduces P. haitanensis blades decay [17,19]. It also recognizes and induces defense in the response to biotic and abiotic stresses by upregulating the synthesis of gibberellin A3, indole-3-acetic acid and methyl jasmonic acid as well as by cells redox states adjusting [4]. The present short review summarizes the research of oct-1-en-3-ol as stress response molecule in marine algae for the first time including different aspects: (i) its biosynthesis from fatty acids; (ii) its distribution in marine
algal; (iii) a direct effect of oct-1-en-3-ol on microorganisms infecting the thalli; (iv) an indirect communication molecule for alga-alga signaling; and (v) as an inducer that initiates the defense response of algae.

2. Biosynthesis of Oct-1-en-3-ol and Its Distribution in Marine Algae

In general, lipoxygenases (LOX) comprise a large gene family of non-heme iron-containing dioxygenases, ubiquitous in animals and higher plants [20]. They catalyze regio- and stereospecific dioxygen insertion into polyunsaturated fatty acids (FAs) that contain (1Z,4Z)-penta-1,4-diene system resulting with (2E,4Z)-hydroperoxy-2,4-diene [21]. These hydroperoxides may be subsequently cleaved by LOX or by hydroperoxide lyases (HPL) to the oxygenated products with shorter chain [22] including volatile unsaturated aldehydes and alcohols and the corresponding unsaturated oxofatty acids [21,22]. The biosynthesis of oxylipins has been well investigated in higher plants and animals as well as in algae. However, different biotransformation principles have been found. Higher plants use exclusively polyunsaturated C_{18} FAs for oxylipin production, while animals and algae use predominantly polyunsaturated C_{20} FAs [20,23] which are not ubiquitous in the plants [24]. Moreover, the formation of volatile short chain aldehydes relies on LOX and HPL combined action in higher plants, whereas animals and algae seem to be more flexible and may use either LOX/HPL system or specific LOX [23,25]. In general, to produce oxylipins, red algae metabolize C_{20} acids via 12-LOX-initiated pathways, green algae metabolize C_{18} acids at C-9 and C-13, and brown algae metabolize both C_{18} and C_{20} acids principally with LOX action at C-6 [23].

Several lipid peroxidation enzymes have been characterized in terrestrial plants, animals, and cyanobacteria, but there are few reports on LOX genes sequences and protein functions from algae [4]. LOXs are critical starting biocatalysts for oxylipins synthesis, and LOXs from prokaryotes or lower eukaryotes always demonstrate nonspecific and multifunctional properties. Unique LOX isoform from *P. haitanensis* is a multifunctional enzyme that combines HPL, LOX, and allene oxide synthase (AOS) as three catalytic activities within one catalytic domain of the protein [4] which may explain *P. haitanensis* diversity of oxylipins. Phylogenetic analysis indicated that red algae LOX separated from LOX clades of the ancestor of higher plants and animals in the early stages of evolution. The substrate flexibility, oxygenation position flexibility, and functional versatility of the enzyme gene of *P. haitanensis* (named PhLOX) represent typical properties of lower organisms [4].

In red alga *P. haitanensis*, oct-1-en-3-ol is generated from arachidonic acid (C_{20}:4) by a multifunctional LOX enzyme that has high HPL, LOX, and AOS activities within one catalytic domain of the protein [26,27] that was determined using isotopically-labeled [D_8]-arachidonic acid substrate, Figure 1. These results suggested that PhLOX possesses an unusually high HPL activity for C_{20} substrates. LOXs from the alga *Chlorella pyrenoidosa* showed HPL activity under oxygen deprivation [26].

![Figure 1](image-url)  
**Figure 1.** Formation of oct-1-en-3-ol from arachidonic acid.

The headspace collection of VOCs by static headspace (SHS), dynamic headspace (DHS), solid phase microextraction (HS-SPME), as well as the traditional methods such as hydrodistillation (HD) combined with analytical chromatographic techniques (i.e., gas chromatography and mass spectrometry, GC-MS), have been frequently used for the research of VOCs from algae [28,29]. In addition, solvent extraction (SE), focused microwave-assisted
hydrodistillation (FMAHD) or supercritical fluid extraction (SFE) has been likewise applied [28]. Striking differences were found among HS-SPME and HD chemical profiles of identified VOCs [29,30]. HS-SPME has been mainly the method of choice to identify oct-1-en-3-ol in the algae [31,32] and it has been described as an important VOC in seafoods [32,33] that additionally contribute to the complex seafood aroma, but also to “mushroom and mushroom-metallic” notes [34].

*Pyropia haitanensis* has been the most investigated alga regarding oct-1-en-3-ol as communication molecule that initiates the alga defense response and it was the major volatile metabolite produced in *P. haitanensis* [17]. HS-SPME/GC-MC was applied for detail investigation of VOCs from *P. haitanensis* [27]. Oct-1-en-3-ol, oct-2-en-1-ol, and octan-3-ol were present in the conchocelis phase, but were absent in the thallus. The content of VOCs in the conchocelis phase were much higher and oct-1-en-3-ol was found at 56.30 ± 46.51 µg/100 mg and at 119.47 ± 40.70 µg/100 mg after the heat shock applied to the alga (its amount was increased by 2.12 folds). HS-SPME/GC-MS was also used [35] to detect VOCs directly released from *P. haitanensis* thalli during 4 h of desiccation and the concentrations of many VOCs increased significantly in comparison with the control, particularly for oct-1-en-3-ol (2.24 fold higher), octan-3-one (4.81 fold higher) and dodecanoic acid (12.40 fold higher). Oct-1-en-3-ol was the major oxylipin in *Macrocystis pyrifera* that was mentioned in recent paper [36] as still unpublished results, and it was studied in this alga as oxylipin messenger that induces rapid *M. pyrifera* response after exposure to this molecule. High concentrations of oct-1-en-3-ol were measured [31] by HS-SPME/GC-MS in *Rhodomonas* species (420 ± 94 ng/g) which were perceived as having a very strong “cooked shrimp/cooked seafood” aroma. Oct-1-en-3-ol was found in four microalgae species [34] by HS-HSPME/GC-MS: in *Chlorella protothecoides* (13.8 ± 1 µg/kg), in *Chlorella vulgaris* (4.4 ± 0.5 µg/kg), in *Tetraselmis chuii* (3.9 ± 0.8 µg/kg) and in *Schizochytrium limacinum* (19 ± 0.7 µg/kg).

More than 100 VOCs were identified [32] from selected brown and red edible seaweeds by HS-SPME/GC-MS and thermal desorption gas chromatography-mass spectrometry (TD GC-MS). Among others, *Alaria esculenta* was characterized by oct-1-en-3-ol, heptan-3-one and benzaldehyde. Oct-1-en-3-ol, as one of 16 major VOCs representative for *Fucus serratus* aroma compounds, was determined by dynamic headspace analysis (DHS) followed by GC-MS from aqueous suspension of the alga [37]. Evaluation of VOCs in brown algae (*Lessonia sealessiana*, *Macrocytis pyrifera*, *Lessonia flavicans* and *Durvillaea antarctica*) and red algae (*Mazzaella laminarioides* and *Iridaea cordata*) as sub-Antarctic macroalgae revealed (after lyophilisation) that oct-1-en-3-ol was present in the headspace of all samples with the highest percentage (9.15%) in *D. antartica* [38]. The essential oils from green alga *Capsosiphon fulvescens* isolated by static vacuum simultaneous distillation-extraction (V-SDE) and conventional simultaneous distillation-extraction (SDE) were analyzed by GC-MS [33]. Twenty-five alcohols were detected from V-SDE and SDE and (1Z,5Z)-octa-1,5-dien-3-ol was the most abundant followed by oct-1-en-3-ol and (E)-phytol. Our own research by HS-SPME/GC-MS also indicated the presence of oct-1-en-3-ol in *Codium bursa* (up to 9.71 ± 0.18% [39]) and its minor percentages were found in *Amphirhoa rigida* [30], *Halopteris filicina*, *Dictyota dichotoma*, and *Flabellia petiolata* [40].

In summary, oct-3-en-1-ol can be found among the headspace VOCs of green, red and brown algae mainly as minor constituent, but in *Pyropia haitanensis* and *Rhodomonas* species it was found in the headspace as the major compound.

3. A Direct Effect of Oct-1-en-3-ol on Microorganisms Infecting the Thalli

The effect of exogenously applied oct-1-en-3-ol on the decay rate and quantity of epiphytic bacteria on *P. haitanensis* thalli has been investigated [4,17]. Oct-1-en-3-ol treatment groups exhibited a concentration-dependent reduction in thallus bleaching [17]. Treatment with 10 µM of oct-1-en-3-ol caused a moderate reduction in decay whereas a remarkable reduction was observed with 50 or 100 µM of oct-1-en-3-ol [17]. The applied oct-1-en-3-ol on the epiphytic bacteria on *P. haitanensis* thalli reduced the amount of the bacteria in a
concentration-dependent manner. The greatest inhibitory effect (82.1% compared with the untreated control) was noted on day three at 100 µM of oct-1-en-3-ol [17]. However, the bacterial growth inhibition was attenuated upon prolonged time, and stabilized after five days at 60% of control levels. We can assume that the similar action of oct-1-en-3-ol on the same bacteria could occur in other marine algae.

Oxidative burst is a common mechanism by which algae respond to pathogens or external stimuli often leading to H$_2$O$_2$ release [41], as in Arabidopsis thaliana leaves [18] where it induced an oxidative burst (e.g., H$_2$O$_2$). However, oct-1-en-3-ol treatment did not trigger P. haitanensis oxidative burst, but the exposure to oct-1-en-3-ol resulted in a significant H$_2$O$_2$ reduction [4]. Therefore, general trend on its effect on algal oxidative burst could not be noticed. However, there was no correlation between the levels of H$_2$O$_2$ and applied oct-1-en-3-ol concentrations which may indicate that a maximal response was achieved at the lowest levels of oct-1-en-3-ol exposure. The genes encoding enzymes expression associated with intracellular redox state were found to exhibit similar changes. NADPH oxidase is an enzymatic source of cellular reactive oxygen species (ROS), producing superoxide anions by transferring electrons from intracellular NADPH and reducing molecular oxygen [41]. NADPH oxidase is activated after algae are stimulated by external factors [42]. However, the obtained results [4] indicated that oct-1-en-3-ol exposure did not cause intracellular ROS generation, but rather inhibited ROS synthesis. In addition, the effects of oct-1-en-3-ol exogenous application on the endogenous production of two primary antioxidant enzymes in cells (superoxide dismutase (SOD) and glutathione peroxidase (GSH-Px)) were investigated. SOD gene expression, on the contrary, was up-regulated after early phase of oct-1-en-3-ol stimulation, and SOD activity was increased correspondingly (oct-1-en-3-ol stimulated cellular antioxidant mechanisms) with applied three concentrations of oct-1-en-3-ol, and it was further increased in a time-dependent manner up to 60 min. Furthermore, the enzyme activity of intracellular GSH-Px, an antioxidant associated with H$_2$O$_2$ metabolism, was also increased after oct-1-en-3-ol treatment. GSH-Px activity did not respond as strongly to exogenous oct-1-en-3-ol treatment, and only 100 µM of oct-1-en-3-ol increased its activity at 30 and 60 min. This finding suggested that large decrease in H$_2$O$_2$ could be attributed to the activation of an antioxidant system in response to oct-1-en-3-ol indicating that this molecule plays a different role in algae compared with higher plants. Furthermore, the algae response to oct-1-en-3-ol was different from other previously studied stimulants such as lipopolysaccharides [43], arachidonic acid, linolenic acid and methyl jasmonate [44] or oligoagars [45]. Therefore, the reduction of epiphytic bacteria on P. haitanensis could not be attributed to an oxidative burst.

In addition, brown algae are phylogenetically distantly related to terrestrial plants, and they feature several specific stress response mechanisms, such as an inorganic antioxidant iodide and various halocarbons [46,47]. For example, kelp species (e.g., Macrocystis pyrifera) are the most well-known effective iodine accumulators among all living organisms (the vanadium-dependent haloperoxidase (vHPO) gene family is present which is correlated with the induction of inorganic iodide and halogenated metabolite metabolism). As a particular class of peroxidases, vHPOs also act as ROS detoxifying markers in brown algae since they catalyze the oxidation of halides in the presence of H$_2$O$_2$ and respond to several biotic and abiotic stresses [4,48].

4. An Indirect Communication Molecule for “Alga-Alga Signaling” and the Defense Response of Algae

The absence of vascular connections (common in terrestrial plants) indicates impossibility for red algae to regulate systemic response to attack via internal signals [5]. Therefore, in distinction to higher plant species, external chemical cues are necessary for communication within an alga, between individuals of a species, as well as with other organisms. However, the communication mechanisms among individuals of an alga species have generally been unclear, and there have been few reported signals mediating such interactions between marine algae. For example, hydrocarbons of brown algae were found as pheromones released from female gametes that can attract male gametes [9]. However,
marine algae are not passive in biotic interactions, and they can actively react to various attackers [49,50]. Algae have evolved the ability to receive stress-induced signals and respond to them by activating their own defense system [4] (Figure 2).

Oct-1-en-3-ol has been investigated for “alga-alga signaling” mainly in *P. haitanensis* and *Macrocystis pyrifera* on selected metabolites (e.g., fatty acids, amino acids, glycometabolism intermediates, or C8 compounds). Based on published results described further it is possible to note its influence to algal defense response. However, due to different metabolism of different marine algae it is difficult to conclude trends for the impact of oct-1-en-3-ol to the different metabolites abundance in various marine algae.

*P. haitanensis* could produce oct-1-en-3-ol as defense messenger molecule under stress (as well as other C8 compounds), and the unharmed *P. haitanensis* could receive the signal and respond to the stresses. For example, *P. haitanensis* can convert large quantities of C20:4 FAs into oct-1-en-3-ol using lipoxygenase (LOX) enzyme upon the induction by high-temperature stress or by agaro-oligosaccharides [26,27,51]. In response to external stimuli, rapidly produced oct-1-en-3-ol self-amplifies via the fatty acid-oxylipin metabolic cycle positive feedback [4]. This loop allows its continuous production providing the rapid, reliable and highly mobile signal that could transfer messages at relatively high concentrations. Based on these observations, it was suggested that oct-1-en-3-ol was released as the messenger molecule to initiate generalized defense response, and led to the biosynthesis of additional cell wall materials, phytoalexins, defense-related enzymes [4] or others.

To investigate the metabolites affected by oct-1-en-3-ol, *P. haitanensis* thalli were exposed to this compound [17] and the metabolic profile approach was used. First of all, after treating *P. haitanensis* with oct-1-en-3-ol (50 µmol·L\(^{-1}\)) for 0.5 h and 1 h [17], the weight of all thalli increased with cultivation time in comparison to the control indicated the change of the alga growth performance (e.g., the treated thalli weight on the eighth day after 1 h treatment was 16 ± 0.56% higher than the control). The metabolites of *P. haitanensis* thalli extracts [17] were investigated and the levels of 36 metabolites varied significantly after oct-1-en-3-ol treatment including organic acids, lipids (including one glycolipid), amino acids (asparagine, threonine, glycine, glutamine, lysine, tryptophan), sugars, glycometabolism intermediates (glycerol-3-phosphate, ribose-5-phosphate, glucose-6-phosphate), amines, and nucleotides [17]. In addition, *P. haitanensis* thalli were grown in seawater and exposed to oct-1-en-3-ol at the concentrations of 10, 50 and 100 µM for 0.5 and 1 h [4] and it was found that oct-1-en-3-ol upregulated the synthesis of methyl jasmonic acid, indole-3-acetic

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**Figure 2.** A hypothetical model of oct-1-en-3-ol signal transduction and amplification among *P. haitanensis* [4]. The Creative Commons Public Domain Dedication waiver (http://creativecommons.org/publicdomain/zero/1.0/; accessed on 4 July 2021) applies to the data.
acid, and gibberellin A3. The production of these compounds adjusted the redox state in cells, resulting in host defence activation. The release of volatile oxylipins in response to oct-1-en-3-ol treatment was also investigated in *P. haitanesis* [4]. Furthermore, *M. pyrifera* thalli were grown in seawater and also exposed to oct-1-en-3-ol at final concentration of 50 µM for 0.5 or 1 h [36] and the genome-wide gene expression profile and fatty acid spectrum were investigated. Oct-1-en-3-ol exposure of *M. pyrifera* regulated the fatty acid and phytohormone contents and the transcript levels of more than 600 genes [36] involved in various physiological processes (especially lipid metabolism, amino acid metabolism, energy metabolism and secondary metabolite biosynthesis). Oct-1-en-3-ol induced 10 genes, six lipases, two fatty acid desaturase, one lipoxygenase (LOX), and one diacylglycerol acyltransferase type 2 (DGAT2) encoding gene in lipid metabolism of *M. pyrifera* [36].

In further discussion, the major affected marine natural compounds after oct-1-en-3-ol treatment of *P. haitanesis* and *M. pyrifera* are presented in short according to their chemical classes (fatty acids, amino acids, glycometabolism intermediates, phytohormones, others).

Tetradecanoic acid, hexadecanoic acid and octadecanoic acid were significantly decreased after the treatment of *P. haitanesis*, while hexadecanoic acid decreased and several organic acids were increased such as citric acid, ethanedioic acid and threonic acid [17]. Citric acid is an important metabolic intermediate of tricarboxylic acid cycle and its increase indicated the enhancement of primary metabolism and rising energy demand for energy by the cells. 1-Monoocadecanoylglycerol and 1-monohexadecanoylglycerol were increased indicated generally that the synthesis of lipids was accelerated. In another study [4] treatment with oct-1-en-3-ol increased the total amount of FAs in *P. haitanensis*, in particular, C20:1, arachidonic acid, and eicosapentaenoic acid that were significantly increased after 30 min of the treatment (50 µM of oct-1-en-3-ol) whereas C18:0 was dramatically increased after 10 µM treatment. In addition, a large number of membrane lipids in *P. haitanensis* were decreased with oct-1-en-3-ol treatment including phosphatidylcholine (PC), and lyso phosphatidylglycerol (Lyso PG) suggesting an activation of phospholipase 2 activity [4]. Oct-1-en-3-ol treatment also decreased the total fatty acids content in *M. pyrifera* by 56.5% at 0.5 h and 41.9% at 1 h [36]. In particular, stearic acid (C18:0), arachidonic acid (C20:0), erucic acid (C22:1), as well as unsaturated docosadienoic acid (C22:2), and lignoceric acid (C24:0) significantly decreased, whereas pentadecanoic acid (C15:0), palmitic acid (C16:0), and unsaturated oleic acid (C18:1), linoleic acid (C18:2), and behenic acid (C22:0) only decreased after 0.5 h [36].

Amino acids, such as asparagine and glutamine, were significantly increased in *P. haitanesis* after the treatment [17]. Glutamine is the major precursor for the biosynthesis of many compounds, such as nucleic acids, amino acids, and proteins and it can be transformed into many other amino acids. Therefore, glutamine increase indicated that *P. haitanensis* response to oct-1-en-3-ol might initiate the preparation for the biosynthesis.

After the treatment, several glycometabolism intermediates were increased in *P. haitanesis*, especially glycerol-3-phosphate. Glycerol-3-phosphate is galactosylglycerol synthesis precursor [52] involved in the photosynthesis and cell walls formation of many red algae [53]. Therefore, the increase of glycometabolism intermediates indicated that oct-1-en-3-ol induced photosynthesis that made the alga assimilate more carbon to synthesize carbohydrates and promote the cell wall formation. In addition, an apparent increase of cellulose was observed and since cellulose is the main component of the red algae cell wall, its increase also indicate the cell walls synthesis. In addition, galactosylglycerol, which is the primary metabolite resulted from the photosynthesis of red algae was also increased. The increase in the synthesis of monoacylglycerol, lipids, amino acids, and organic acids indicated that oct-1-en-3-ol could enhance the photosynthesis of carbohydrates and promote the cells growth.

C₈ derivatives (including short-chain unsaturated alcohols, aldehydes and ketones) were the most diverse in *P. haitanensis* while oct-1-en-3-one and oct-2-enal were the most abundant [4]. The concentrations of all VOCs were increased after 10 µM and 50 µM
treatment and significantly increased VOCs were oct-1-en-3-ol, octa-1,5-diene-3-ol, nona-2,6-dienal, pent-1-en-3-one and hepta-2,4-dienal. The volatile oxylipins can crosstalk with phytohormones in green plants [8]. Presently, it is not clear whether phytohormones can exhibit similar roles in the algae as in terrestrial ecosystems. They may be involved in inducing algal defenses preparing the alga to respond to anticipated stressors or pathogen attack. Some hormones, such as jasmonic acid, are down-stream metabolites of oxylipin metabolism [54]. After oct-1-en-3-ol treatment, the concentrations of three phytohormones (indole-3-acetic acid (IAA), methyl jasmonic acid (MeJA), and gibberellin A3 (GA3)) in P. haitanensis were increased [4]. There were no obvious changes in the concentrations of the other measured phytohormones. The levels of gibberellic acid (GA), indole-3-acetic acid (IAA), abscisic acid (ABA), and zeatin, as well as glycine betaine levels in M. pyrifera were determined [36]. After oct-1-en-3-ol treatment, the concentrations of three phytohormones (IAA, ABA and zeatin) decreased during the whole induction period, but the content of gibberellic acid was increased.

5. Conclusions

In red alga P. haitanensis, oct-1-en-3-ol is generated from arachidonic acid by a multi-functional LOX enzyme that has high HPL, LOX, and AOS activities within one catalytic domain of the protein. Oct-3-en-1-ol can be found among the headspace VOCs of green, red and brown algae mainly as minor constituent, but in Pyropia haitanensis and Rhodomonas species it was found in the headspace as the major compound. The applied oct-1-en-3-ol on the epiphytic bacteria on P. haitanensis thalli reduced the amount of the bacteria in a concentration-dependent manner. However, oct-1-en-3-ol treatment did not trigger P. haitanensis oxidative burst, and did not cause intracellular ROS generation, but inhibited ROS synthesis. SOD activity was increased correspondingly (oct-1-en-3-ol stimulated cellular antioxidant mechanisms). In response to external stimuli, rapidly produced oct-1-en-3-ol self-amplifies via the fatty acid-oxylipin metabolic cycle positive feedback. Oct-1-en-3-ol was released as a messenger molecule to initiate generalized defense response, and led to the biosynthesis of additional cell wall materials, phytoalexins, defense-related enzymes or others.

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