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A portion of plant airborne communication is endorsed by uptake and metabolism of volatile organic compounds

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Plants have the ability to sense volatile organic compounds (VOCs) so as to efficiently adapt to their environment. The mechanisms underlying such plant 'olfactory' systems are largely unknown. Here I would like to propose that the metabolism of VOCs in plant tissues is one of the mechanisms by which plants sense VOCs. During the gas-exchange that is essential for photosynthesis, VOCs in the atmosphere are taken into the intercellular spaces of leaves. Each VOC is partitioned between the gas phase (intercellular space) and liquid phase (cell wall) at a certain ratio determined by Henry's law. The VOCs in the cell wall diffuse through the plasma membrane to the cytosol depending on their oil/water partition coefficients. Plants detoxify some VOCs, especially those that are oxidized, through glycosylation, glutathionylation, and reduction. These metabolic processes lower the concentration of VOCs in the cytosol, which facilitates further cytosolic uptake. As a result, vigorous metabolism of VOCs in the cytosol can lead to a substantial accumulation of VOC metabolites and the depletion of glutathione or NADPH. One such metabolite (a VOC glycoside) is known to mount a direct defense against herbivores, whilst deprivation of glutathione and NADPH can fortify plants with responses similar to the oxidative stress response.

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Introduction

As has been reviewed elsewhere, plants sense volatile organic chemicals (VOCs) emitted into the atmosphere by different parts of the same plant, neighboring plants, and rhizobacteria. The first plant volatile compound to be identified as an infochemical was ethylene. Ethylene regulates ripening, germination, elongation, senescence, and responses against biotic/abiotic stresses [1,2]. Because of the physiological significance of ethylene as a phytohormone, the mechanism used by plants to perceive ethylene has been extensively studied. We now know that ethylene is specifically recognized by a membrane receptor protein, leading to activation of the phosphorylation cascade and the regulation of a subset of genes. Most living organisms perceive chemical cues in their surroundings using cue-specific receptors, like the ethylene receptor. The G-protein coupled receptor found in the human olfactory system, two-component signaling systems in bacterial sensors, as well as in plant sensors for ethylene and cytokinin, and some of the transient receptor potential channels are all examples of receptors that are specific to the chemical structures of particular signal molecules. The combination of the specificity of signal recognition and high affinity to chemical cues allows receptor-mediated chemical sensing to achieve high sensitivity. Accordingly, it has been assumed that plants similarly perceive VOC cues by specific protein receptor-mediated recognition. However, to our knowledge, no receptors for VOC cues other than ethylene have been identified.

We know that the tissues of any organism are exposed to chemicals in air and/or water in their surroundings, and that most of these chemicals can attach to the tissue surface or penetrate the tissues. This form of passive uptake of VOCs is known to occur, for example, in the human body, with substantial uptake both via the derma and through inhalation. This uptake has often been discussed in the context of the toxicological effects of volatile pollutants in the atmosphere. The efficiency of transdermal uptake from the air depends on the properties of each volatile compound, such as hydrophobicity and molecular weight, implying that the uptake is a physicochemical process [3]. Some of the VOCs taken up by the human body would be recognized as xenobiotics, and they were served to xenobiotic metabolism attained by phase I, II, and III enzymes, each responsible to oxidation, reduction or hydrolysis, conjugation, and modification of conjugates, respectively [4]. This could also be the case with plants [5]. A portion of the atmospheric VOCs might be partitioned into plant tissues through the stomata or cuticle, the cell wall, and the plasma membrane [6,7,8•].

Flux measurement over an orange grove in California showed that approximately 42% of VOCs emitted in the grove were deposited into vegetation, at a rate of 3.24 nmol m^{-2} s^{-1} [9]. Given the low concentration of

VOCs in the atmosphere, only a small portion of VOCs would be taken up by plant tissues if the physicochemical partitioning process were the only mechanism involved [7]. The highly efficient vegetative uptake of VOCs that is observed, therefore, suggests that there exists a system to facilitate the uptake. VOC metabolism inside of plant tissues may help to promote this uptake [10•].

At least a portion of VOCs coming into contact with the plant must be taken up by the receiver tissues through a physicochemical process in the first place. Some of the VOCs entering the tissues would be metabolized, leading to continuous uptake of VOCs from the atmosphere. This, in turn, would result in a high metabolic turnover of the VOCs, along with the accumulation of a high level of VOC metabolites in the receiver tissues. This scenario would mean that the biochemical metabolic process could be substantially active even when the concentration of VOCs outside of the plant tissues was quite low. Consequently, intake of exogenous VOCs would lead to phenotypic changes in the receiver plants. A similar scenario is found with CO_2 assimilation for photosynthesis. CO_2 diffuses through boundary layer resistance, stomatal resistance, intercellular air space resistance, and liquid phase resistance to meat rubisco [11], even though differences in physicochemical parameters, such as hydrophobicity, vapor pressure, and so on, between CO_2 and VOCs should be taken into account. In this review, I will show that metabolism of exogenous VOCs is one mechanism by which plants can perceive VOCs, as well as providing a number of examples.

Incorporation into primary metabolism

Early studies showed that spraying aqueous methanol on leaves increased the growth of several C3 plants grown under drought conditions [12]. After being sprayed onto the leaf surface, methanol is taken up by the plant cells, where it is oxidized to formaldehyde. Based on experiments with ^{14}C-labeled formaldehyde, the formaldehyde appears to be further oxidized to CO_2 and then enters the Calvin cycle to yield sugars [13]. Formaldehyde is also sometimes oxidized to formic acid that is subsequently metabolized to constitute the methyl groups of methionine and phosphatidylcholine [14]. Another study showed that a rhizobacterium-derived VOC, dimethyl disulfide, promoted plant growth under sulfur-starved conditions [15]. Assimilation and incorporation of the sulfur in dimethyl disulfide into plant proteins accounted for this growth enhancement. The growth-promoting effect of both methanol and dimethyl disulfide is partly attributed to the assimilation of essential elements or functional groups into primary plant metabolites.

However, primary metabolism is not only the way that plants perceive methanol. Wound-induced methanol regulated expression of several genes, such as β-1,3-glucanase, resulting in improved resistance to bacterial pathogens but greater susceptibility to viruses, due to an increase in the gating capacity of plasmodesmata [16]. These methanol responses observed in plants cannot be explained by metabolic processes alone so it is thought that there must be other mechanisms triggering signaling cascades, such as priming mediated by MAPK activation [17].

Incorporation into phytohormone biosynthesis

Another mechanism to respond to VOCs was reported by using transgenic Arabidopsis plants overexpressing *ent*-copalyl diphosphate/*ent*-kaurene synthase as the emitter plants [18]. The transgenic Arabidopsis emitted *ent*-kaurene into the atmosphere, and *ent*-kaurene in the vapor phase fully complemented the dwarf phenotype of a mutant defective in gibberellin biosynthesis at the step prior to formation of *ent*-kaurene. This is a completely artificial scenario, but it clearly indicates that a plant takes in and metabolizes a compound from the vapor phase. The amount of *ent*-kaurene in air samples collected at a site of Japanese coniferous tree vegetation [consisted mainly of Japanese cedar (*Cryptomeria japonica*) and Japanese cypress (*Chamaecyparis obtusa*)] ranged from 0.01 to 7.1 $\mu g\ g^{-1}$ dry weight h^{-1} (average: 0.61 $\mu g\ g^{-1}$ dry weight h^{-1}) [19]. Even though direct comparison is inadequate, the amount of *ent*-kaurene emitted by natural vegetation seems to be comparable to that emitted by the transgenic Arabidopsis (60 ng h^{-1} $plant^{-1}$) [18], suggesting that *ent*-kaurene emissions may well disturb the proper regulation of gibberellin biosynthesis in some plants growing close to the coniferous trees.

Methyl salicylate and methyl jasmonate are also reported to function as airborne signals under a given condition [20,21,22]. The esters diffuse into plant tissues, then, are converted into salicylic acid and jasmonic acid by specific esterases [23,24]. Jasmonic acid thus formed must be further metabolized into jasmonoyl-isoleucine, which is the active form of signaling because it is a specific ligand of a nuclear receptor, the COI1-JAZ complex [25]. Inactivation of jasmonoyl-isoleucine also needs metabolic enzymes, cytochrome P450 94 family enzymes [26].

Glycosylation

In the cells of many plant species, a subset of glycosylated VOCs can be found [27]. In general, these glycosylated compounds are formed from endogenous VOCs [28,29], but they can also be made from exogenous compounds. In Australian vineyards, 1,8-cineole emitted by eucalyptus trees grown in close proximity to grapevines has been shown to be taken up by the grapevines, resulting in modification of the flavor quality of the red wines subsequently produced [30•]. An increased level of 1,8-cineole in red wines was detected even when the distance between the grapevines and eucalyptus trees was as much as