Chemical and Molecular Ecology of Herbivore-Induced Plant Volatiles: Proximate Factors and Their Ultimate Functions

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In response to herbivory, plants emit specific blends of herbivore-induced plant volatiles (HIPVs). HIPVs mediate sizable arrays of interactions between plants and arthropods, microorganisms, undamaged neighboring plants or undamaged sites within the plant in various ecosystems. HIPV profiles vary according to the plant and herbivore species, and the developmental stages and conditions of the live plants and herbivores. To understand the regulatory mechanisms underling HIPV biosynthesis, the following issues are reviewed here: (i) herbivore-induced formation of plant volatile terpenoids and green leaf volatiles; (ii) initial activation of plant responses by feeding herbivores; and (iii) the downstream network of the signal transduction. To understand the ecological significance of HIPVs, we also review case studies of insect–plant and inter-/intraplant interactions mediated by HIPVs that have been documented in the field and laboratory in recent years.

Keywords: Green leaf volatile (GLVs) • Herbivore-induced plant volatile (HIPVs) • Indirect defense • Insect oral factor • Terpenoid (terpene).

Abbreviations: AOS, allene oxide synthase; DMNT, (E)-4,8-dimethyl-1,3,7-nonatriene; ER, endoplasmic reticulum; FAC, fatty acid–amino acid conjugate; FDP, farnesyl diphosphate; GDP, geranyl diphosphate; GGDP, geranylgeranyl diphosphate; GLV, green leaf volatile; GST, glutathione S-transferase; Hex-Ac, (Z)-3-hexen-1-yl acetate; HIPV, herbivore-induced plant volatile; 13HPL, 13-hydroperoxide lyase; 13HPOT, linolenic acid 13-hydroperoxide; IDP, isopentenyl diphosphate; JA, jasmonic acid; LOX, lipoxygenase; MEP, 2-C-methyl-D-erythritol 4-phosphate; MVA, mevalonate; SA, salicylic acid; TMTT, (E,E)-4,8,12-trimethyltrideca-1,3,7,11-tetraene; TPS, terpene synthase; TSSM, two-spotted spider mite.

Introduction

One of the significant aspects of growth and reproduction in plants is defense against herbivorous arthropods. Plants may defend themselves either directly by producing toxins, repellents, digestibility reducers, etc., or indirectly by enhancing the effectiveness of carnivorous natural enemies of herbivores. Such defenses were long considered to be constitutive. Since the 1980s, however, induced defenses, especially indirect defense, have been in the spotlight because of their effectiveness and the impressive arrays of interactions within distinct trophic levels (Karban and Baldwin 1997). One of the well-documented induced indirect defenses of plants against herbivores is to emit specific blends of volatiles in response to herbivory [hereafter called herbivore-induced plant volatiles (HIPVs)] that attract carnivorous natural enemies of the herbivores. HIPVs are also known to mediate sizable arrays of interactions between plants and, for example, arthropods, microorganisms, undamaged neighboring plants or undamaged sites within the plant. So it has been proposed that the ecological significance of HIPVs is probably more complex than initially thought (Takabayashi and Dicke 1996). Furthermore, the blends vary according to the plant and herbivore species, and the developmental stages and conditions of those species, and such specificities and diversity are very important for mediating specific interactions of plants with herbivores, carnivores and other plants (Sabelis et al. 2007).

In the last decade, HIPVs have been looked at again with special interest by plant molecular biologists as well as chemical and behavioral ecologists, and thus a growing body of information on HIPVs has been accumulated. Now we should shed light on the ecological significance of HIPVs by integrating the molecular mechanisms involved in the production (proximate factors) of HIPVs and their ecological functions (ultimate factors). Eventually, such integrated knowledge will give us hints regarding controlling pest insects for sustainable agriculture and for bioenergy production. In particular, we focus here on two major groups of herbivore-induced volatiles, i.e. volatile terpenoids and green leaf volatiles (GLVs), and their ecological functions.

Biosynthesis and regulation of HIPVs

How can plants synthesize a wide diversity of terpenoid compounds?

Terpenoids, derived from a common five-carbon building block (isoprene unit), are some of the most structurally diverse natural products. There are two biosynthetic pathways for terpenoids: the mevalonate (MVA) pathway in the cytoplasm and the 2-*C*-methyl-D-erythritol 4-phosphate (MEP) pathway in the plastids (**Fig. 1**). Both pathways generate the five-carbon compound isopentenyl diphosphate (IDP) and its isomer dimethylallyl diphosphate. Conventional

pathway allocation had suggested that the MVA and MEP pathways are strictly independent. For instance, the cytoplasmic formation of sesquiterpenes (C15) uses IDP derived specifically from the MVA pathway; in contrast, the plastidial formation of monoterpenes (C10) and diterpenes (C20) uses IDP derived from the plastidial MEP pathway. However, there is emerging evidence that the two pathways cross-talk by allowing IDP to be shuttled between different compartments (Piel et al. 1998, Bick and Lange 2003, Bartram et al. 2006). Surprisingly, it appears that ~80% of IDP from the MEP pathway contributes substantially to total sesquiterpene biosynthesis after herbivory (Bartram et al. 2006, Arimura et al. 2008a), indicating a strong contribution of the MEP pathway to sesquiterpene biosynthesis.

The structural diversity of terpenoids is subsequently brought about by the diversity of terpene synthases (TPSs), which utilize the different prenyl diphosphates as substrates to synthesize monoterpenes from geranyl diphosphate (GDP), sesquiterpenes from farnesyl diphosphate (FDP) and diterpenes from geranylgeranyl diphosphate (GGDP) (**Fig. 1**). TPSs are often multiproduct enzymes, and thus even a single TPS can contribute significantly to the plasticity of blends, especially blends produced in response to herbivory (Köllner et al. 2004, Keeling and Bohlmann 2006, Arimura et al. 2008a). As described above, conventional pathway allocation suggests that the monoterpene/diterpene precursors
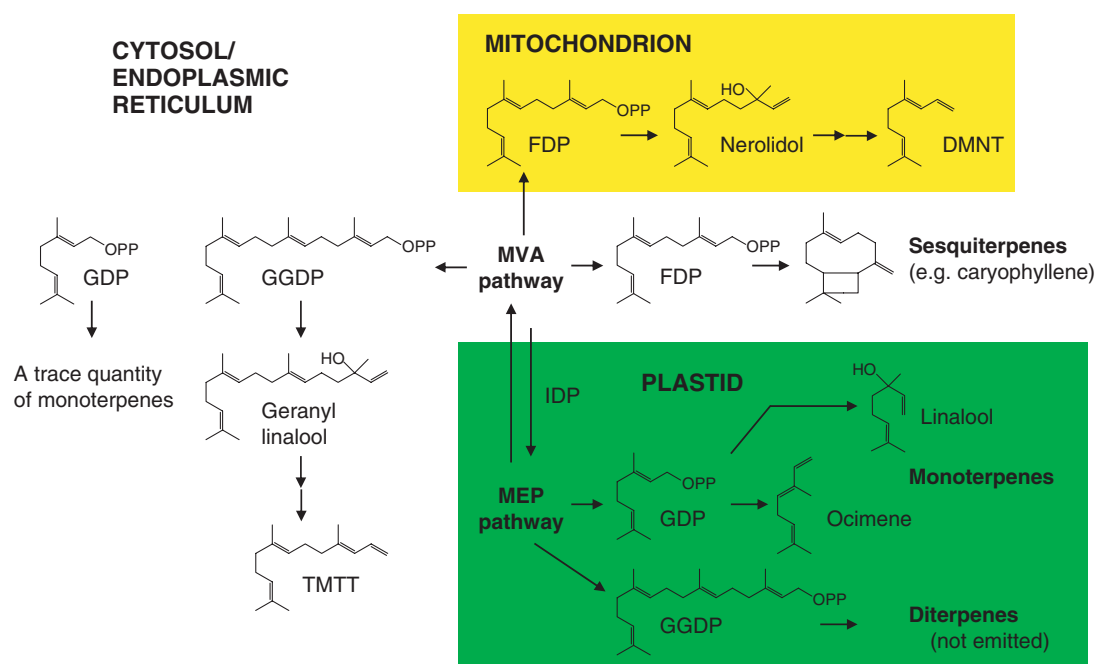

Fig. 1 Schematic representation of the terpenoid biosynthetic pathway in plants. Note that the biosynthetic routes of the homoterpenes (DMNT and TMTT) from nerolidol and geranyllinalool, respectively, are still unclear. DMNT, (*E*)-4,8-dimethyl-1,3,7-nonatriene; FDP, farnesyl diphosphate; GGDP, geranylgeranyl diphosphate; GDP, geranyl diphosphate; IDP, isopentenyl diphosphate; MEP, 2-*C*-methyl-D-erythritol-4-phosphate; MVA, mevalonate; TMTT, (*E,E*)-4,8,12-trimethyltrideca-1,3,7,11-tetraene; TPS, terpene synthase.

(GDP/GGDP) and a sesquiterpene precursor (FDP) are, respectively, provided by the plastidial MEP pathway and the cytosolic MVA pathway. During the last decade, however, several other considerations have been addressed, e.g. the efficient transport of GDP from the plastids to the cytosol (Bick and Lange 2003) and the presence of GDP and GGDP synthases in the cytosol/endoplasmic reticulum (ER) (Bouvier et al. 2000, Okada et al. 2000). Those studies suggest that terpenoid precursors GDP and GGDP can be available in not only plastids but also the cytosol/ER. This gives us a key hint for understanding why the transgenes in transgenic tobacco and Arabidopsis plants expressing limonene (monoterpene) and geranyllinalool [diterpene, the precursor of the C16 homoterpene (*E,E*)-4,8,12-trimethyltrideca-1,3,7,11-tetraene (TMTT)] synthase genes, respectively, can function in the cytosol (Ohara et al. 2003, Herde et al. 2008) (see **Fig. 1**). Furthermore, it was very recently documented that the synthesis of both mono- and sesquiterpenes can be enhanced by the ectopic expression of a single TPS in the cytosolic compartment of tomato fruit (Davidovich-Rikanati et al. 2008). Namely, significant cytosolic targeting of mono- or di-TPSs can occur because of the availability of substrates in those compartments. Nevertheless, it should also be noted that, in transgenic tobacco, cytosol-targeted limonene synthase results in 3-fold lower production of limonene than the plastid-targeted limonene synthase (Ohara et al. 2003). Even in the above-mentioned transgenic tomato fruit, the yield of monoterpenes is ~10% compared with that of sesquiterpenes (Davidovich-Rikanati et al. 2008).

Furthermore, targeting sesqui-TPS (FaNES1) to the mitochondria resulted in the production of nerolidol and its oxidative C11 homoterpene (*E*)-4,8-dimethyl-1,3,7-nonatriene (DMNT), which is emitted after herbivore attack by a wide variety of plant species and plays a role in attracting predators (or parasitoids) (Kappers et al. 2005). As indicated by the presence of mitochondria-targeted FDP synthase and TPS (FaNES2, a homolog of FaNES1) (Aharoni et al. 2004), this cell compartment may also contain a potential pool for sesquiterpene biosynthesis. In summary, product diversification can vary due to possible complexities of both the localization and functionality of TPSs and prenyltransferases (e.g. FDP synthase) in addition to the shuttling of the intermediates (IDP and GDP) between cell compartments. These may contribute to the large array of unique compositions of terpenoid compounds in HIPVs.

Regulation of volatile terpenoid biosynthesis in response to herbivory

Since the blends of HIPVs may vary with the attacking herbivore (De Moraes et al. 1998, Ozawa et al. 2000, Leitner et al. 2005), various components and cross-talk between the involved signaling pathways are thought to be responsible for the characteristic terpenoid blend (Engelberth et al. 2001,

Schmelz et al. 2003, Arimura et al. 2008a). Several oxylipin compounds [jasmonic acid (JA), its precursors, and related compounds] very probably act as master switches for herbivore-stimulated plant responses, activating distinct sets of defense genes leading to terpenoid formation (Ament et al. 2004, van Schie et al. 2007). In lima bean leaves that were damaged by continuous mechanical wounding effected by a robotic device that mimics damage by chewing arthropods, JA, a prominent wound hormone, accumulated locally in direct response to the damage and led to an immediate up-regulation of the ocimene synthase gene (*PlOS*) independent of the light regime (Arimura et al. 2008b). Those findings suggested that there are at least two steps of biosynthetic regulation: by damage-dependent JA levels which directly control the expression level of *PlOS*, irrespective of light or dark conditions, and light-dependent photosynthesis to generate the early precursors of the MEP pathway.

Moreover, synergistic and antagonistic cross-talk among the signaling pathways (Ca^{2+}, JA and ethylene signaling) is involved in terpenoid biosynthesis, and this integrated signaling is responsible for volatile terpenoid formation in plants (**Fig. 2**). When plants are damaged by sucking arthropods (e.g. spider mites or aphids), antagonistic cross-talk of salicylic acid (SA) with JA seems to regulate the biosynthesis of HIPVs in the infested leaves (Ozawa et al. 2000, Leitner et al. 2005, Girling et al. 2008). In *Medicago truncatula*, herbivore-stimulated Ca^{2+} transients serve as a second messenger influencing the composition of terpenoids, whose biosynthesis depends on the JA pathway in caterpillar (chewing arthropod)-damaged leaves (Arimura et al. 2008a). Volatile profiles in *M. truncatula* revealed a sizeable number of different substances emitted, particularly sesquiterpenoids, depending on the type of herbivory (sucking vs. chewing herbivory) (Leitner et al. 2005). The same holds true for JA and SA concentrations: chewing arthropods increase endogenous JA levels but do not significantly induce SA levels, whereas sucking arthropods induce both JA and SA in wild-type plants (Reymond et al. 2004, De Vos et al. 2005, Leitner et al. 2005, Smith and Boyko 2006, De Vos et al. 2007, Runyon et al. 2008). Although several reports suggest overall negative interactions between JA and SA in defense signaling, this cross-talk greatly depends on concentration and timing (Mur et al. 2006).

Ethylene also contributes to the terpenoid biosynthesis induced by chewing caterpillars in at least two ways: by modulating both early signaling events such as cytoplasmic Ca^{2+} influx and the downstream JA-dependent biosynthesis of terpenoids (Arimura et al. 2008a). The first event after leaf feeding is an influx of cytosolic Ca^{2+} in the damaged area (Maffei et al. 2007a). In general, Ca^{2+}-binding proteins (e.g. calmodulins and Ca^{2+}-dependent protein kinases) may secondarily decode information contained in the temporal and spatial patterns of the signals and cause changes in metabolites
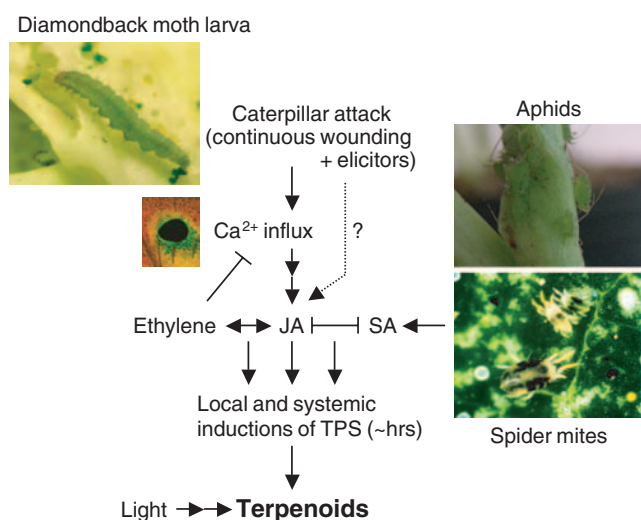
Fig. 2 Model of the signaling network required for terpenoid biosynthesis in chewing arthropod-damaged leaves and sucking arthropod-damaged leaves. Images of the change in leaf Ca^{2+} following insect damage are shown. Arrows and bars indicate positive and negative interactions, respectively. The overall scenario may differ in certain plant taxa. JA, jasmonic acid; SA, salicylic acid.

and gene expression (Harmon et al. 2000). However, whether there is a close interaction between the Ca^{2+} signaling and terpenoid biosynthesis after herbivore damage remains to be determined. In summary, the regulatory mechanisms seem to be rather complex, because of the complex cross-talk among signaling pathways depending on the type of herbivory. We recently found, in mite-infested bean leaves, that polyamines (e.g. spermine) also act, in part, concomitant with the JA pathway and activate the influx of Ca^{2+} and reactive oxygen species (Ozawa, R., Bertea, C.M., Foti, M., Narayana, R., Arimura, G.I., Muroi, A., Horiuchi, J.I., Nishioka, T., Maffei, M.E. and Takabayashi, J. in preparation).

Biosynthesis and regulation of green leaf volatiles in response to herbivory

GLVs include C6 aldehydes, alcohols, and their esters. GLVs are compounds produced by the lipoxygenase (LOX) pathway when leaves are injured or suffer from biotic/abiotic stresses (Matsui 2006). The first product, (*Z*)-3-hexenal, is formed through oxygenation of linolenic acid by LOX to form linolenic acid 13-hydroperoxide (13HPOT), and subsequent cleavage of 13HPOT by fatty acid 13-hydroperoxide lyase (13HPL). *n*-Hexanal is formed similarly, but from linoleic acid. Enzymatic or non-enzymatic isomerization of (*Z*)-3-hexenal yields (*E*)-2-hexenal. Those C6 aldehydes are further converted to the corresponding C6 alcohols by alcohol dehydrogenases [e.g. (*Z*)-3-hexen-1-ol from (*Z*)-3-hexenal]. An acyltransferase is thereafter responsible for

formation of the acetate [e.g. (*Z*)-3-hexen-1-yl acetate (Hex-Ac) from (*Z*)-3-hexen-1-ol] (D'Auria et al. 2007).

It should be noted that 13HPOT serves as a precursor of not only GLVs but also JA, and thus the use of this compound as a substrate for allene oxide synthase [(AOS) in JA biosynthesis] and 13HPL (in GLV biosynthesis) is potentially competitive (**Fig. 3**). JA plays a core role in defense signaling pathways and in the production of herbivore-induced volatile terpenoids, as described above. GLVs are also involved in direct and indirect defense responses in plants after herbivory (see below) (Shiojiri et al. 2006a, Chehab et al. 2008). In tomato leaves, 13HPL localizes on the outer envelope membrane of plastids and potentially receives 13HPOT from the outside of plastids, whereas AOS localizes on the inner envelope membrane of plastids and potentially receives 13HPOT from the interior of plastids (Froehlich et al. 2001). In potato chloroplasts, both 13HPL and AOS localize on thylakoid membranes but are differentially distributed in the membrane (Farmaki et al. 2007). The differences in the spatial organization of these two branches of oxylipin metabolism discourage their metabolic competition, which might support prompt management of HIPV production by using these two oxylipin pathways after herbivory (**Fig. 3**).

In general, herbivore-induced production of terpenoids follows the activation of biosynthetic genes such as TPS genes, so that the de novo production of herbivore-induced volatile terpenoids takes at least a few hours. In contrast, GLVs start to be released much faster (within seconds) from leaf and stem tissues after herbivore damage (**Fig. 4**). Real-time volatile analyses indicated that (*Z*)-3-hexenal was formed immediately in wounded Arabidopsis leaves (peaking at approximately 30–45 s following damage), followed by the formation of (*Z*)-3-hexen-1-ol and Hex-Ac (peaking at approximately 5 min) (D'Auria et al. 2007). Vigorous formation of (*Z*)-3-hexen-1-ol and Hex-Ac was observed when Arabidopsis leaves were partially injured, while they were only weakly formed when the leaves were completely homogenized, and (*Z*)-3-hexenal was the predominant product (Matsui, K. and Ueda, M. in preparation). Thus, it is assumed that little alcohol and acetate are formed in the disrupted tissues. They are formed in the vicinity of the wounded sites probably owing to the supply of hexenal from the directly disrupted tissues (**Fig. 4**). This is supported by the fact that NAD(P)H and acetyl-CoA, which are generally present in healthy leaves, are needed to form the alcohol and acetate, respectively. The relatively lower HLC (Henry's law constant) value for Hex-Ac ($3.1\,M\,atm^{-1}$), compared with the value for (*E*)-2-hexenal ($14.5\,M\,atm^{-1}$) (Karl et al. 2003), makes the acetate more prone to be released from the plant tissues. Such differences in biophysical features and fates of each type of GLV must be responsible for their distinct physiological functions. For instance, when maize leaves were subjected to beet armyworm, hexenals,
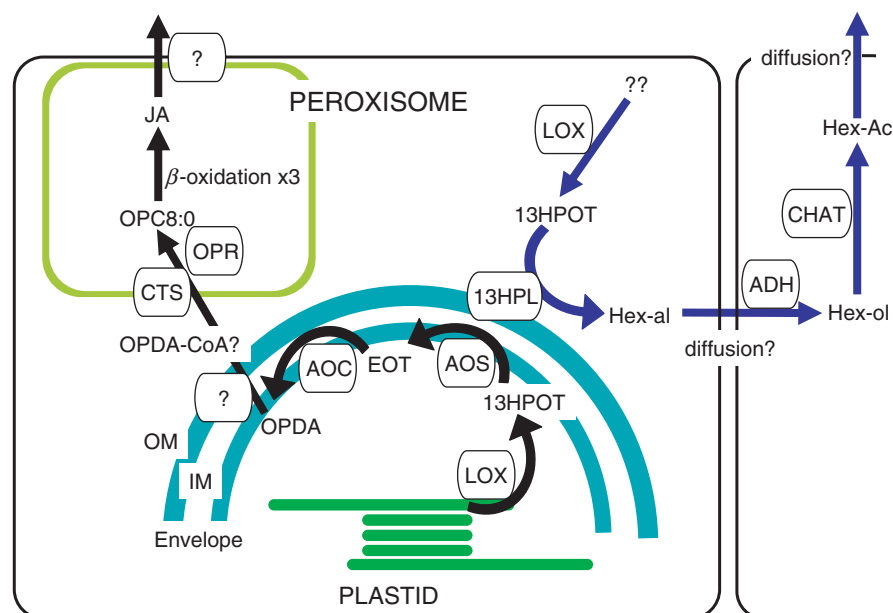
Fig. 3 Schematic representation of the 13HPL and AOS pathways. In tomato, 13HPL localizes in the outer membrane of the plastid envelope, while AOS localizes in the inner membrane of the envelope. For the 13HPL pathway (indicated by blue arrows), 13HPOT is probably supplied by cytoplasmic LOX, but little is known about the details, especially regarding substrate loading to this pathway. Part of Hex-al formed by 13HPL can diffuse to the neighboring cells, where it is reduced and acetylated. For the AOS pathway (indicated by dark arrows), a plastid LOX serves 13HPOT for AOS, and subsequent catalysis by AOC results in formation of OPDA. OPDA is excreted from the plastid thereafter, so that OPDA (or OPDA-CoA) is transported into the peroxisome by CTS. Subsequent modification by OPR and β-oxidation finally yields JA. JA thus formed is in part fated to be transported from the peroxisome and plasma membrane so as to serve as an intercellular signaling molecule. This scheme incorporates the evidence obtained from tomato (Froehlich et al. 2001). The overall scenario may differ in certain plants; for instance, potatoes were reported to employ a distinct process (Farmaki et al. 2007). ADH, alcohol dehydrogenase; AOS, allene oxide synthase; AOC, allene oxide cyclase; CHAT, acetyl CoA-(*Z*)-3-hexen-1-ol acetyl transferase; CTS, comatose; EOT, 12,13-epoxyoctadecatrienoic acid; Hex-Ac, hexenyl acetate; Hex-al, hexenals; Hex-ol, hexenols; 13HPL, 13-hydroperoxide lyase; 13HPOT, linolenic acid 13-hydroperoxide; IM, inner membrane; JA, jasmonic acid; LOX, lipoxygenase; OM, outer membranes; OPC8:0, 3-oxo-2[2′(Z)-pentenyl]-cyclopentane-1-octanoic acid; OPDA, 12-oxophytodienoic acid; OPR, 12-oxophytodienoic acid reductase.

(*Z*)-3-hexen-1-ol and Hex-Ac were emitted (Farag et al. 2005). In contrast, when maize leaves were treated with methyl jasmonate, neither hexenals nor hexenol was emitted, while Hex-Ac was significantly emitted (Farag et al. 2005). This was also the case for cotton leaves, in which Hex-Ac was the only GLV emitted from sites distal to the herbivory, while emission of all the GLVs could be observed when the leaves were artificially damaged (Röse et al. 1996). In summary, GLV differs spatially between local and distal sites of the herbivore-damaged leaf (**Fig. 4**). Such spatial specificity should be taken into account when the physiological roles of GLVs are discussed.

Moreover, the rapid formation of hexenal after the onset of mechanical damage should be directly controlled by pre-existing enzymes rather than induced enzymes. This can be explained by a physical event in which the substrate and enzyme, which occur separately and do not co-exist in tissue (or cell) compartments, encounter each other after tissue disruption. However, it has not been elucidated which substrates (e.g. galactolipids, phospholipids or others) and enzymes (e.g. lipases or LOXs) are involved in this mixing process, and thus the detailed mechanism that leads to the rapid formation of hexenal after herbivory and mechanical wounding has not been clarified. GLVs can also be formed even without tissue disruption. In tobacco plants exposed to ozone, and in reed leaves exposed to high temperature or high light, GLV emissions are observed (Beauchamp et al. 2005, Loreto et al. 2006). In those cases, the compounds are emitted late after stress. An Arabidopsis mutant, *npq1*, which has a defect in the xanthophyll cycle essential to restrain photooxidative stress, showed a high level of GLV emissions during exposure to high light (Loreto et al. 2006). These findings suggest that oxidative damage of membranes is one of the primary causes of the induction of GLV emissions. It has been proposed that oxidative stress is one of the outcomes of herbivore damage (Mithöfer et al. 2004). Over-
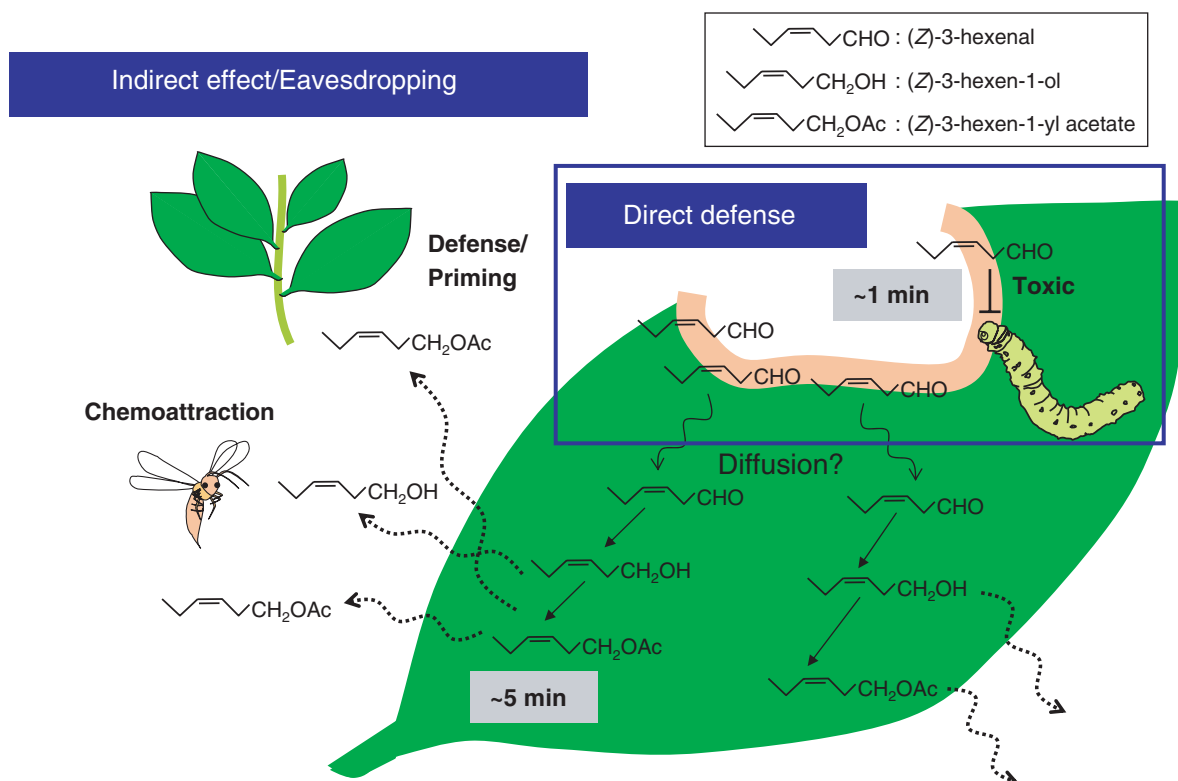
Fig. 4 Biosynthesis and biological effects of GLVs. The first product of the GLV pathway, (Z)-3-hexenal, is formed at the wounded site immediately after disruption of plant tissues caused by herbivore attack or mechanical damage. A portion of the aldehyde can diffuse out of the wound site to the whole leaf, where the non-toxic GLV volatile alcohol and acetate are formed. These volatile GLVs can be useful for regulating feeding (for herbivores), prey (for predators) and for the defense of neighboring plants or within plants.

all, in addition to the process of mixing of substrates and enzymes, the supply of oxidized lipids and/or subsequent loss of membrane integrity might affect the onset of GLV formation.

GLVs are unstable in the atmosphere and undergo oxidation by ·OH, O_3 and NO_3. For example, the atmospheric lifetime of (Z)-3-hexenal was estimated to be 2 h (Imamura, T. personal communication). Although it has not yet been clarified whether or not oxidized compounds or other breakdown products have ecological functions, the instability of HIPVs must be taken into consideration when the ecological functions of HIPVs are discussed. Pinto et al. (2007b) proposed that O_3-degraded GLVs no longer play a role in the host allocation of parasitic wasps. The same may hold true for some volatile terpenoids (Pinto et al. 2007b).

Insect factors affecting the production of HIPVs

Mechanical wounding and chemical elicitors from insect oral secretions are believed to induce HIPV emissions synergistically in plants (**Table 1**). Fatty acid–amino acid conjugates (FACs), such as *N*-acyl Gln/Glu, that induce plants to release HIPVs have been isolated from the regurgitate of

several lepidopteran larvae (Alborn et al. 1997, Halitschke et al. 2001, Spiteller and Boland 2003), crickets and fruit fly larvae (Yoshinaga et al. 2007). FACs play roles not only in induced plant defense but also in nitrogen assimilation in lepidoptera larvae (Yoshinaga et al. 2008). Furthermore, of recent interest regarding caterpillars' oral secretions is the finding that fall armyworm (*Spodoptera frugiperda*) caterpillars, which infest cowpea leaves, include gut proteolytic fragments called inceptin (Schmelz et al. 2006). Inceptin [+ICDINGVCVDA−] and the related peptides [+(GE)ICDINGVCVDA−] are derived from chloroplastic ATP synthase γ-subunit regulatory regions. These peptides elicit rapid and sequential production of JA, ethylene and SA, and consequently DMNT emissions (Schmelz et al. 2007).

Another elicitor of caterpillar origin that induces the production of HIPVs is β-glucosidase from the oral secretion of the larvae of cabbage white butterfly *Pieris brassicae* (Mattiacci et al. 1995). Cabbage plants infested by *P. brassicae* larvae attract a parasitic wasp, *Cotesia glomerata*. Although this plant emits the same blend of volatiles when infested by herbivores as when damaged mechanically, the infested plants, as a result of exposure to β-glucosidase, emit the volatiles

Table 1 Insect oral factors inducing the production of HIPVs

Elicitors	Arthropod species	Properties
β-Glucosidase	Large white (*Pieris brassicae*[a])	The first claimed elicitor[a]
Fatty acid–amino acid conjugates (e.g. volicitin)	Lepidopteran larvae[b], crickets[c] and fruit fly larvae[c]	Bind to a membrane protein from maize[d]
		Enable activation of ion channel-forming activity[e]
		Functional in maize and tobacco but not lima bean and cotton[f]
Disulfo-oxy fatty acids (caeliferins)	American bird grasshopper (*Schistocerca americana*[g])	Saturated and monounsaturated sulfated α-hydroxy fatty acids[g]
Disulfide-bridged peptides(e.g. inceptin)	Fall armyworm (*Spodoptera frugiperda*[h])	Peptides derived from a cowpea chloroplastic ATP synthase γ-subunit[h]

[a]Mattiacci et al. (1995); [b]Alborn et al. (1997), Halitschke et al. (2001), Spoel et al. (2003), Sawada et al. 2006; [c]Yoshinaga et al. (2007); [d]Truitt et al. (2004); [e]Maischak et al. (2007); [f]Spiteller et al. (2001); [g]Alborn et al. (2007); [h]Schmelz et al. (2006), Schmelz et al. (2007).

in larger quantities and for a longer time. In this system, the major volatiles involved are GLVs. However, this elicitor induces the production of homoterpenes DMNT and TMTT in lima bean and maize plants (Hopke et al. 1994).

In contrast to caterpillars, however, little is known about oral elicitors from sucking arthropods (spider mites and aphids). It has been proposed very recently that the release of aphid elicitors (e.g. oligogalacturonides) due to cell wall digestion by gel saliva enzymes may induce Ca^{2+} influx (Will and van Bel 2008), but there is a missing link to downstream signaling and biosynthetic pathways for the induced volatiles. Since such oral factors may induce both JA/ethylene and SA pathways (Arimura et al. 2002, De Vos et al. 2007), some novel signaling network should lead to the HIPV formation in a different manner from that of caterpillars (see above).

In addition to oral elicitors, it should be noted that the continuous mechanical damage effected by a robotic device (MecWorm) is able to induce in lima bean leaves the emission of volatiles whose profiles perfectly match those of the HIPVs induced by feeding caterpillars *Spodoptera littoralis* (Mithöfer et al. 2005). This discovery amazed us, since it is generally believed that insect oral factors play a major role in addition to physical wounding in the induction of HIPVs, as described above. In contrast, plants in which the leaves were manually wounded by punching once at the onset of the experiment do not show induced emission of ocimene due to only a transient JA accumulation (Arimura et al. 2008b). However, not all plants investigated so far responded to MecWorm treatment exactly as lima bean or cotton did (with an emission of about 90% identical volatile compounds); e.g. the levels of identical volatiles in tobacco were 78%, in maize 60%, and in potato 43% (Maffei et al. 2007a). Therefore, it will be of a great interest to understand how both concomitant and continuous challenges of oral elicitors and physical damage (or either of them) are responsible for the induction of a particular HIPV.

Ecological functions of HIPVs

Once HIPVs are emitted, plants cannot control their use. Thus, HIPVs can be received by any organisms, i.e. carnivores, conspecific and heterospecific herbivores, and neighboring plants. Thus, ecological functions of HIPVs are completely dependent on the receiver. For example, when HIPVs are used as prey-searching cues by carnivorous natural enemies of infesting herbivores, and the carnivores decrease the damage caused by herbivores by removing them from the plants, HIPVs mediate an interaction that is adaptively favorable to both the emitter (infested plants) and the receiver (carnivores), and are called synomones, a subcategory of allelochemicals (**Table 2**; Dicke and Sabelis 1988). In contrast, when the same HIPVs are used by other herbivore species to find their food resources, HIPVs are adaptively favorable to receivers (herbivores) but not to emitters (infested plants), and are called kairomones (**Table 2**; Dicke and Sabelis 1988). Such context dependency of the function of HIPVs makes ecological interactions even more complicated. To understand such complexity, we review the following four interactions mediated by HIPVs: (i) plant–carnivore interactions; (ii) plant–herbivore interactions; (iii) plant–plant interactions; and (iv) plant–pathogen interactions.

Interaction between a plant and a carnivorous natural enemy of herbivores mediated by HIPVs

HIPVs are known to attract carnivorous natural enemies of the herbivores. A well-studied example is a tritrophic system consisting of lima bean, the two-spotted spider mite (TSSM) (*Tetranychus urticae*) and a carnivorous mite (*Phytoseiulus persimilis*), where TSSM-infested lima bean leaves start emitting HIPVs that attract the carnivorous mites (Sabelis et al. 2007). As HIPVs enhance the prey-searching efficacy of *P. persimilis*, and the attraction of *P. persimilis* is observed after the

Table 2 Allelochemical terminology

Allelochemical	An infochemical[a] that mediates an interaction between two individuals that belong to different species.
Allomone	An allelochemical that is pertinent to the biology of an organism (organism 1) and that, when it contacts an individual of another organism (organism 2), evokes in the receiver a behavioral or physiological response that is adaptively favorable to organism 1, but not to organism 2.
Kairomone	An allelochemical that is pertinent to the biology of an organism (organism 1) and that, when it contacts an individual of another organism (organism 2), evokes in the receiver a behavioral or physiological response that is adaptively favorable to organism 2, but not to organism 1.
Synomone	An allelochemical that is pertinent to the biology of an organism (organism 1) and that, when it contacts an individual of another organism (organism 2), evokes in the receiver a behavioral or physiological response that is adaptively favorable to both organism 1 and organism 2.
Antimone	An allelochemical that is pertinent to the biology of an organism (organism 1) and that, when it contacts an individual of another organism (organism 2), evokes in the receiver a behavioral or physiological response that is adaptively favorable to neither organism 1 nor organism 2.

[a]An infochemical is a chemical that, in natural context, conveys information in an interaction between two individuals, evoking in the receiver a behavioral or physiological response. Pheromone and allelochemical are subcategories of infochemical.

removal of TSSMs from the plant, the HIPVs are classified as synomones. Similar interactions between plants and carnivorous natural enemies of herbivores have been reported in systems consisting of plants, caterpillars and parasitic wasps (for review, see Dicke and van Loon 2000, Sabelis et al. 2007). For example, maize plants infested by African cotton leafworm (*S. littoralis*) emit volatiles that attract parasitic wasps *Cotesia marginiventris* and *Microplitis rufiventris* (D'Alessandro et al. 2006). Recently, parasitic wasps that attack eggs of herbivorous insects were reported to use volatile organic compounds of plant origin whose production was induced by egg deposition by female herbivores (Meiners and Hilker 1997, Meiners and Hilker 2000, Fatouros et al. 2008). These volatiles are also categorized as HIPVs.

HIPV-mediated plant–carnivore interactions are also observed even in the soil. van Tol et al. (2001) showed that the roots of a coniferous plant (*Thuja occidentalis*) release chemicals upon attack by weevil larvae (*Otiorhynchus sulcatus*) and that these chemicals attract parasitic nematodes (*Heterorhabditis megidis*). The first such below-ground plant signal identified was the root-feeding beetle (*Diabrotica virgifera virgifera*)-induced below-ground maize plant signal, (*E*)-β-caryophyllene, which strongly attracts a parasitic nematode (Rasmann et al. 2005). Rasmann and Turlings (2007) further reported that simultaneous feeding by above-ground herbivores (African cotton leafworm) and below-ground herbivores (*D. virgifera virgifera*) affected the production of HIPVs that in turn affected the attraction of the respective natural enemies.

Interaction between a plant and a herbivore mediated by HIPVs

Herbivorous arthropods use host-food plant volatiles as one of the foraging cues. In general, the amounts of volatiles emitted from intact leaves of a plant are rather low, making the intact plant inconspicuous to herbivorous insects. In contrast, the blend of HIPVs is qualitatively and quantitatively different from that of intact leaf volatiles, making the plants conspicuous not only to carnivores, but also to herbivores. Thus, HIPVs can be used by con- and heterospecific herbivores as one of their host-food-finding cues. Horiuchi et al. (2003) reported that lima bean plants slightly infested by TSSMs attracted the conspecific mites, whereas those heavily infested repelled the conspecifics. Regarding insect herbivores, HIPVs released at night from tobacco budworm-infested tobacco plants repelled conspecific female moths (De Moraes et al. 2001). Common armyworms (*Mythimna separata*) utilize HIPVs emitted from maize plants infested by conspecifics to determine their nocturnal behavior (Shiojiri et al. 2006b). Recently, Carroll et al. (2006, 2008) reported that neonates and larvae of fall armyworms (*S. frugiperda*) exploit fall armyworm-induced corn plant volatiles as host plant location and recognition cues.

Interaction between two plants mediated by HIPVs

In response to HIPVs or volatiles from artificially damaged plants, neighboring intact plants enhance either their direct defense (i.e. become a less suitable resource for herbivores) or their indirect defense (i.e. attract carnivorous natural enemies of herbivores) (Bruin et al. 1992, Arimura et al. 2000, Dolch and Tscharntke 2000, Karban et al. 2000, Choh et al. 2004, Engelberth et al. 2004).

Bate and Rothstein (1998) showed that (*E*)-2-hexenal, one of the commonly found HIPVs in many plant–herbivore combinations, induced several defense-related genes in Arabidopsis. Exposing plants to GLVs induces phytoalexin production as well as the expression of defense-related genes in several plant species (Matsui 2006). Similarly, Frost et al. (2008) reported that GLVs prime defense genes and metabolites in poplars. Terpenoids (β-ocimene, DMNT, TMTT and

linalool) that are constituents of TSSM-induced lima bean leaf volatiles also function to induce several defensive genes in intact lima beans (Arimura et al. 2000). It was also shown that feeding damage caused by TSSMs on lima bean leaves that had been exposed to TSSM-induced conspecific leaf volatiles was less severe than that on control leaves. Kishimoto et al. (2005) used both GLVs and volatile terpenoid (*allo*-ocimene), and showed that the manner of induction varied depending on both the gene monitored and the volatile used. These findings suggest that HIPVs function as signals to initiate defense responses of undamaged plants. In most studies, however, rather high concentrations of HIPVs were used under laboratory conditions. A subset of glutathione *S*-transferase (GST) genes is induced in pumpkin seedlings after their exposure to (*E*)-2-hexenal (Fujita and Hossain 2003). GST detoxifies various kinds of toxic compounds and xenobiotics by forming conjugates between them and gluta-thione. The predominant adduct to glutathione was obtained from (*E*)-2-hexenal in wounded Arabidopsis leaves (Davoine et al. 2006).

TSSM-induced lima bean leaf volatiles induced conspecific plants to produce extrafloral nectar that functions as an indirect defense (i.e. alternative food for natural enemies of TSSMs) (Choh and Takabayashi 2006, Choh et al. 2006). Using naturally growing lima bean plants, Heil and Silva Bueno (2007) showed that HIPVs elicited a defensive response in intact plants (or part of intact plants), and these HIPVs functioned as external signals for within-plant communication. Karban and co-workers reported plant–plant interaction mediated by plant volatiles in sagebrush, a shrub from the family Asteraceae (Karban et al. 2006, Shiojiri and Karban 2006). In their system, artificially damaged plant volatiles are key to intra- and interplant communication.

Interactions between plants and pathogens mediated by HIPVs

The interactions have been studied from the viewpoint of possible defensive function of HIPVs, especially GLVs, against subsequent attack of microorganisms. Transgenic Arabidopsis overexpressing 13HPL showed stronger resistance against a necrotrophic fungal pathogen, *Botrytis cinerea*, while those with suppressed 13HPL showed higher susceptibility to the fungal pathogen (Shiojiri et al. 2006a). The differences in susceptibilities of the transgenic Arabidopsis to *B. cinerea* are mostly due to the direct toxicity of C6 aldehydes against *B. cinerea* (Kishimoto et al. 2008). It has been reported that (*E*)-2-hexenal induced phytoalexin accumulation in cotton plants (Zeringue 1992). Furthermore, Gomi et al. (2003) reported that (*E*)-2-hexen-1-ol enhanced resistance of citrus trees (*Citrus jambhiri*) against *Alternaria alternata*. In summary, a subset of GLVs, especially C6 aldehydes, have a direct defensive effect, as they are formed and accumulated at the wounded sites to prevent the invasion of pathogens and herbivores locally (**Fig. 4**).

Conclusion

Volatile terpenoids and GLVs have distinct natures, especially regarding their de novo synthesis (temporal and spatial patterning of induction) and biochemical features. However, they play similar roles in ecosystems, i.e. both mediate interactions between plants and insects, plants and pathogens, and plants and plants. For example, evidence is accumulating that several plants, when attacked by a single herbivore species, release chemical information that is sufficiently specific for predators and parasitoids to tell prey and non-prey apart. This specificity would be determined in part by volatile blends, which are produced by the temporally (and spatially) controlled release of volatile terpenoids and GLVs. This specificity also holds within vegetation with prey and non-prey on different plants and even when part of the plants harbor both prey and non-prey. However, there are also cases of multiple herbivore attacks in which the plant releases herbivore-induced plant volatiles that make one or another herbivore go unrecognized by its specific natural enemy (Shiojiri et al. 2002). On the other hand, herbivore-induced terpenoids and GLVs are highly reactive with atmospheric pollutants such as ozone (Pinto et al. 2007a, Pinto et al. 2007b). Both ozone-reactive and ozone-non-reactive HIPVs have been reported to be important for the attraction of the diamondback moth parasitoid *Cotesia vestalis* (Pinto et al. 2007b). Overall, it cannot be doubted that HIPVs involving volatile terpenoids and GLVs are significant components of interaction webs in ecosystems, but it will be worthwhile to examine this subject more closely, including aspects of multiple food chains, atmospheric chemistry and global environmental change.

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