

Sites of synthesis, biochemistry and functional role of plant volatiles

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Abstract

All plants are able to emit volatile organic compounds (VOCs) and the content and composition of these molecules show both genotypic variation and phenotypic plasticity. VOCs are involved in plant–plant interactions and for the attraction of pollinating and predatory insects. The biochemistry and molecular biology of plant VOCs is vast and complex, including several biochemical pathways and hundreds of genes. In this review the site of synthesis, the biosynthesis and the functional role of VOCs are discussed.

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1. Introduction

Volatile organic compounds (VOCs) are products emitted into the atmosphere from natural sources in marine and terrestrial environments (Guenther et al., 1995; Lerdaun et al., 1997; Chappell, 2008) and the majority of VOCs entering the atmosphere are of biogenic origin. In fact, over 90% of natural emission of VOCs is related to plants species with dominant sources of VOCs being forests all over the world; the most important among them is the Amazonian rainforest. Plants emit 400–800 Tg C/yr as hydrocarbons, an amount equivalent to the sum of biogenic and anthropogenic methane emissions (Guenther et al., 1995), while up to 36% of the assimilated carbon is released as complex bouquets of VOCs (Kesselmeier and Staudt, 1999; Kesselmeier, 2001; Kesselmeier et al., 2002). Unlike methane, plant-produced VOCs are extremely reactive in the troposphere, with life-times ranging from minutes to hours (Lerdaun et al., 1997), contributing to the aerosol that scatters the light to produce the blue sky.

VOCs are released from leaves, flowers and fruits into the atmosphere and from roots into the soil. To humans, pollinator-attracting floral VOCs have been a source of olfactory pleasure since antiquity, and we also use a large number of aromatic

plants as flavorings, preservatives, and herbal remedies (Pichersky and Gershenzon, 2002; Pichersky et al., 2006).

The primary functions of airborne VOCs are to defend plants against herbivores and pathogens, to attract pollinators, seed dispersers, and other beneficial animals and microorganisms, and to serve as signals in plant–plant communication (Dudareva and Pichersky, 2008). In some plants, released VOCs may also act as wound sealers (Penuelas and Llusia, 2004).

Some VOCs might be dangerous for human's health when present at higher concentrations (Jahodar and Klecakova, 1999), and plant-emitted VOCs are also major precursors of tropospheric phytotoxic compounds (Padhy and Varshney, 2005). Since some VOCs can act as precursors of photochemical smog, their level is one of the fundamental parameters for the assessment of atmosphere quality (Ulman and Chilmontczyk, 2007). VOCs can regulate the oxidative capacity of the troposphere, carbon monoxide, O₃ and aerosol budgets, and together with high concentration of nitrogen oxides in the sunlight they form more phytotoxic O₃ (Vuorinen et al., 2005). Furthermore, VOCs have also been shown to be involved in the formation of secondary aerosols in the atmosphere, which have implications for the radiative balance of the earth (Padhy and Varshney, 2005).

Routine measurements of VOCs in air have shown that average concentrations are very much smaller than those used in laboratory experiments designed to study the effects of VOCs on plants. However, maximum hourly concentrations of some

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VOCs can be 100 times larger than the average, even in rural air (Cape, 2003).

This review aims to collect most of the information available on the ability of plants to produce VOCs and to explore their sites of synthesis, biochemistry and functional role.

2. Plant VOCs

Chemically, VOCs belong to the large group of terpenoids (homo-, mono-, di-, sesquiterpenoids), fatty acid derived C₆-volatiles and derivatives, phenylpropanoid aromatic compounds (like methyl salicylate, MeSA, and indole), as well as certain alkanes, alkenes, alcohols, esters, aldehydes, and ketones (Pichersky and Gershenzon, 2002; Holopainen, 2004; Arimura et al., 2005, 2009; Baldwin et al., 2006; Wu and Baldwin, 2009). Today more than 1700 volatile compounds have been isolated from more than 90 plant families, constituting approximately 1% of all plant secondary metabolites (Pichersky and Gershenzon, 2002). The composition of VOCs emitted by plants also depends on the mode of damage such as single wounding, continuous wounding (Mithöfer et al., 2005), herbivore feeding (Paré and Tumlinson, 1996), and egg deposition (Hilker and Meiners, 2002). Some VOCs emitted after insect feeding can serve as repellents to the attacking insect itself as a direct defense, as well as attractants to the natural enemies of the attacking insect as indirect defenses (Kessler and Baldwin, 2001). An herbivore-induced VOC blend may comprise more than 200 compounds (Dicke and Van Loon, 2000). In addition to attracting the natural enemies of the egg and larval stages, herbivore-induced plant volatiles (HIPVs) can also decrease the oviposition rates of the attacking herbivores and thus can be considered both direct and indirect defense systems (Dicke and Van Loon, 2000; Kessler and Baldwin, 2001). Besides addressing organisms from other trophic levels, induced VOCs also act on neighbored leaves of other plants (Arimura et al., 2000; Engelberth et al., 2004; Heil and Silva Bueno, 2007). Moreover, the volatile production generally shows a pronounced rhythmicity by emitting the volatiles mostly during the light phase (Arimura et al., 2008b). Furthermore, the production of VOCs is activated by elicitors from oral secretions of the attacking insect herbivore (Truitt et al., 2004; Truitt and Pare, 2004; Schmelz et al., 2006).

Although defenses might benefit plants, the expression of plant resistance can be costly in the absence of plant enemies (Bergelson and Purrington, 1996; Strauss et al., 2002). Since the synthesis of a chemical represents an investment of energy and resources for the organism if the benefits it gets from this investment are reasonable, evolution will keep this trait, yet the opposite is also true: if the use of resources does not benefit the organism, this adaptation may persist or it will eventually disappear (Macias et al., 2007). Since the production of VOCs can be limited by both light and soil nutrients is likely to incur considerable costs, at least under certain growing conditions (Heil, 2008).

3. Sites of synthesis of plant VOCs

Plants express different types of secondary metabolites as defense strategy against biotrophs, ranging from the constitutive

and inducible synthesis of bioactive natural products to the production of structural traits (Ballhorn et al., 2008). Many VOCs, particularly most monoterpenes and sesquiterpenes, are synthesized and stored in special secretory tissues, which occur in most vascular plants. The secreted material is usually eliminated from the secretory cells outside the plant or into specialized intercellular spaces (Fahn, 1988). Certain plant species accumulate VOCs in resin ducts, or glandular trichomes and such compounds can be released in large amounts as soon as these structures are ruptured by herbivore feeding or movements on the plants' surface (Duke et al., 2000). Since many of the constitutive defense compounds may be toxic at high concentrations to the plant itself, the plant must be able to generate and store such substances without poisoning itself. The obvious strategy to overcome this problem is to store VOCs as inactive precursors, for instance as glycosides (Jerkovic and Mastelic, 2001), or in extracellular compartments, as in the case of glandular trichomes. Secretory tissues are usually classified according to the substance they produce and trichomes, ducts and cavities are mainly involved in VOC production.

3.1. Glandular trichomes

Several plant species store VOCs in specialized glandular trichomes (Gershenzon et al., 2000) which release their contents in response to tissue damage, thus deterring herbivores or inhibiting microbial growth (Langenheim, 1994). Glandular trichomes secreting VOCs are present in Lamiaceae, Asteraceae, Geraniaceae, Solanaceae and Cannabinaceae. Their morphology may vary among families although two general types of trichomes are frequently present: capitate trichomes, which consist of a basal cell, one to several stalk cells and one to few secretory cells (Fig. 1A–B) and peltate trichomes, comprising a basal epidermal cell, a short stalk cell and a secretory head consisting of several secretory cells arranged in one layer (Fig. 1C–F). Whatever the exact nature of the capitate gland secretory products, it is clear that the bulk of the VOCs is produced by and stored in the peltate glandular trichomes (Maffei et al., 1989; Turner et al., 2000). This general scheme of glandular trichome structure can reach a further complexity in some families where trichomes are multicellular and biserial, with one to several pairs of cells in the stalks and the secretory heads (Fahn, 1988) (Fig. 1C). In many cases, VOCs are accumulated inside the cuticular layer but outside the plant cell wall, either alone or along with other compounds which can be of a very different chemical nature and lipo-hydrophilicity. Being protodermal extrusions, glandular trichomes are present on plant surfaces, with particular reference to leaf blades, flowers and, in some cases, seeds. Although the presence of terpene synthases in trichomes has been well documented (Berteaux et al., 2006), the regulation of their expression in trichomes remains obscure. In tomato (*Lycopersicon esculentum* Mill.), the expression of the monoterpene synthase *LeMTS1* in stems and petioles was predominantly detected in trichomes and could be induced by jasmonic acid (JA) treatment (Van Schie et al., 2007). To elucidate the biosynthetic pathway and to isolate and characterize genes involved in the biosynthesis of

terpenoids including artemisinin in *Artemisia annua* L., glandular trichomes were used as an enriched source for biochemical and molecular biological studies (Bertea et al., 2006). The accumulation of VOCs in developing plants could, in theory, be influenced by both the rate of terpene synthesis and the rate of terpene loss. Maffei et al. (1986, 1989) using scanning electron microscopy to estimate gland numbers and densities on developing leaves, found that young leaves contained fewer glandular trichomes than older leaves, indicating an evident gland production during leaf growth. It is interesting to note that in many plant species new glandular trichomes are continually produced during leaf growth and that newly initiated glands do occur together with mature glands in growing regions, such that neighboring glands within the same leaf zone are often of different ages. Circumstantial evidence based on ultrastructural correlation, specific labeling and subcellular fractionation studies indicates that at least the early steps of monoterpene biosynthesis occur in trichome plastids (Turner et al., 1999), while nuclear hypertrophy has been observed in the secretory cells of both peltate and capitate trichomes (Berta et al., 1993).

3.2. Secreting ducts and cavities

Other secreting structures producing constitutive VOCs are less visible because hidden in deep tissues of the plant. These are secreting ducts and cavities that consist of relatively large intercellular spaces lined by an epithelium of secretory cells (Fahn, 1988). In this case also, bioactive VOCs are stored and represent a constitutive defense ready to be delivered in case of rupturing of tissues. Resin ducts are typical of evergreens such as the Pinaceae, but are also present in several other plant families such as the Myrtaceae, Asteraceae, Umbelliferae and Leguminosae. These tissues generate by the progressive separation of cells (schizogeny) with the creation of a large intercellular space inside which secretion accumulates (Fahn, 1988). Fig. 1G shows a cross-section of a Scots pine needle. In this family, resin ducts are present all over the plant body, from leaves to roots, and they accumulate VOCs which are used as a chemical weapon against herbivore and pathogen attack.

Secretory cavities are typical of families such as Rutaceae, Clusiaceae, Myrtaceae and some others. Unlike resin ducts, secretory cavities originate both by schizogeny and lysigeny (disruption — lysis of cell walls and mixing of protoplasts). Typical structures are those present in the skin of citrus fruits (Fig. 1H). Compression of surrounding tissues forces the secretion to get out and the ensuing release of compounds into the environment represents, in this case also, a constitutive chemical defense.

3.3. Secretory cells in flowers and roots

Other tissues able to produce lipophilic substances are represented by secretory cells that accumulate the secreted products inside their vacuoles. This is the case of VOCs produced by the odorous roots of the grass *Vetiveria zizanioides* Nash (vetiver). Vetiver VOCs are produced in secretory cells

localized in the first cortical layer outside the endodermis of mature vetiver roots (Viano et al., 1991a,b; Maffei, 2002). Fig. 1I shows a cross-section of vetiver root, where the essential oil-producing cells are evidenced by treatment with Sudan Black B (Maffei, 2002). Recently, by using culture-based and culture-independent approaches to analyze the microbial community of the vetiver root, Del Giudice et al. (2008) demonstrated the presence of a broad phylogenetic spectrum of bacteria, including α , β , and γ proteobacteria, high-G+C-content gram-positive bacteria, and microbes belonging to the Fibrobacteres/Acidobacteria group. The same group isolated root-associated bacteria and showed that most of them were able to grow by using vetiver sesquiterpenes as a carbon source and to metabolize them releasing into the medium a large number of compounds typically found in commercial vetiver oils. Several of these bacteria were also able to induce gene expression of a vetiver sesquiterpene synthase (Del Giudice et al., 2008). These results support the intriguing hypothesis that bacteria may have a role in essential oil biosynthesis opening the possibility to use them to maneuver the vetiver oil molecular structure. These results are in accordance with those obtained by Viano et al. (1991a,b) who analysed vetiver root ultrastructure using electron transmission microscopy and detected essential oil crystals in the inner cortical layer close to the endodermis. According to these authors the secretion of the essential oil occurs in this region and successively reaches the whole cortex.

VOCs can be synthesized by a variety of other anatomical structures such as solitary cells and areas of epidermal cells. The typical fragrance of flowers results from VOCs occurring in form of small droplets in the cytoplasm of the epidermal and neighboring mesophyll cells of sepals (Fahn, 1988). In flowers, the biosynthesis of VOCs usually occurs in epidermal cells, allowing an easy escape of VOCs into the atmosphere (Kolossova et al., 2001). Flowers usually produce their attractive fragrance in osmophores or in conical cells located on the petals (Fig. 1J). These cells do not stock VOCs but release them into the air (Caissard et al., 2004). In species belonging to the Orchidaceae and Araceae, VOCs produced by osmophores produce also amines and ammonia (Pridgeon and Stern, 1983). Although these stored and induced VOCs have useful roles, non-terpene-emitting species also survive the onslaught of herbivores and competition, and can set seed (Owen and Penuelas, 2005). In fact, lack of specific anatomical structures for VOC storage does not imply negligible internal VOC concentrations (Niinemets et al., 2004).

3.4. Extrafloral nectar

Constitutive defenses are not restricted to direct defenses. Central American *Acacia* species secrete extrafloral nectar to attract and nourish ants that defend the host plant against herbivores. This form of indirect defense can be inducible as well as constitutive. In the latter case the plants are obligatory inhabited by symbiotic ants. Interestingly, phylogenetic analysis revealed that the inducibility of extrafloral nectar secretion is the ancestral (plesiomorphic) state and the constitutive nectar flow represents the derived (apomorphic) state within the genus

Acacia (Heil et al., 2004). In response to herbivory, plants like Lima bean (*Phaseolus lunatus* L.) also secrete extrafloral nectar, that attracts predatory arthropods, mainly ants, and therefore serves as an indirect defense (Heil, 2004a). In many cases, plants do not rely on a single defense strategy but employ a complex array of different defensive mechanisms. Wild Lima beans significantly benefited from induced increased nectar production in terms of less leaf damage, and higher growth rates and seed production, respectively (Kost and Heil, 2008). Moreover, volatiles released by damaged lima bean leaves could induce extrafloral nectar in neighboring plants (Kost and Heil, 2006) as well as in undamaged leaves of the same shoots (Heil and Silva Bueno, 2007). When lima bean plants were exposed to (Z)-3-hexenyl acetate, a substance naturally released from damaged lima bean, a significant increase in EFN secretion was found (Heil et al., 2008). Also, plants growing in the wild, which had been induced by exogenous application of the phytohormone jasmonic acid (JA), responded by increasing both their VOC emission and EFN secretion (Heil, 2004b). It has been demonstrated that an artificial increase of the amount of available EFN benefits lima bean in nature by attracting predacious and parasitoid arthropods and recent findings suggest that EFN plays an even more important role as an indirect defense of lima bean than VOCs or any other JA-responsive trait (Kost and Heil, 2008).

4. Main biochemical pathways of plant VOCs

De novo biosynthesis and emission of VOCs include products of the lipoxygenase (LOX) pathway, such as oxylipins, green leaf volatiles (GLVs), as well as many terpenoids, including isoprene, some carotenoid derivatives, indoles and phenolics, including methyl salicylate (MeSA) and aromatic VOCs (Tholl et al., 2006; Tholl, 2006). A schematic representation of the volatilome tree is depicted in Fig. 2.

4.1. Isoprenoids

All isoprenoids are produced from the precursors dimethylallyl diphosphate (DMAPP) and its isomer isopentenyl diphosphate (IPP), which are synthesized by the deoxyxylulose-5-phosphate (DXP) pathway (also known as the MEP pathway) in the chloroplasts and by the mevalonate (MVA) pathway in the cytoplasm (see ref. Kesselmeier and Staudt, 1999, for a review of the evolutionary and functional history of the two pathways for IPP and DMAPP synthesis). Some exchange and/or cooperation is thought to exist between these two pathways and the two pathways probably operate under different physiological conditions within the cell and depend on the cell and plastid developmental state (Wanke et al., 2001). The evidence that a small amount of cross-talk between the two pathways might occur, implies that the pathways are not completely autonomous (Holopainen, 2004). It is proposed that C₁₀ precursors of monoterpenes are predominantly synthesized within plastids by the MEP pathway, whereas precursors of sesquiterpenes are produced via the classical MVA pathway. However, it has to be noted that monoterpenes and sesquiterpenes, along with the hemiterpene isoprene, are VOCs that represent only a small por-

tion of the diverse group of isoprenoid plant products (Owen and Penuelas, 2005).

Isoprene (2-methyl-1,3-butadiene) is the simplest terpenoid (hemiterpene) emitted by plants; it is synthesized from DMAPP by the action of isoprene synthase. The biosynthesis and functional physiology of isoprene have been recently reviewed (Sharkey et al., 2008).

Some VOCs, such as β -ionone, are not derived directly from isoprenoid pyrophosphates but instead from the cleavage of tetraterpenes such as carotenoids, by the action of carotenoid cleavage dioxygenases (CCDs) (D'Auria et al., 2002) (Fig. 2, branch A).

Highly volatile monoterpenes (C₁₀) have two isoprene units, whereas sesquiterpenes have three isoprene units (C₁₅), based on the classification of Ruzicka. Monoterpenes are typical leaf products whereas sesquiterpenes are typical flower fragrances (Dudareva et al., 2006); although considerable amounts of monoterpenes and sesquiterpenes are produced in leaf glandular trichomes (see Fig. 1) and are emitted from the herbivore-damaged foliage and roots (see below).

Homoterpenes, such as 4,8-dimethylnona-1,3,7-triene (DMNT) and 4,8,12-trimethyltrideca-1,3,7,11-tetraene (TMTT) are the most typical compounds related to herbivore feeding. The biosynthesis of TMTT and DMNT, has been proposed to proceed via an oxidative degradation by P450 enzymes of the diterpene geranyl linalool and the sesquiterpene (*E*)-nerolidol as precursors, respectively (Holopainen, 2004; Arimura et al., 2005, 2009) (Fig. 2, branch A and B).

A large, structurally diverse number of terpenoids are yielded by a large family of terpene synthases (TPS) using geranyl diphosphate (GPP) and farnesyl diphosphate (FPP) as substrates and many distinct TPSs that synthesize monoterpenes and sesquiterpenes (the bulk of terpenoid VOCs) have been characterized from various plants (Owen et al., 1997, 2001; Lin et al., 2007; Arimura et al., 2008a,b, 2009; Wu and Baldwin, 2009). Metabolic engineering of VOCs can be achieved through the modification of existing pathways, for instance by up- or down-regulation of one or more biosynthetically steps or by the re-direction of metabolite fluxes to a desired compound by blockage of competing pathways. Otherwise, the introduction of new genes or branch-ways that are normally not present in the host plant can be accomplished. There are several examples of successful applications of these methods. By overexpressing a dual linalool/nerolidol synthase (*FaNES1*) from strawberry in chloroplasts of the model plant *Arabidopsis thaliana* (L.) Heynh. it has been demonstrated that linalool and its derivatives significantly repelled aphids (Aharoni et al., 2005). Direction of *FaNES1* to another compartment, the mitochondria, which contains the sesquiterpene precursor FPP, leads to the formation of nerolidol and its derivative, the C₁₁ homoterpene DMNT; both volatiles attracted carnivorous predatory mites thus improving plant indirect defense (Kappers et al., 2005).

4.2. Oxylipins

Oxylipins originate from polyunsaturated fatty acids which are released from chloroplast membranes by lipase activity and

that represents the substrate for numerous other oxygenated compounds including jasmonates (which comprise JA, methyl JA, JA amino acid conjugates and further JA metabolites) as well as the source for GLV biosynthesis. LOXs form hydroperoxides from linolenic (18:3) or linoleic acids (18:2). With linolenic acid as the substrate, (13*S*)-hydroperoxyoctadecatrienoic acid (13-HPOT) or (9*S*)-hydroperoxyoctadecatrienoic acid (9-HPOT) are formed, whereas with linoleic acid as the substrate (13*S*)-hydroperoxyoctadecadienoic acid (13-HPOD) and (9*S*)-hydroperoxyoctadecadienoic acid (9-HPOD) are formed (Wasternack, 2007). Discrete 9-LOX and 13-LOX pathways have been proposed to explain the occurrence of numerous oxylipins (Howe and Schillmiller, 2002). Octadecanoids and jasmonates originate from 13-allene oxide synthase (13-AOSs) activity, whereas aldehydes, ω -oxo fatty acids and alcohols are formed by the activity of hydroperoxy lyases (13-HPLs). GLVs are synthesized via the LOX (lipoxygenase) pathway from C₁₈ polyunsaturated fatty acids including linoleic acid and linolenic acids (Dudareva, 2005). The C₁₈ acids are cleaved to C₁₂ and C₆ compounds by hydroperoxide lyases (Engelberth et al., 2004). The first C₆ GLV compound synthesized by the LOX/lyase pathway is 3-*Z*-hexenal which is then converted to other GLVs such as 2-hexenal (leaf aldehyde), 3-hexenol (leaf alcohol) and 3-hexenyl acetate (leaf ester) (Shiojiri et al., 2006). 3-Hexenyl acetate is formed from a reaction between 3-hexenol and acetyl-CoA, a reaction catalysed by an acyltransferase (D'Auria et al., 2007). While GLVs are usually defined as saturated and unsaturated C₆ alcohols, aldehydes and esters, it has been recently shown that C₅ compounds (2-pentenyl acetate and 2-pentenol) can be constituents of the GLVs as well (Connor et al., 2008). The biosynthesis of oxylipins has been recently reviewed (Wasternack, 2007) (see also Fig. 2, branch C).

4.3. Volatile aromatic compounds

Another large class of VOCs consists of compounds containing an aromatic ring. VOCs containing nitrogen or sulfur are synthesized by cleavage reactions of modified amino acids or their precursors. For example, the volatile indole is made in maize by the cleavage of indole-3-glycerol phosphate, an intermediate in tryptophan biosynthesis (Koeduka et al., 2006). Indole has been identified as one of the blend of VOCs emitted from maize in response to herbivore damage and the production and release of indole in plants has been shown to be an active process in which the de novo synthesis is triggered in response to insect feeding (Pare and Tumlinson, 1997b). Maize seedlings contain indole as an intermediate in at least two biosynthetic pathways. The BX1 enzyme catalyzes the conversion of indole-3-glycerol phosphate (IGP) to indole, which is further converted to the defense-related secondary metabolite DIMBOA [2,4-dihydroxy-7-methoxy-2H-1,4-benzoxazin-3(4H)-one]. Indole also serves as the penultimate intermediate in the formation of tryptophan by tryptophan synthase. In maize plants, a gene has been characterised as IGP lyase, which catalyses the formation of free indole from IGP and the induction pattern of *Igl* parallels the emission of free indole

from the whole plant (Frey et al., 2000). The effect of wounding on indole emission is relatively small and this response could indicate that a certain threshold of *Igl* induction has to be exceeded for notable indole production to occur (Frey et al., 2000) (Fig. 2, branch D).

Other aromatic VOCs include phenylalanine-derived compounds. Eugenol is a reduced version of coniferyl alcohol, a lignin precursor, while phenylacetaldehyde, a compound present in tomato fruit, is derived from phenylalanine by decarboxylation and oxidative removal of the amino group (Pichersky et al., 2006). Propenyl- and allyl-phenols, such as methyl chavicol (estragole), *p*-anol as well as eugenol, have gained importance as flavoring agents and also as putative precursors in the biosynthesis of 9,9'-deoxygenated lignans, many of which have potential medicinal applications (Gang et al., 2001). The biosynthesis of chavicol was shown to occur via the phenylpropanoid pathway to *p*-coumaryl alcohol, which can be reduced to form *p*-dihydrocoumaryl alcohol, followed by dehydration to afford chavicol, as well as formation of *p*-methoxycinnamyl alcohol, with further side-chain modification to afford methyl chavicol (Vassao et al., 2006) (Fig. 2, branch E).

SA is synthesized by two pathways: one deriving from benzoate via cinnamate, the other via isochorismate. MeSA is synthesized via a reaction catalyzed by a methyltransferase whereby a methyl group is transferred from the donor molecule *S*-adenosine-methionine (SAM) to the carboxyl group of SA. SA methyltransferase (SAMT) has been characterized in several plant species including the model plant *Arabidopsis* (Vassao et al., 2006) (Fig. 2, branch E and F).

VOCs derived by oxidative cleavage and decarboxylation of various fatty acids result in the production of shorter-chain volatiles with aldehyde and ketone moieties that often serve as precursors for the biosynthesis of other VOCs (Pichersky et al., 2006).

Besides detection, isolation and characterisation of enzymes and genes involved in the formation of many VOCs, the structures of enzymes after crystallisation are now being investigated and this information gives us hints on the catalytic mechanisms as well as probable evolutionary origins of these enzymes (Petersen, 2007).

5. Induced production of VOCs

While flower scents are usually released in an ontogenetically programmed way, the quantity and quality of VOCs that are released from vegetative plant parts and roots can change dramatically when plants are stressed (Heil, 2008). In induced processes, rather than in the case of constitutive defenses, the recognition of the attacking insect and the subsequent signaling of the alarm is the prerequisite for a fast and efficient defense. Many forms of induced defense are not restricted to local responses at the wounding site, but can be detected systemically throughout the plant. Thus, induced defenses also involve the synthesis and accumulation of various VOCs that influence insect attraction/deterrence and inhibit insect growth and development.

There are two types of plant inducible defenses: direct defenses and indirect defenses. Direct defenses include any plant

traits that by themselves affect the susceptibility of host plants to insect attacks (Kessler and Baldwin, 2002), whereas indirect defenses include plant traits that by themselves do not affect the susceptibility of host plants, but can serve as attractants to natural enemies of the attacking insect (Chen, 2008). After release from leaves, flowers, and fruits to the atmosphere and from roots into the soil, plant VOCs defend plants against herbivores and pathogens or provide reproductive advantages by attracting pollinators (Chen, 2008). Moreover, certain volatiles may act as airborne signals that boost direct and indirect defenses in remote parts of the same plants or neighboring plants (Heil and Silva Bueno, 2007; Ton et al., 2007). However, it has to be noted that herbivore-induced emission of plant VOCs is not limited to higher plants. It has been recently shown the arsenic hyper-accumulating fern, *Pteris vittata* responds to herbivore wounding events by emitting several sesquiterpenes (Imbiscuso et al., 2009). The same sesquiterpenes are used by higher plants to attract insects in the field (Il'ichev et al., 2009).

Insect egg deposition induces a plant volatile pattern that attracts egg parasitoids and induces the change of plant surface chemicals, thus arresting the egg parasitoids by contact cues in the vicinity of the eggs (Hilker and Meiners, 2002, 2006). Indirect plant responses to insect egg deposition require modification of the biosynthetic activity of the terpenoid pathways, since changes of the quantity and/or quality of the plant's terpenoid volatiles have been detected for several plant species with eggs (Fatouros et al., 2008).

Generally speaking, inducible defenses consist of three steps: surveillance, signal transduction, and the production of defensive chemicals (Chen, 2008). In the first step, the plant's surveillance system detects parasite attacks by specific recognition of signals. The detected signals are then transduced through a network of signal transduction pathways, which eventually lead to the production of defense chemicals (Maffei et al., 2007a,b; Wu and Baldwin, 2009). In all cases, induction of plant VOC can be triggered by both biotic and abiotic stress (Arimura et al., 2009). In the next sections we will examine the role of induced VOCs in plant defense against pathogens and piercing/sucking/chewing herbivores as well as the induced physiological response of VOCs to environmental stresses.

5.1. Plant VOCs and the response to biotic stress

The VOC bouquet of biotically stressed plants typically consists of green leaf volatiles (GLVs), terpenoids, methyl jasmonate (MeJA), MeSA, methanol, ethylene, and other substances. Total VOC emission from herbivore-damaged plants can be nearly 2.5-fold higher than emissions from intact plants and this observation also sustains the hypothesis that local biotroph-induced VOCs might have substantial role in tropospheric processes (Holopainen, 2004). The insect feeding-induced emission of volatiles has been demonstrated for several higher plant species (Van Poecke and Dicke, 2004b), among others the model plant *A. thaliana* (Van Poecke and Dicke, 2004a), maize (*Zea mays* L.) (Turlings et al., 1990), Lima bean (*P. lunatus*) (Arimura et al., 2008b), *Nicotiana attenuata* Torr. (Kessler and Baldwin, 2001; Gaquerel et al., 2009; Wu and Baldwin, 2009),

Medicago truncatula Gaertn. (Arimura et al., 2008a), and spruce (*Pinus glabra* Walter) (Martin et al., 2003), as well as for lower plants like ferns (Imbiscuso et al., 2009). In general, VOCs can carry various types of information: (I) for herbivores to localize their host plants, (II) for indirect defense employing a third trophic level by attracting natural enemies of the plant's offender, and for (III) neighboring plants and (IV) distant parts of the same plant, respectively, to adjust their defensive phenotype accordingly (Heil and Silva Bueno, 2007). Herbivore-induced VOCs represent phenotypically plastic responses of plants to herbivory, which result in changes in interactions between individuals in the insect–plant community (Snoeren et al., 2007). Moreover, genetic variations within herbivore species affect VOCs production and there is a relationship between variations in the dispersing behavior of some insects (e.g. spider mite) and VOCs production (Maeda et al., 2007).

Using VOCs as the only source of information, carnivores can discriminate between plants infested by different herbivore species (e.g. hosts and non-hosts) and between different plants infested by the same herbivore. However, it must be considered that the majority of herbivore-induced VOCs are also constitutively released from flowers (Dudareva et al., 2006; Pichersky et al., 2006). Overall, the current picture demonstrates a high functional diversity in VOC-mediated communication within and among organisms, but it leaves us with the open question of how misunderstandings in all these communications are avoided (Heil and Silva Bueno, 2007).

Some insects can locate their hosts even though the host plants are often hidden among an array of other plants, and plant volatiles play an important role in this host-location process (Bruce et al., 2005). Furthermore, these VOC-mediated interactions of plants with organisms of higher trophic levels suggest that they communicate similarly with each other (Maffei et al., 2007b). However, VOC exposure alone, without actual herbivore attack, may directly increase the production of defenses. Alternatively, VOC exposure may allow nearby plants to ready their defenses for immediate use once the herbivores move from the neighboring plant to attack the “listening” receiver (Arimura et al., 2000; Baldwin et al., 2006; Heil and Silva Bueno, 2007; Gaquerel et al., 2009; Wu and Baldwin, 2009).

Volatiles from primary host plants may also attract other insects, as is the case of male aphids (Powell and Hardie, 2001; Powell et al., 2006). Parasitoids also use herbivore-induced responses to assess habitat profitability and adapt patch residence time (Tentelier and Fauvergue, 2007). Furthermore, herbivore-induced plant volatiles emissions are inducible by other biotrophs as well as abiotic agents (Holopainen, 2004) (see next section).

Some substances are immediately released after damage and cause the characteristic odor of freshly mowed pastures, the so called GLVs (Arimura et al., 2009). GLVs seem not to be enhanced by elicitors, and, therefore, their release has been described as instantaneous “bleeding” from damage sites. However, two related herbivores can lead to the emission of distinctive ratios of GLVs in the same plant species (Degen et al., 2004). A rapid formation of C₆-volatiles after wounding not

only serves as protection against herbivores or pathogens, but may also be toxic for the plant itself. The majority of GLVs are isomers of hexenol, hexenal or hexenyl acetate. Some preformed GLVs ‘bleed’ instantaneously from disrupted tissue, but the rest of these compounds are released rapidly upon damage, since the first intermediate of the octadecanoid cascade, 13-hydroperoxylinolenic acid, also acts as an intermediate for the synthesis of 6-carbon volatiles (Walling, 2000; Gatehouse, 2002). In contrast, the release of esters such as MeJA and MeSA, of monoterpenes such as limonene, linalool or β -ocimene, and of sesquiterpenes, such as α -bergamotene, β -caryophyllene and farnesene, typically starts 24 h after attack (Dudareva et al., 2006; Pichersky et al., 2006). Growth conditions (particularly daylength) may affect the ratio of VOCs present in the emission blend, even though the response to herbivory and nutrient availability are similar (Ibrahim et al., 2008). Transgenic *Arabidopsis* plants with an altered biosynthesis for GLV showed striking responses when subjected to herbivory and HPL sense plants showed a significant increase in GLV production after herbivory, compared with controls. By contrast, in HPL antisense *Arabidopsis* plants GLV formation decreased and attracted fewer parasitoids than the control (Shiojiri et al., 2006). These data indicate that the genetic modification of VOCs biosynthesis could be an approach to improve plant and, in particular, crop resistance against pest attacks. Induced resistance is often associated with the ability for a faster and stronger activation of defense responses upon an attack by pathogens or insects. This physiological state is referred to as priming (Heil and Silva Bueno, 2007; Ton et al., 2007). Priming of corn plants by GLV released from damaged plants caused yet undamaged corn plants to produce JA and VOCs more intensively and rapidly in response to caterpillar-caused damage compared with plants that were damaged without this pre-treatment.

The type of feeding damage clearly affects the VOCs produced, and a part of the biochemical explanation is that leaf chewers in general induce only JA signaling, while piercing-sucking herbivores and pathogens tend to induce salicylic acid-mediated resistance pathways as well (Smith and Boyko, 2007). Indications for a role of JA for pathogen defense in potato arose from reports that exogenous application of JA leads to local and systemic protection against subsequent pathogen attack (Cohen et al., 1993; Pozo et al., 2004). The blend of volatile compounds emitted by tomato plants infested with the potato aphid (*Macrosiphum euphorbiae* Thomas) has been studied comparatively with undamaged and aphid-infested plants. Aphid-infested plants were significantly more attractive towards *Aphidius ervi* Haliday than undamaged plants. However, collection of the volatiles and analysis by gas chromatography revealed only quantitative differences between uninfested and aphid-infested plants (Sasso et al., 2007; Guerrieri and Digilio, 2008).

Also plant pathogens induce the production of VOC, which because of their antimicrobial activities probably inhibit the spread of the pathogen into plant tissues. In addition, tomato mutants deficient in the biosynthesis of the octadecanoid pathway are highly susceptible to small leaf-feeding mites and thrips whereas MeJA treatment restores resistance (Holopainen, 2004).

Several tomato VOCs produced by leaves such as 2-hexenal, 2-nonenal, 2-carene, β -caryophyllene, β -phellandrene, guaiacol, MeSA, benzyl alcohol, and eugenol, are effective in inhibiting the pathogen *Botrytis cinerea*. Among these constituents, 2-hexenal and 2-nonenal showed the strongest inhibitory effect. Some VOCs, such as 2-hexenal and MeSA, are plant-produced signals that activate plant defense genes (He et al., 2006).

In general, VOCs can be considered as infochemicals that mediate many interactions in a plant–insect community, both above and below ground (Bezemer and van Dam, 2005). Because volatile isoprenoids are reactive, and are likely to undergo rapid changes and transformations (physical, chemical and/or biological) in the soil system, a considerable proportion of rhizosphere sources of VOCs may not diffuse through soil to the atmosphere (Lin et al., 2007). Feeding on roots even can induce changes in the volatile bouquet released from the aerial parts of a plant, although the ecological relevance of this observation remains elusive (Soler et al., 2007a, b) and the potential abundance and specific effects of VOCs in the rhizosphere environment are still not known. Due to the lack of reliable sampling, there have been few direct measurements of monoterpene emissions or exudations from root systems in natural environments, or even from roots of plants growing in pots (Lin et al., 2007). The rhizosphere of *Pinus* species is a strong and previously un-characterized source of volatile isoprenoid emissions and these are likely to impact significantly on rhizosphere function (Lin et al., 2007). In general, below ground interactions and their putative impact on above ground events and activities (and vice versa) is a topic of increasing interest and worth to be more intensively investigated (Mithoefer et al., 2009). Even below ground the emission of volatiles is an efficient trait: in maize roots the sesquiterpene (*E*)- β -caryophyllene is necessary to attract entomopathogenic nematodes to roots damaged by the ferocious maize pest *Diabrotica virgifera virgifera* Le Conte (Fig. 3). Maize varieties that lack this signal have been shown to be far more vulnerable to maize pest (Rasmann et al., 2005; Rasmann and Turlings, 2007). In Vetiver roots, emission of a complex blend of sesquiterpene hydrocarbons and alcohols repels insects and protect the plant from microbial attacks (Maffei, 2002; Del Giudice et al., 2008). Studying the effects of belowground herbivory on aboveground tritrophic signaling and vice-versa emphasizes the important role of plants in bridging interactions between spatially distinct components of the ecosystem (Rasmann and Turlings, 2007).

Plants that are merely primed for enhanced defense after the reception of distress signals, for example via VOCs from nearby plants or adjacent leaves, are better protected in an environment of herbivore pressure, without suffering from costly energy investments in defense mechanisms. The phenomenon of volatile-induced priming against insects also fits in the ecological context of costs and benefits. Therefore, an additional agronomical benefit can be expected if the emissions of the appropriate volatiles were to be enhanced in crop plants (Turlings and Ton, 2006).

Plant VOCs that have elicited antennal responses were also attractive to parasitoids in behavioral experiments. The summed

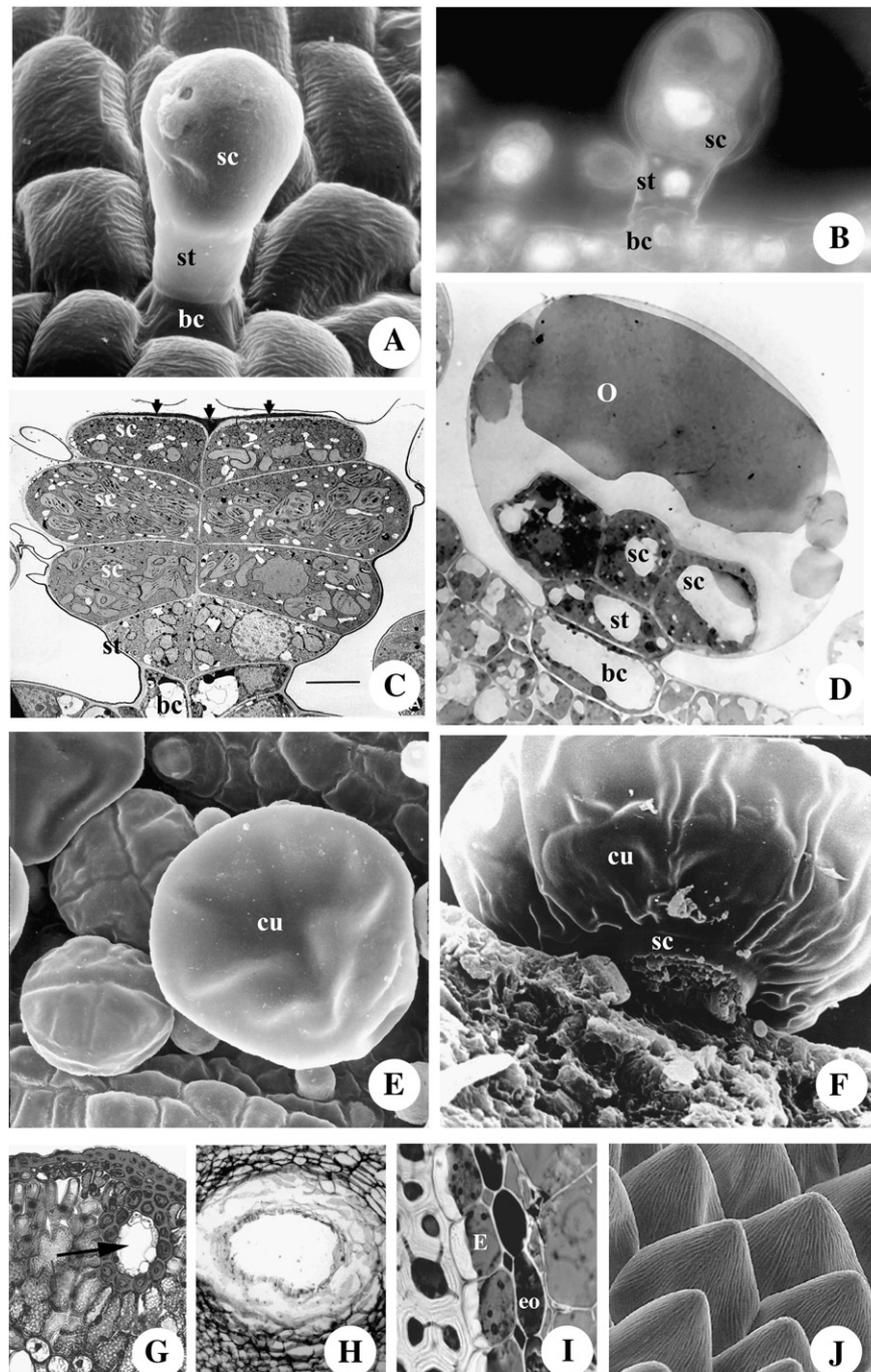


Fig. 1. Secretory structures producing VOCs in higher plants. (A) Capitate glandular trichome present on the leaf surface of *Mentha lavanduliodora* Sacco. (B) DAPI staining reveals polymorphic nuclei in the secretory cells of capitate glandular trichomes in *Mentha x piperita* L. (C) Cross-section of a biseriolate glandular trichome of *Artemisia annua* L.; arrows indicate a dense osmiophilic deposit in the extracellular space facing the secretory cells [(from Duke et al., 2000), reprinted with permission]. (D) Cross section of a monoseriate glandular trichome of *Mentha spicata* L.; the essential oil accumulates in the subcuticular space between the cuticle and the secretory cell's cell wall. Oil droplets accumulate and merge into a single essential oil deposit. (E) Scanning electron microscopy view of developing stages of glandular trichomes in *M. lavanduliodora* Sacco; young trichomes show cell divisions and the lack of essential oil accumulation. (F) Scanning electron microscopy view of a mature glandular trichome in *M. lavanduliodora* showing particulars of the stalk cell. (G) Needles of gymnosperms show the presence of resin ducts; arrow indicates the cavity where resin is secreted. (H) Citrus fruit skin shows the presence of secreting cavities of lysigenous origin. (I) Cross-section of a *Vetiveria zizanioides* root stained with Sudan Black B, showing oil-producing cells within the last layer of the cortical parenchyma. (J) Scanning electron micrograph of conical cells from the inner epidermis of *Antirrhinum* flower petals [(from (Kolossova et al., 2001), reprinted with permission)]. bc = basal cell; cu = cuticle; E = endodermis; eo = essential oil-storing cells; O = drop of essential oil; sc = secretory cell; st = stalk cell.

neural activity of antennal olfactory receptors can be measured using the gas chromatography-electroantennographic detection (GC-EAD) technique. Using plants upon which herbivores are

feeding and investigating by GC-EAD the VOCs released, it is possible to identify a range of compounds that are electrophysiologically active and which may subsequently prove to be

active in behavioural assays as repellents of insect pests (Mithoefer et al., 2009). Although electrophysiological techniques have the advantage of online identification of the electrophysiologically active VOCs, these compounds are not always behaviorally active to insects (Bjostad, 1998). The behavioral significance of these compounds therefore needs to be evaluated in behavioral experiments. Y-tube olfactometric assays demonstrated that headspace volatile extracts collected from leaf miner-damaged, or artificially damaged, bean plants were more attractive to naive females of the parasitoid insect *Opius dissitus* than those collected from healthy plants (Bjostad, 1998).

Aerial interaction of the wild tobacco (*N. attenuata*) and sagebrush (*Artemisia tridentata* subsp. *Tridentata* Nutt.) is the best-documented example of between-plant signaling via above-ground VOCs in nature but at the same time highlights the difficulty of predicting how plant–plant signaling functions from first principles (Baldwin et al., 2006) (Table 1).

5.2. Plant VOCs and responses to abiotic stress

Independent of tissue damage by other organisms, numerous plants emit VOCs in response to light and temperature changes or other abiotic stresses, like flooding or drought (Ebel et al., 1995; Holzinger et al., 2000; Kreuzwieser et al., 2000; Gouinguene and Turlings, 2002; Teuber et al., 2008). Environmental effects on the emission responses can be caused

by temperature-dependent increases in the volatility and diffusion rates of specific compounds or by the pool size of specific leaf volatiles (Niinemets et al., 2004). However, the composition of the herbivore-induced volatiles also strongly depends on other abiotic factors, such as the availability of nitrogen and phosphorous (Schmelz et al., 2003), soil salinity and pH as well as air humidity (Vallat et al., 2005). In fact, limited water availability can restrict VOC biosynthesis, while more severe drought reduces emissions (Owen and Penuelas, 2005). Furthermore, the treatment of some plants with heavy metals (Hg^{2+} , Cu^{2+} , and Fe^{3+}) results in a characteristic blend of volatiles (Engelberth et al., 2001).

The elevating atmospheric CO_2 concentration results in the warming of the lower atmosphere, which might lead to a higher emission of VOCs from plants and other factors, such as temperature, light and herbivores might conceal the effects of CO_2 (Scholefield et al., 2004; Vuorinen et al., 2005). However, VOC emissions that are induced by the leaf-chewing herbivores are not always influenced by elevated CO_2 concentration (Vuorinen et al., 2004). Leaf photosynthetic properties may confer a valuable basis to model the seasonal variation of VOC emission capacity; especially in tropical regions where the environmental conditions vary less than in temperate regions (Kesselmeier et al., 2002; Kuhn et al., 2004). Further consequences of reduced photosynthetic gas exchange and maintaining VOC emissions are a very high carbon loss, up to 50%, from VOC emissions related to net CO_2 uptake and a

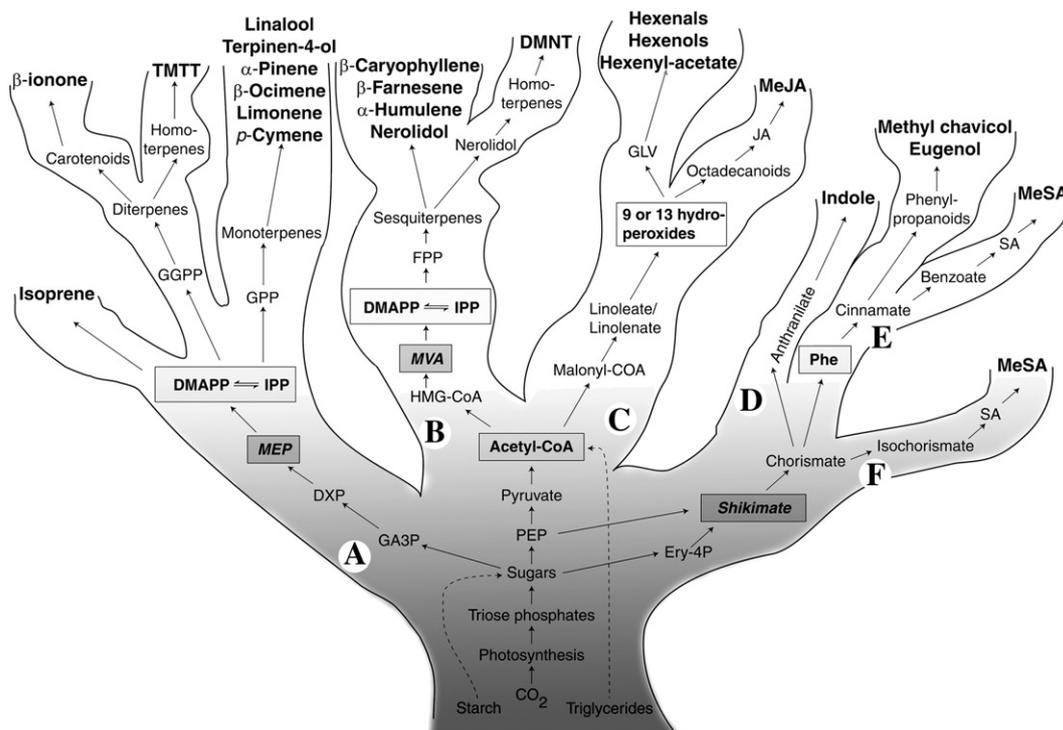


Fig. 2. The volatilome tree. Branch (A) VOCs are produced by different biochemical pathways. The MEP pathways give rise to the formation of monoterpenes and diterpenes. The latter are precursors of the homoterpene TMTT and of the carotenoid-derived β -ionone. Isoprene is generated from DMAPP. Branch (B) sesquiterpenoids are generated by FPP derived from the cytosolic MVA pathway. The homoterpene DMNT derives from the sesquiterpene nerolidol. Branch (C) oxylipins generate from fatty acids which are cleaved into GLVs and JA derivatives. Branch (D) the volatile indoles generate from anthranilate. Branch (E) aromatic VOCs such as eugenol derive from phenylpropanoids, whereas MeSA derived from SA generated from benzoic acid. Branch (F) alternatively, MeSA can be formed by methylation of SA deriving from isochorismate.

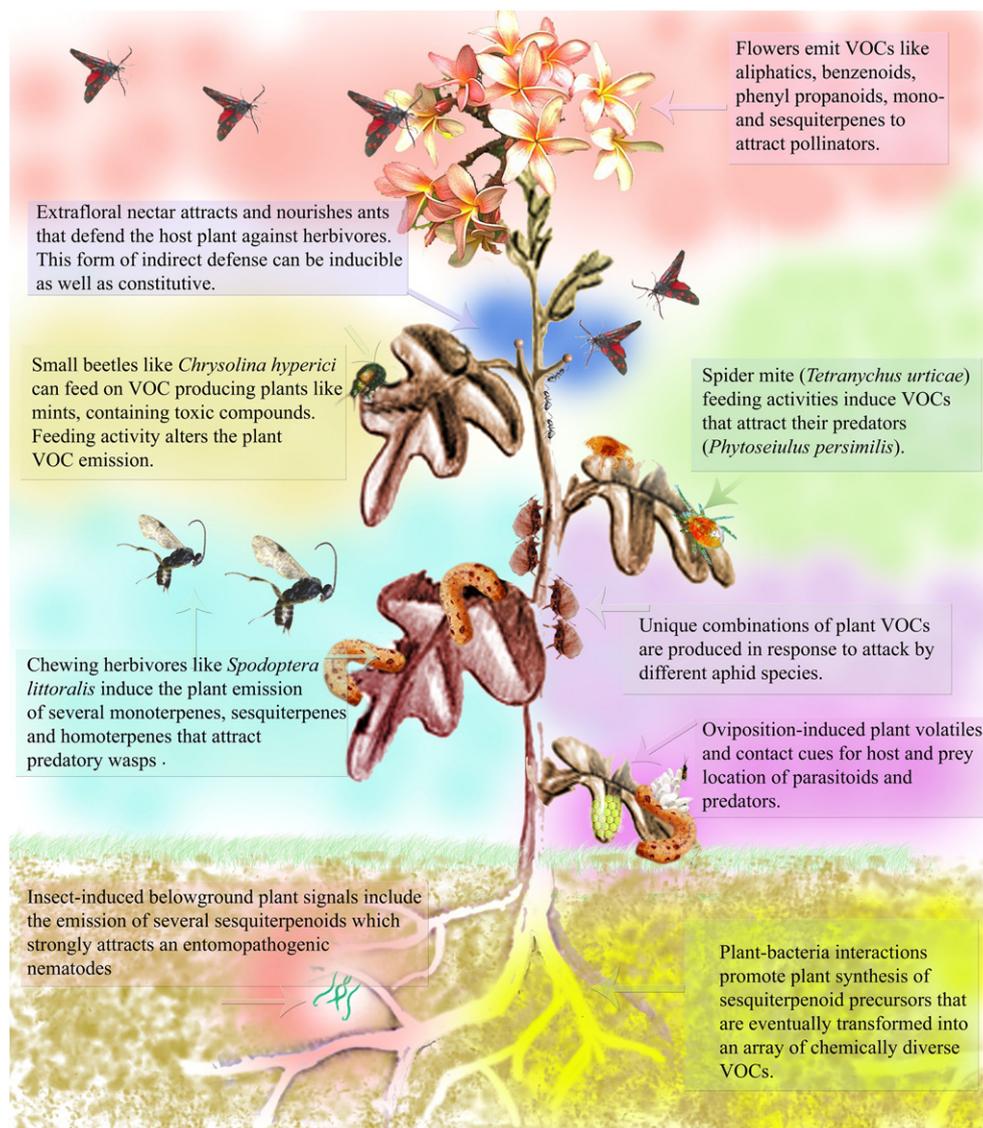


Fig. 3. Functional role of plant VOCs. Plants emit a wide array of volatile compounds for pollinator's attraction and in response to biotic and abiotic stress. Flowers emit compounds belonging to several major classes of VOCs to attract pollinators (Knudsen et al., 2006). Extrafloral nectaries attract both ants and butterflies and their activation is inducible by insect herbivory (Kost and Heil, 2008). Several beetles, such as *Chrysomela menthastris* and *C. hyperici*, feed on aromatic plants despite their toxic compounds and induce increased VOC plant emissions. Aphids feeding on plants trigger the emission of several monoterpenes and homoterpenes (Sasso et al., 2007). Sucking herbivore like spider mites induce VOC emissions that attract their predators (Arimura et al., 2000). Chewing herbivores like *Spodoptera littoralis* induce the plant emission of several monoterpenes, sesquiterpenes and homoterpenes that attract predatory wasps (Arimura et al., 2000). Oviposition-induced plant volatiles and contact cues for host and prey location of parasitoids and predators (Hilker and Meiners, 2006). Insect-induced belowground plant signals include the emission of several sesquiterpenoids which strongly attracts an entomopathogenic nematode (Rasmann et al., 2005). Plant-bacteria interactions promote plant synthesis of sesquiterpenoid precursors that are eventually transformed into an array of chemically diverse VOCs (Del Giudice et al., 2008).

strong increase in leaf internal isoprene concentrations (Teuber et al., 2008). It has been demonstrated that transgenic non-isoprene-emitting poplars show reduced rates of net assimilation and photosynthetic electron transport during heat stress, but not in the absence of stress. The decrease in the efficiency of VOCs has been inversely correlated with the increase in heat dissipation of absorbed light energy, measured as non-photochemical quenching (NPQ). Down-regulation of isoprene emission has been shown to affect thermotolerance of photosynthesis thus inducing increased energy dissipation by NPQ pathways (Behnke et al., 2007). It has been hypothesized

that VOCs like isoprene may stabilize thylakoid membranes and/or may exert antioxidant properties thus increasing plant tolerance to environmental stresses. The involvement of isoprene in non-enzymatic plant defense strategy has also been suggested (Velikova, 2008). Isoprene appears to act on photosynthetic membranes to protect against thermal damage (Singsaas and Sharkey, 2000; Sharkey et al., 2001).

Although the phytotoxic impact of ozone on plants has been well documented, the effect of O_3 on plant VOC emissions has received little attention. Chronic exposure to moderately increased concentrations of ozone on insect induced terpene

Table 1
Some selected examples of the functional role of plant volatiles.

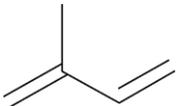
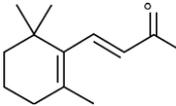
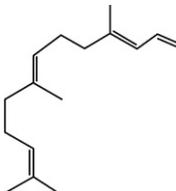
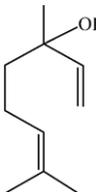
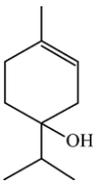
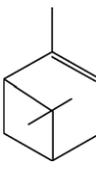
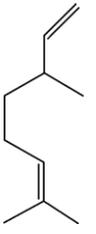
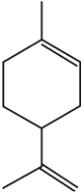
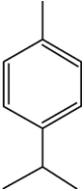
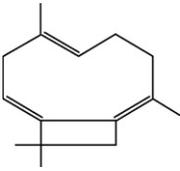
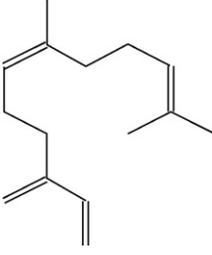
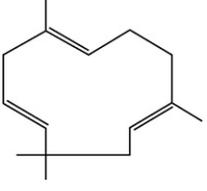
VOC class	Biochemical pathway	Biosynthetic site (tissue types)	Defense compound name; Constitutive (C), Induced (I)	Structure formulae	Infochemical interactions	Reference
Emiterpene	MEP	Chloroplast (mesophyll cells)	Isoprene (C,I)		Thermotolerance. Tolerance of ozone and other reactive oxygen species. 'Safety valve' to get rid of unwanted metabolites.	(Sharkey et al., 2008; Velikova, 2008)
Apocarotenoid	MEP and carotenoid cleavage products (CCPs)	Necrotic lesions of leaf tissues; flowers	β -ionone (C, I)		Repellent against <i>Phyllotreta cruciferae</i> . Inhibits mitochondrial respiration. Inhibits the sporulation and growth of the fungus <i>Peronospora tabacina</i> . Attracts pollinators.	(Bouvier et al., 2005; Gruber et al., 2009)
Homoterpene	MEP	Herbivore and microbe wounded tissues.	4,8,12-trimethyltrideca-1,3,7,11-tetraene (TMTT) (I)		Involved in indirect defence in a number of plants, such as maize [<i>Zea mays</i> (L.)], tomato (<i>Solanum lycopersicum</i> L.), lima bean (<i>Phaseolus lunatus</i> L.), and broad bean (<i>Vicia faba</i> L.). Induced by treatment with jasmonic acid, 12-oxo-phytodienoic acid (OPDA), or linoleic acid.	(Arimura et al., 2009; Moraes et al., 2009)
Monoterpene	MEP	Glandular trichomes, mesophyll wounded tissues, chloroplasts	Linalool (C, I)		Repels aphids. Electrophysiologically active compound. Alarm pheromone inhibitor. Increases after attack from <i>Dioryctria sylvestrella</i> . Released from maize by <i>Spodoptera exigua</i> damage.	(Kleinhentz et al., 1999; Degenhardt and Gershenzon, 2000; Aharoni et al., 2005; Webster et al., 2008)
Monoterpene	MEP	Glandular trichomes, mesophyll wounded tissues.	Terpinen-4-ol (C, I)		Causes a significant increase in male <i>Eupoecilia ambiguella</i> upwind flying to the pheromone source. Elicits electroantennogram responses. Displays toxic effects against <i>Tribolium confusum</i> fecundity and egg hatchability.	(Tunc and Erler, 2003; Stamopoulos et al., 2007; Schmidt-Busser et al., 2009)
Monoterpene	MEP	Glandular trichomes, resin ducts, mesophyll wounded tissues.	α -pinene (C, I)		Repels the spruce beetle <i>Dendroctonus rufipennis</i> at high concentrations, but intermediate concentrations elicit entry and gallery construction. Elicits olfactory receptor neurons of the weevil <i>Pissodes notatus</i> . Enhances attraction by <i>Thanasimus dubius</i> , <i>Platysoma cylindrica</i> , and <i>Corticium parallelus</i> to the pheromones of their <i>Ips</i> prey.	(Erbilgin and Raffa, 2001; Bichao et al., 2003; Wallin and Raffa, 2004)
Monoterpene	MEP	Glandular trichomes, mesophyll wounded tissues.	β -ocimene (C, I)		Exposure of <i>Arabidopsis thaliana</i> to the monoterpene causes increased abundance of several gene transcripts and increased plant resistance against the pathogen <i>Botrytis cinerea</i> . Genes of the octadecanoid pathway and genes known to respond to octadecanoids are among the most prevalent within the stress-gene category up-regulated in <i>Arabidopsis</i> . The β -ocimene synthase is induced in	(Faldt et al., 2003; Arimura et al., 2004, 2009; Godard et al., 2008)

Table 1 (continued)

VOC class	Biochemical pathway	Biosynthetic site (tissue types)	Defense compound name; Constitutive (C), Induced (I)	Structure formulae	Infochemical interactions	Reference
Monoterpene	MEP	Glandular trichomes, secretory ducts, mesophyll wounded tissues.	Limonene (C, I)		<i>Lotus japonicus</i> plants infested with two-spotted spider mites (<i>Tetranychus urticae</i>). Induced oviposition on aphid-free plants. Selection of the oviposition site by predatory hoverflies relies on the perception of a volatile blend composed of prey pheromone and typical plant green leaf volatiles. Elicits olfactory receptor neurons of the weevil <i>Pissodes notatus</i> . Involved in the selective herbivory on the conifer <i>Pinus caribaea</i> by the leaf-cutting ant <i>Atta laevigata</i> .	(Barnola et al., 1997; Bichao et al., 2003; Verheggen et al., 2008)
Monoterpene	MEP	Glandular trichomes, mesophyll wounded tissues	<i>p</i> -cymene (C, I)		Elicits a response of receptors on <i>Bemisia tabaci</i> (whitefly) antennae as determined by electroantennography. Significantly higher in tomato lines with a higher repellence level. Toxic agent for the western flower thrips (<i>Frankliniella occidentalis</i>). Repellent against mosquitoes.	(Janmaat et al., 2002; Park et al., 2003; Bleeker et al., 2009)
Sesquiterpene	MVA	Glandular trichomes, secretory cells, mesophyll and root wounded tissues	β -caryophyllene (C, I)		Elicits electroantennogram responses. Involved in insect host location. Involved in the selective herbivory on the conifer <i>Pinus caribaea</i> by the leaf-cutting ant <i>Atta laevigata</i> . Below ground signal emitted by insect-damaged maize roots. Induced by a plant pathogen and perceived by its vector insect, the phloem-feeding psyllid <i>Cacopsylla picta</i> . Biotransformed by plant-hosted bacteria. Released by <i>Arabidopsis</i> upon insect feeding.	(Barnola et al., 1997; Bichao et al., 2003; Del Giudice et al., 2008; Webster et al., 2008; Mayer et al., 2008a,b; Schmidt-Busser et al., 2009; Degenhardt et al., 2009; Abel et al., 2009)
Sesquiterpene	MVA	Glandular trichomes, secretory cells, mesophyll and root wounded tissues	β -farnesene (C, I)		Common aphid alarm pheromone, the major example of defence communication in the insect world. Produced in response to feeding <i>Spodoptera littoralis</i> on the fern <i>Pteris vittata</i> . Behavioral and electrophysiological responses of winged <i>Aphis fabae</i> to volatiles of faba bean. Biosynthesized de novo following insect damage.	(Pare and Tumlinson, 1997a; Kunert et al., 2005; Webster et al., 2008; Verheggen et al., 2008; Imbiscuso et al., 2009)
Sesquiterpene	MVA	Glandular trichomes, secretory cells, mesophyll and root wounded tissues	α -humulene (C, I)		Produced in high amounts in response to simultaneous herbivory by the piercing-sucking insect western flower thrips <i>Frankliniella occidentalis</i> and the chewing herbivore <i>Heliothis virescens</i> . Produced by a recombinant insect-induced gene (<i>AlCarS</i>) with high sequence similarity to the florally expressed (E)- β -caryophyllene synthase.	(Delphia et al., 2007; Abel et al., 2009)

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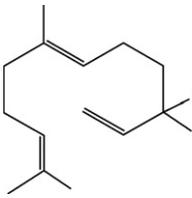
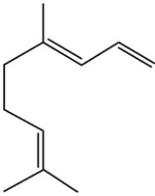
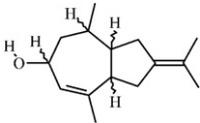
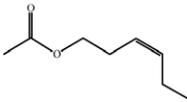
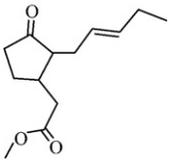
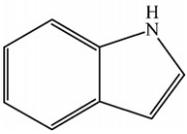
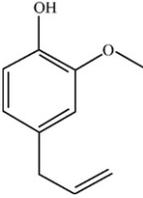
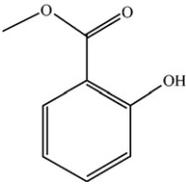
VOC class	Biochemical pathway	Biosynthetic site (tissue types)	Defense compound name; Constitutive (C), Induced (I)	Structure formulae	Infochemical interactions	Reference
Sesquiterpene	MVA and MEP	Glandular trichomes, secretory cells, mesophyll wounded tissues	E-nerolidol (C, I)		Precursor of DMNT. Released from maize by <i>Spodoptera exigua</i> damage. Induced in transgenic Bt (expressing the cry1Ac endotoxin gene) and conventional oilseed rape leaves infested with the third instar larvae of Bt-susceptible <i>Plutella xylostella</i> . Induces specific responses in the sensilla trichodea of the <i>Cactoblastis cactorum</i> females.	(Degenhardt and Gershenzon, 2000; Pophof et al., 2005; Bartram et al., 2006; Ibrahim et al., 2008)
Homoterpene	MVA and MEP	Herbivore and microbe wounded tissues.	4,8-dimethylnona-1,3,7-triene (DMNT) (I)		Detected in the headspace of many plant species after herbivory. Active components in mediating a possible interplant signal transfer. Increases in <i>Fagus sylvatica</i> L. in the presence of the aphid <i>Phyllaphis fagi</i> L. Emitted by <i>Trifolium pratense</i> (red clover) after herbivory by <i>Spodoptera littoralis</i> caterpillars. Major volatile induced in cowpea by neonate fall armyworms, <i>Spodoptera frugiperda</i> , herbivory. Used by birds to locate insect-rich trees in the wild. In birch, leaf fungal pathogen <i>Marssonina betulae</i> does not induce emission as in leaves damaged by larvae of <i>Epirrita autumnata</i> .	(Degenhardt and Gershenzon, 2000; Tschardt et al., 2001; Kappers et al., 2005; Vuorinen et al., 2007; Carroll et al., 2008; Mantyla et al., 2008; Arimura et al., 2009; Kigathi et al., 2009; Joo et al., 2010)
Sesquiterpene	MVA	Root secretory cells	Vetiverol (C, I)		Produced in root cells upon bacterial transformation. Toxic to insects and mammals (rats, mice, rabbits). Potent skin irritant. Phototoxic.	(Zhu et al., 2001; Maffei, 2002; Del Giudice et al., 2008; Bhatia et al., 2008)
Fatty acid derivatives, GLV	Oxylipin pathway	Herbivore and microbe wounded tissues.	Hexenyl-acetate (I)		Induces extrafloral nectar secretion. Increases in response to insect feeding.	(Loughrin et al., 1994; Azuma et al., 1997; Farag et al., 2005; Heil et al., 2008)
Jasmonates	Oxylipin pathway	Secretory tissues, herbivore wounded tissues.	Methyl-jasmonate (C, I)		Released in response to wounding and herbivore attack. The potency of MeJA as an exogenous elicitor of COI1-dependent responses likely reflects its efficient uptake and <i>in vivo</i> conversion to bioactive JA–amino acid conjugates. The complex interplay with the alarm signals salicylic acid and ethylene provides plants with a regulatory potential that shapes the ultimate outcome of plant–microbe and plant–insect interactions. Induces accumulation of proteinase inhibitor (PIN2). Induces swelling of mitochondria and release of cytochrome <i>c</i> .	(Pozo et al., 2004; Kessler et al., 2006; Wasternack, 2007; Katsir et al., 2008)
Indoles	Anthranilate pathway	Wounded tissues	Indole (I)		Biosynthesized <i>de novo</i> following insect damage. Triggered by the fatty acid derivative volicitin in maize. Is attractive to <i>Cortesia marginiventris</i> , a	(Pare and Tumlinson, 1997a; Frey et al., 2000; Gouinguene and Turlings, 2002)

Table 1 (continued)

VOC class	Biochemical pathway	Biosynthetic site (tissue types)	Defense compound name; Constitutive (C), Induced (I)	Structure formulae	Infochemical interactions	Reference
Phenyl-propanoids	Cinnamate pathway	Glandular trichomes and other secretory structures.	Eugenol (C, I)		<p>parasitic wasp that attacks larvae of several species of Lepidoptera.</p> <p>Produced by plants as defense compound against animals and microorganisms and as floral attractants of pollinators.</p> <p>Larvicidal activity against the tobacco armyworm, <i>Spodoptera litura</i>.</p> <p>Repellent against female <i>Culex pipiens pallens</i> adults and against the tick <i>Ixodes ricinus</i> L.</p> <p>In addition to its antimicrobial, antioxidant, antifungal and antiviral activity, possesses antiinflammatory, cytotoxic, and anaesthetic properties.</p>	(Huang et al., 2002; Koeduka et al., 2006; Chaieb et al., 2007; Del Fabbro and Nazzi, 2008; Kang et al., 2009; Bhardwaj et al., 2010)
Semiochemical	Cinnamate and isochorismate pathway	Wounded tissues	Methyl-salicylate		<p>Required for systemic acquired resistance signal perception in systemic tissues.</p> <p>Increase populations of predators and decreased populations of spider mites in grape vineyards and hop yards.</p> <p>In field tests, traps baited with methyl salicylate were highly attractive to adult <i>Coccinella septempunctata</i>.</p>	(James and Price, 2004; Zhu and Park, 2005; Park et al., 2007; Webster et al., 2008; Schmidt-Busser et al., 2009)

emissions indicated only very small changes in emissions, but showed induction of some terpenes, particularly the monoterpene β -ocimene and the homoterpene DMNT, in response to insect feeding (Blande et al., 2007). O₃ can affect phytophagous insect performance and behavior due to changes in the plant physiology and chemistry and the destruction of olfactory cues, disrupting insect chemical communication (Pinto et al., 2007a,b). Recent laboratory studies have shown that exposing Lima bean to ozone increases the emission of the homoterpenes DMNT and TMTT, emissions of which are also induced by spider mite (*Tetranychus urticae* Koch) feeding (Vuorinen et al., 2004). By using a free-air ozone concentration enrichment (FACE) it was found that enhanced O₃ levels activate chemical defenses of some plants, resulting in altered VOC emission profiles, and that a combination of abiotic and biotic stress may substantially increase VOC emission (Blande et al., 2007).

6. Plant VOCs and pollinators' attraction

In order to attract pollinators, plants have evolved the ability to produce a mind-boggling array of VOCs that have also found abundant use for humans when collected as essential oils. Habitat location is generally mediated by long-range cues, such as plant volatiles or herbivore pheromones perceived by olfaction, whereas cues used in the closer vicinity are mostly short-range cues of herbivore products or of the plant surface often perceived by gustatory receptors (Fatouros et al., 2008). The role of VOCs produced by flowers as chemical attractants used to draw in their often highly-specific pollinators has recently been documented, by examining how these compounds

are produced in flowers, detected by potential pollinators, and how biotechnology can be used to alter their activity (Cseke et al., 2007). Since floral VOCs are part of pollination syndromes they represent a very crucial factor to ensure sexual reproduction (Pichersky and Gershenzon, 2002). Moreover, the ability of flowers to attract pollinators from a distance is the reason why VOCs have been retained through natural selection and are found in floral scents (Caissard et al., 2004).

In general, pollinators respond mainly to olfactory cues and researchers have focused on pollinator attraction through combinations of specific floral traits, such as scent and color, in the form of pollination syndromes (Raguso et al., 2003). Visual and olfactory cues often function synergistically to attract pollinators (Majetic et al., 2007) and VOCs are especially useful at night when visual cues become insufficient. The potential impact that pollinators, conserved biosynthetic pathways, and the genetics of small colonizing populations may have in determining population-specific associations between floral color and floral scent has been demonstrated (Majetic et al., 2007).

As pollinator attractants, VOCs are important cues that help insects locate flowers and signal the presence of food or mates. The floral scent chemical compositions of hundreds of species have been enumerated; however, only recently has the molecular genetic basis of the biosynthesis of these compounds begun to be elucidated (Barkman, 2003). Although it seems self-evident that flowers emit scent to attract pollinators, there has been little experimental work to demonstrate the attractiveness of individual scent components to specific pollinators. The role of individual volatiles in pollinator attraction has been

elegantly tested by genetic manipulation of floral emission using appropriate mutants and transformants (Pichersky and Gershenzon, 2002).

In the case of obligate and specific plant–pollinator relationships, the role of floral signals may be crucial in allowing the encounter of the partners. A clear demonstration of floral scent–insect interaction is found in the fig tree (*Ficus* spp.). Because associations between figs and their pollinating wasps are horizontally transmitted, partner encounter is a crucial step, and is mediated by the emission by receptive figs of the volatile compounds that are detected by the pollinator (Proffitt et al., 2008). About 750 *Ficus* species (Moraceae) are involved in such interactions, each with a distinct species of pollinating wasp (Chalcidoidea, Agaonidae). In some cases pollinators of some species are stimulated by the odor of their associated fig species and generally not by the odor of another species (Grison-Pige et al., 2002). In this context, the ability to manipulate floral scent provides a better understanding of qualitative and quantitative changes in VOCs and of the roles of individual volatiles in pollinator attraction. This will also enable to broaden the pollinator attractiveness of important crops that rely on a limited range of insect species for their pollination that cannot be cultivated outside of their natural habitat without additional expenses being invested in artificial pollination techniques. Moreover, customizing floral scent for specialized pollinators will reduce the chance of pollen loss and unsuccessful interspecific pollination, thereby increasing plant reproductive success (Dudareva et al., 2006).

Floral scent headspace samples show the presence of thousands chemical compounds belonging to seven major compound classes, of which the aliphatics, the benzenoids and phenylpropanoids, and, among the terpenes, the mono- and sesquiterpenes, occur in most orders of seeds plants (Knudsen et al., 2006) (Fig. 3). The most common single compounds in floral scent are the monoterpenes limonene, β -ocimene, β -myrcene, linalool, α -pinene, β -pinene, and the benzenoids benzaldehyde, MeSA, benzyl alcohol, and 2-phenyl ethanol, the sesquiterpene β -caryophyllene and the irregular terpene 6-methyl-5-hepten-2-one (sulcatone) (Knudsen et al., 2006). Floral VOCs also provide important guides in the nectar-seeking behavior of butterflies and compounds may have evolved as adaptations to attract pollinating butterflies, thus eliciting a high attractiveness for foraging butterflies (Anderson and Dobson, 2003). For example, lilac aldehyde is also known to elicit strong antennal signals in butterfly species. This compound is emitted in high amounts, especially in nocturnal plant species, and it is known to be highly attractive to the nocturnal moth species *Autographa gamma* L. and *Hadena bicurris* Hufn. (Dotterl et al., 2006). Although electrophysiological techniques have the advantage of online identification of the electrophysiologically active components of volatile blends, these compounds are not always behaviorally active to insects (Bjostad, 1998). Compounds both present in relatively high abundance in the floral scents and detected exclusively in the floral parts of the plant, such as linalool, linalool oxide (furanoid) I and II, oxoisophoroneoxide, and phenylacetaldehyde, elicited the strongest insect antennal responses, suggest-

ing that they may reflect adaptations by the plant to attract butterfly pollinators (Anderson and Dobson, 2003).

7. Concluding remarks

A growing body of evidence indicates that VOCs are important signaling molecules and the deciphering of this chemical information will be of paramount importance for the early detection of plant responses to biotic and abiotic stress, allowing the search for new sustainable methods for pest and environmental control.

Research on the volatile emission by plants shows that VOCs are very potent signaling molecules that have evolved to serve multiple functions. As the great majority of cellular signals origin from membrane proteins within a lipophilic environment, volatile lipids may be privileged to interact with such processes. This is shown by the fact that several VOCs are able to modulate both plant and animal signal transduction pathways. The production of a highly complex blend of VOCs may have started with a plant defense strategy to later evolve to also regulate plant–insect interactions.

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