Role of Natural Products in Nature: Plant–Insect Interactions

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Abstract The chapter discusses the interactions of relatively low molecular weight and largely lipophilic secondary plant metabolites with insects and some other invertebrates. This includes compounds stored within plant tissues that are toxic to insects by a range of mechanisms. It covers metabolites that are both constitutively produced and those that are induced in response to defence signalling stimuli including insect attack. Also included are volatile compounds released from plants that act as signals (semiochemicals) detected by herbivorous insects and those that interact with insects at higher trophic levels. Finally, plant to plant communication is described.

Metabolites with Toxic Modes of Action

General Properties of Plant Toxicants

The production of chemicals that are capable of deterring insect pests by toxic activity is an important survival strategy for plants. Structurally, such toxicants are usually compounds that are non-volatile, due to their molecular weight or hydrophilicity. If they accumulate in the tissue of healthy plants prior to insect attack, they are considered to be constitutive (Stamp, 2003; Wittstock and Gershenzon, 2002). Alternatively, they may only be present, or present in much higher concentrations, after plants have encountered attack, or after exposure to natural plant or insect derived defence activators. In this case they are considered to be induced toxicants (Walling, 2000). Induction provides economic advantage to the plant as metabolic energy has to be diverted from primary metabolism for toxin production. In addition, insect herbivores are less likely to develop resistance to induced defence products as they will be subjected to less exposure to them. However, the balance between these two strategies may depend on the likelihood of the plant coming under attack. Those that encounter more frequent colonisation by pests may be forced to rely more heavily on constitutive rather than induced defence, despite its greater energetic cost to the plant (McKey, 1979). Also, defence metabolites are often restricted in their distribution, both spatially and temporally and plant organs associated with survival or reproduction tend to contain the highest concentrations of constitutive defence metabolites (Wittstock and Gershenzon, 2002). They may be developmentally regulated, being present at highest concentrations when the plant is young and less able to protect itself against predators, or they may be concentrated around the region of contact with the invader.

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A.E. Osbourn and V. Lanzotti (eds.), *Plant-derived Natural Products*,
DOI 10.1007/978-0-387-85498-4_15, © Springer Science+Business Media, LLC 2009

Compounds may be stored in specialised subcellular compartments from which they are released, or normally present in inactive forms, ensuring the most economically efficient means of maximum contact with the invader, whilst protecting the host from its own toxic substances (discussed in detail in the following section) (Koroleva et al., 2000; Hallahan, 2000; Grubb and Abel, 2006; Sicker et al., 2000; Neal et al., 1990).

Plant defence may rely on strategies relating to high levels of apparency, as with trees, where weakly acting toxicants are present in high concentrations, as is the case with phenolic compounds. Non-apparent defence, for example, in annuals, relies on highly active compounds that are present in low concentrations (Feeny, 1976). Alkaloids, the largest and most diverse family of plant defence metabolites, are frequently involved in non-apparent defence (Schuler, 1996; De Luca and St Pierre, 2000; Steppuhn et al., 2004; Velozo et al., 1999). These compounds are present in many plant families, including cereals and solanaceous plants, most notably of the genus Nicotiana.

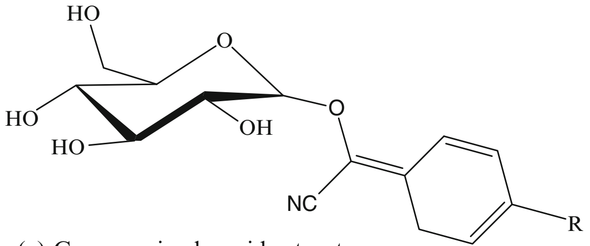
Insecticidal activities of plant metabolites can be demonstrated by their effect on insects when added to artificial diets (De Boer and Hanson, 1987; Broadway and Duffey, 1988; Snook et al., 1997; Jassbi et al., 2006). However, comparative quantification between the toxicity of metabolites applied artificially and amounts measured in whole plant extracts are potentially misleading because of the lower intrinsic acceptability of artificial diets. Compounds within plants may have additional effects that deter insects indirectly, and these defence mechanisms are discussed later in this chapter (see Section “Higher Trophic Level Interactions”).

Plant toxicants may interact with specific molecular targets within the herbivore, including proteins, such as enzymes (Feeny, 1976; Rhoades and Cates, 1976; Downs et al., 2003), structural proteins (Morimoto et al., 2001), ion-channels and receptors (Wittstock et al., 1997;Wink, 2000), and a toxicant may derive its potency by mimicking the structure of endogenous ligands or other plant compounds, such as amino acids (Wink, 2003). Alkaloids derive their bioactivity from their ability to affect neurotransmitter activity (Zenk and Juenger, 2007) and nicotine, for example, is a nicotinic acetylcholine receptor agonist (Itier and Bertrand, 2001). Due to their bioactivity alkaloids have been developed for use as powerful drugs and halucegens. Non specific compounds may also disrupt biomembranes and thereby destroy the activity of ion channels or receptors, that reside within them (Osbourn, 1996). The action of phenolics tends also to be non-specific and frequently involves inactivation of a range of proteins by the formation of hydrogen bonded complexes via their multiple hydroxyl groups (Bennet and Wallsgrove, 1994; Nickolson and Hammerschmidt, 1992).

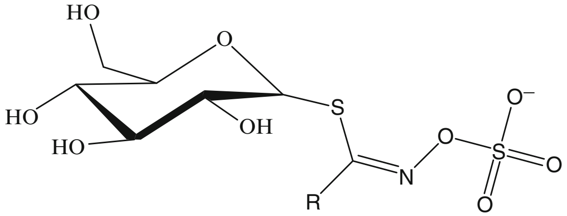
Storage and Release of Plant Toxicants

The potential advantages to the plant of storing toxicants in discreet compartments as inactive precursors have been described. In this section the biological properties, regulation and distribution of some well characterised examples of such metabolites will be discussed.

A family of plant toxicants that clearly falls into this category are the cyanogenic glucosides (Fig. 1a) (Bennet and Wallsgrove, 1994; Seigler, 1991). These amino acid derived compounds are stored as glucosides within the vacuole and are present in representatives from all vascular plants orders. Although they are constitutively produced throughout the life of the plant, young or developing tissues (including seeds or nuts) contain the highest concentrations (Conn, 1981). Cyanide is released when the glucoside is hydrolysed by a glucosidase (Seigler, 1998), which, in addition to its role as a respiratory poison, may also have antifeedant activities.



(a) Cyanogenic glucoside structure



(b) Glucosinolate structure

Fig. 1 The general structure of cyanogenic glucosides (**a**) and glucosinolates (**b**) structure. In (**b**), the R group is derived from amino acids and is highly variable. It may be aliphatic, aromatic or heterocyclic

Furthermore, consumption of cyanide producing compounds can be an advantage to certain herbivores (see Section "Sequestration of Toxins by Herbivores Against Predators") as they defend insects from their own predators (Spencer, 1988). The associated carbonyl compounds have also been shown to be directly toxic to insects.

The glucosinolates are a diverse group of nitrogen and sulphur-containing defence compounds, also derived from amino acids (Fig. 1b). They are found primarily in species of the order Brassicales (for reviews, see Grubb and Abel, 2006; Fahey et al., 2001; Halkier and Gershenzon, 2006) and are thought to have evolved from the cyanogenic glycosides. They are also stored as inactive parent molecules in the vacuole and specialised cells (Koroleva et al., 2000). They are derived from eight different amino acids, and in thale cress, *Arabidopsis thaliana*, the most common precursors are methionine, tryptophan and phenylalanine. Biosynthesis involves three distinct stages: construction or elongation of side chains added to a primary protein amino acid (Textor et al., 2004), core structure elaboration and secondary side chain modification (Grubb and Abel, 2006). These stages, which have been largely confirmed by both biochemical and molecular genetic studies, are responsible for the diversity of this family of metabolites and more than 120 different structural forms have been identified. In the healthy plant gene expression and reporter gene fusion analysis has indicated that the pathway is expressed most highly in reproductive and young developing tissues and in sulphur rich cells in the immediate vicinity of the vascular tissues (Koroleva et al., 2000). Their biosynthesis is up regulated by herbivory (Kim and Jander, 2007; Agrawal and Kurashige, 2003), or plant defence activators (Doughty et al., 1995) and down regulated during sulphur depletion (Bones and Rossiter, 1996).

The toxicity derived from of the glucosinolates is produced in response to cell damage when the glycosidic bond is hydrolysed, by specific β-thioglucosidases termed myrosinases. These enzymes are contained within neighbouring idioblasts or myrosin cells and they release unstable thiohydroximate-O-sulfate products (Grubb and Abel, 2006). These products yield a range of biologically active isothiocyanates, thiocyanates, nitriles oxazolidine-2-thiones and epithioalkanes. Both glucosinolates and to a greater extent their catabolites, particularly the organic isothiocyanates, are toxic to insects but some specialist herbivores are able to detoxify them (Ratzka et al., 2002) (see Section "Sequestration of Toxins by Herbivores Against Predators"). Isothiocyanates have also been shown to attract specialist parasitoids when released from plants (Pope et al., 2008) (see Section on "Synomones").

Another group of plant defence secondary metabolites are the hydroxamic acids or benzoxazinones. These compounds are chiefly produced in cereals and they are involved in defence against a broad range of insect pests, pathogens and weeds. (Kluge et al., 1997; Niemeyer, 1988; Wu et al., 2001). Their role in plant defence was first fully recognised in 1969 when the correlation between susceptibility to the European corn borer, *Ostrinia nubilalis*, and benzoxazinone concentration in maize, *Zea mays*, plants was established (Klun and Robinson, 1969). Similarly, a correlation between elevated tissue concentration in wheat, *Triticum aestivum*, and reduced growth rate of a number of aphid species including the rose-grain aphid, *Metopolophium dirhodum*, the grain aphid, *Sitobion avenae* and the bird cherry oat aphid, *Rhopalosiphum padi* has been found (Argandona et al., 1980; Thackaray et al., 1990). Their toxicity to aphids has been demonstrated in artificial diets (Argandona et al., 1980). The compounds contain a very reactive carbonyl group that may enable them to interact with a range of molecular targets (Niemeyer et al., 1989; Friebe et al., 1997).

In cereals, the benzoxazinones accumulate in young seedlings throughout the plant tissues but decrease in concentration during the later stages of growth (Thackaray et al., 1990). They are also produced in other plant species (Sicker et al., 2000) including dicots (Schullehner et al., 2008), and in some plants the concentration of the compounds remains high as the plant matures (Baumeler et al., 2000). Like another family of plant defence compounds, the avenacins, Fig. 2 (1), that are produced in oats, *Avena* spp. (Osbourn, 1996) the genes in the benzoxazinone pathway are clustered together in a single genomic locus (Frey et al., 1997; Gierl and Frey, 2001). The most generally toxic of the compounds in *Z. mays* and hexaploid wheat is 2,4-dihydroxy-7-methoxy-1,4-benzoxazin-3-one, Fig. 2 (2),whereas in some diploid wheat and rye, *Secale cereale*, its non methoxylated precursor, 2,4-dihydroxy-1,4-benzoxazin-3-one is the major component. These compounds are biosynthesised on the endoplasmic reticulum and stored in the vacuole as inactive glucosides (Sicker et al., 2000). Upon tissue damage by the pest or pathogen the glucoside is released from the vacuole, although active release via a vacuolar membrane transporter may occur. In both foliar and root tissue cytoplasmic glucosidases then catabolise the glucoside to release the active compound (Esen, 1992; Sue et al., 2006). This process in roots may precede rapid release of the compounds into the rhizosphere where they deter soil borne pathogens.

Trichomes are glandular structures situated on regions of the plant surface, including the leaves, where the biosynthesis and storage of a range important secondary metabolites, including terpenes, flavones and phenolics occurs (Bisio et al., 1999; Combrinck et al., 2007; Hallahan, 2000). After insect attack, or in response to pant defence activators (see Section Regulation of Plant Toxicants by Natural Activators) these stored compounds are released

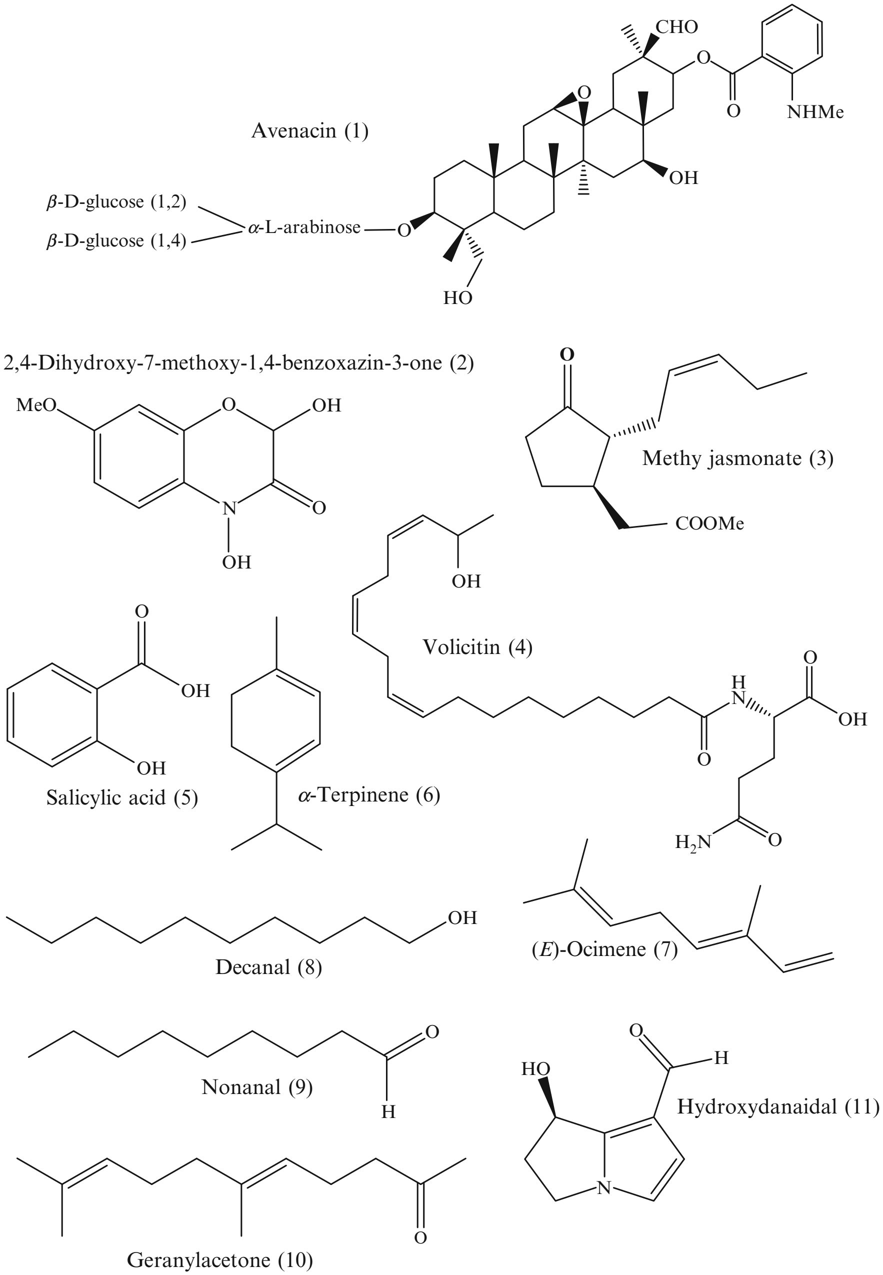


Fig. 2 Chemical structures of compounds 1–11

to protect the plant against herbivory (Jassbi et al., 2008; Schie et al., 2007). Cotton, *Gossypium* spp., for example stores terpenoids in glands at the leaf surface and these are released when the glands are ruptured upon attack (Elzen et al., 1985; Loughrin et al., 1994).

Regulation of Plant Toxicants by Natural Activators

The vast majority of toxicants display some level of induction or increase in concentration after insect attack or exposure to phytohormones that act as disease resistance elicitors. Examples of toxicants that are increased in concentration due to release from non toxic precursors have already been described but accumulation of an active compound may also be due to an up regulation of expression of biosynthetic genes. These changes are mediated by signalling compounds released from the insect or from the plant in response to the insect to enhance the defensive capacity of the attacked host. The major plant signalling compound or phytohormone (also generally classified as a plant secondary metabolite) that is believed to mediate plant response to chewing insects is jasmonic acid and its methyl ester, methyl jasmonate, Fig. 2(3). The role of jasmonates in the induction of plant defence is well established (Creelman and Mullet, 1997), and it has been the subject of much scientific interest (see reviews Leon et al., 2001; Farmer et al., 2003; Wasternack, 2007). However, not all major plant defence metabolites increase upon jasmonate treatment (Keinänen et al., 2001) and other compounds, including abscisic acid (Peña-Cortés et al., 1989) and ethylene (O'Donnell et al., 1996) are also released after insect attack and these compounds have been shown to act synergistically in insect defence (Leon et al., 2001). Conversely, insect induced ethylene production can block the jasmonate response under some circumstances. In tobacco, *Nicotiana attenuate*, leaves, for example, ethylene reduces the positive effect of jasmonic acid on the accumulation of nicotine (Winz and Baldwin, 2001).

Although these phytohormones are released after mechanical wounding, the effects of herbivory are distinct, involving additional responses that can be triggered by chemical elicitors in insect oral secretions. These elicitors include fatty acid-amino acid conjugates, which themselves induce the production jasmonic acid and ethylene.

The most extensively studied of these is volicitin, Fig. 2 (4), an N-linolenoylamino acid conjugate isolated from regurgitate from the beet armyworm caterpillar, *Spodoptera exigua* (Alborn et al., 1997; Halitschke et al., 2001). This compound, and further related molecules have been shown to induce the release of volatiles, including terpenoids and indole, which may compete with the hydroxamic acid pathway, and their role in plant defence will be discussed later (see Section on "Negative Interactions"). Little is known about compounds in aphid saliva that are responsible for induction of plant defence, although a number of metabolites toxic to aphids are induced by feeding (Ding et al., 2000; Kim and Jander, 2007; Gianoli and Niemeyer, 1998; Velozo et al., 1999), including alkaloids, hydroxamic acids and glucosinylates. Analysis of the proteome of saliva from the green peach aphid, *Myzus persicae*, has enabled a number of enzymes to be identified that may play a significant role in the induction of the defence response in the host plant (Harmel et al., 2008). Gene expression analysis suggests that in *A. thaliana* the plant's response to aphids is different from its response to chewing insects (Walling, 2000; de Vos et al., 2007; Moran et al., 2007), and pathways regulated by another phytohormone, salicylic acid, Fig. 2 (5), appear to be primarily involved. This is even more noticeable with the phloem feeding nymph of the silverleaf white fly, *Bemisia argentifolii*. It appears that this insect may either evade jasmonate-induced defences by avoiding the tissue damage that activates the response or it may introduce effectors that suppress jasmonate-dependent defences (Zarate et al., 2007). However, there is evidence that jasmonate, ethylene, abscisic acid and gibberellic acid also play significant role in aphid defence (Thompson and Goggin, 2006). Moreover, it is generally accepted that although chewing insects that cause wounding preferentially trigger jasmonate regulated responses and phloem-feeding insects and biotrophic pathogens trigger salicylate pathways there is considerable overlap, trade off and cross talk between the two signalling pathways (Bostock, 2005; Beckers and Spoel, 2006).

Behaviourally and Developmentally Active Components

Host Recognition

Chemicals, known as semiochemicals, are compounds produced by plants that play a pivotal role in their selection by insects as hosts due to their ability to exert behavioural or developmental effects. They may be released into the atmosphere and used as cues by herbivorous insects to locate their hosts or they may be involved in the modulation of insect feeding. Alternatively, they may protect the plant by attracting insects that prey on or parasitize herbivorous pests.

Aerial Plant Attractants (Kairomones) and the Potentiation of Pheromones

The first stage in host recognition by herbivorous insects is the perception of volatile semiochemicals released from the plant. Kairomones, are chemical substances produced and released by a living organism that benefit the receiver and disadvantage the emitting organism. Hence the definition applies to plant volatiles that are used by herbivores to locate their plant hosts. (Visser, 1988; Pickett et al., 1998; Bengtsson et al., 2005). Insects are able to detect general plant volatiles but just as they possess neurones that enable them to taste individual plant compounds (see Section on "Contact Action Including Phagostimulants"), so they possess sensory neurons tuned to host volatile compounds that enable them to recognise specific plant species. Using electroantenography and single olfactory neuron recordings coupled to gas chromatography it is possible to identify volatile compounds released by plants that are detected by insect olfactory neurons (Pickett, 1990). The activity of these compounds can then be further tested in bioassays to confirm their behavioural role. A comprehensive list of the common volatiles released by plants and the range of different insect species that respond to them have been recently reviewed (Bruce et al., 2005).

In some cases insect neurons are able to distinguish between different structural types of the same family of compounds, for example, selective detection of aromatic isothiocynates (Pickett et al., 1998). This phenomenon has now been found to extend to other insect plant systems, and several examples of this degree of selectivity are described in Pickett et al. (1999). However, there appears to be insufficient structural range in the compounds released by plants to enable insects to locate narrow taxonomic groups of plants. Coupled to this, insects possess neurons that detect a range of compounds present in the volatile emissions of many plants. It has been observed that olfactory cells that detect specific plant volatiles are paired with those that detect other identified plant volatiles. This has led to the hypothesis that insects can detect their hosts on the basis of the ratios of certain volatiles emitted, as opposed to specific compounds. It has now been demonstrated that blends of compounds attract phytophagous insects (Bruce et al., 2005) and if the ratios are changed, attraction fails to occur. In a recent study a mixture of compounds (α-terpene, Fig. 2 (6), *(E)*-ocimene, (7), decanal, (8), nonanal, (9), geranylacetone, (10), benzyl alcohol, phenylacetaldehyde and methyl salicylate assembled in the same ratio as was released by tomato plants, *Lycopersicon esculentum*, attracted the tobacco hornworm, *Manduca sexta* (Fraser et al., 2003). However, although the wheat midge, *Sitodiplosis mosellana*, an oligophagous insect, is attracted by the correct blend of *T. aestivum*, volatiles, small changes in the relative composition removes the effect in wind tunnel bioassays (Birkett et al., 2004).

The ability of plant volatile emissions to affect insects' responses to their own pheromones (Dawson et al., 1987), in particular sex pheromones, has long been recognised (Blight et al., 1984). It is appropriate for insects to encounter their mates in the vicinity of their food source and if the attractivity of a pheromone is enhanced by interaction with a plant volatile the chance of encounters will be increased. There are now several examples of the synergistic affects of volatile plant secondary metabolites and insect sex pheromones (Landholt and Phillips, 1997; Sadek and Anderson, 2007), but the effect also extends to the potentiation of aggregation or dispersal pheromones (Dawson et al., 1987; Witzgall et al., 2008). These observation are being used to develop improved methods of control of pest populations. For example, serricornins, which are insect derived sex pheromones, more effective as traps for the beetles *Stegobium paniceum* and *Lasioderma serricorne* when applied in the presence of dried red chilli, *Capsicum frutescens* L, volatiles, which enhanced the effect of the sex pheromone (Mahroof and Phillips, 2008).

There is also evidence that insects are capable of sequestering plant compounds, including alkaloids, and using them both in defence and to attract members of the opposite sex. Male *Estigmene acrea* moths consume plant derived pyrollizidine alkaloids to produce a sex pheromone, hydroxydanaidal, Fig. 2 (11) (Jordan et al., 2005; Edgar et al., 2007) and certain beetles species also sequester plant compounds for similar purpose. Fruit flies, *Drosophila melanogaster*, utilise methyl eugenol, Fig. 3 (12), as a sexual attractant (Raghu and Clarke, 2003), and euglossine bees collect plant compounds to use as aggregates (Lunau, 1992). However, there remains controversy over the degree to which insects sequester compounds and to which they are synthesise *de novo* within their own tissues.

External Attraction Due to Stress Perception

Some insects have evolved to be attracted to volatiles released from stressed or dead plants taking advantage of the weakened defense mechanisms but sustained nutritional quality of the plant tissue (Ginzel and Hanks, 2005; Miller, 2006; Pureswaran et al., 2004; Kalberer et al., 2001; Kendrick and Raffa, 2006). The release of a combination of ethylene and α-pinene, Fig. 3 (13), has been shown to attract longhorn beetle, *Xylotrechus longitarsis*, to its host (Morewood et al., 2002). Damage of a plant by conspecific or heterospecific insects also influences host-plant selection by herbivorous insects (Schindek and Hilker, 1996; Fernandez and Hilker, 2007). The willow beetle, *Phratora vulgatissima*, preferentailly selects willow, *Salix* spp., plants in plantations (Peacock et al., 1999) possibly due to the effect of plant cues induced by feeding and attractants released by the herbivores themselves. Artificiality damaged plants attract herbivores, due to the release of increased amounts of green leaf volatiles (Peacock et al., 2001; Karban and Baldwin, 1997) which are a mixture of volatiles biosynthesised from 18 carbon fatty acid precursors. They include (*E*)-2-hexenal, Fig. 3 (14), (*Z*)-3-hexenal, (15), hexanal, (*Z*)-3-hexenol and hexanol, (16), (Hatanaka, 1993) and the ratio of these components may play a role in host–plant selection (Bruce et al., 2005).

Contact Action Including Phagostimulants

Compounds that elicit feeding by insects via sensory rather than nutritional mechanisms fall into this category. Phagostimulants are detected

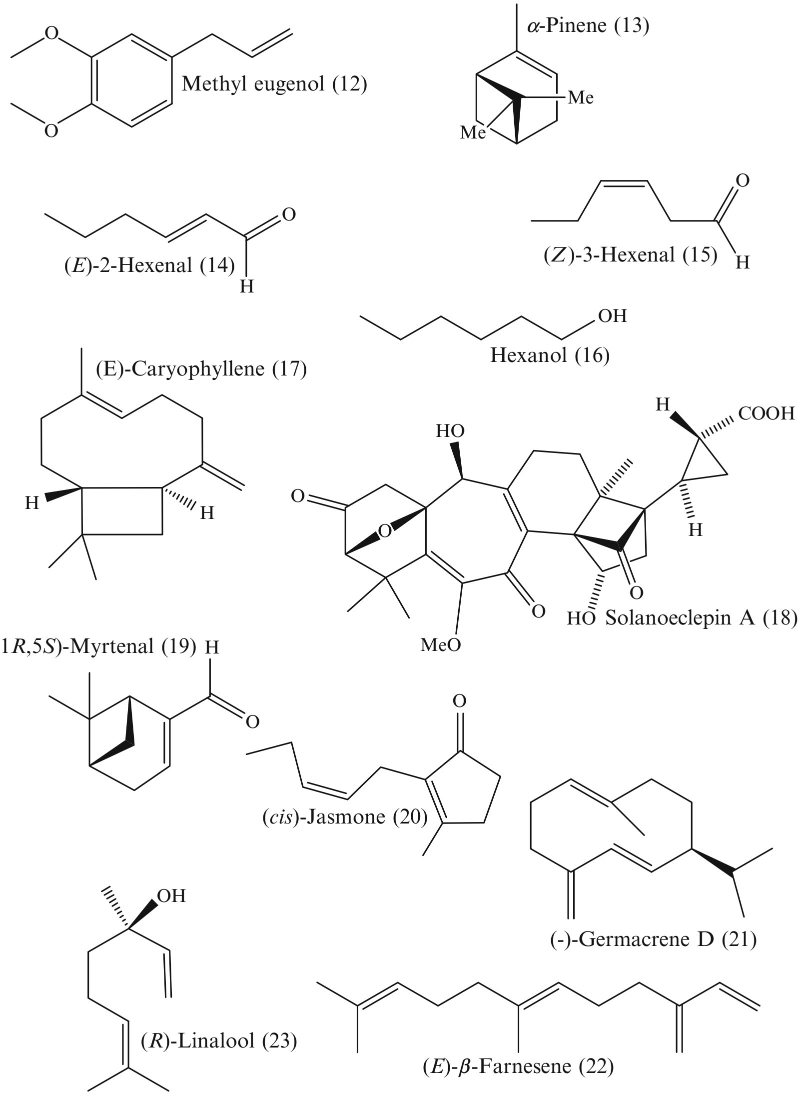


Fig. 3 Chemical structures of compounds 12–23

by contact gustatory receptors on sensory neurones (Chapman, 2003) that detect chemicals in solution and airborne molecules (rarely sufficiently concentrated to produce a response). The process is termed "gustation" or "contact chemoreception" as opposed to taste (Wieczorek and Koppl, 1978).

Presumably, the purpose of phagostimulation is to facilitate the recognition of food by the insect and to enable it to acquire sufficient nourishment. Insects detect amino acids (Simpson et al., 1990) and sugars (Schoonhoven and van Loon, 2002; Glendinning et al., 2000) but their response may be modulated by the presence of other metabolites (Endo et al., 2004). However, it does not appear that essential amino acids have a greater phagostimulatory effect than those that are nonessential.

Non dietary metabolites that can act as phagostimulants include glucosinolates, which have already described here as toxic to many insect species. However, these compounds enable certain specialist feeders that possess gustatory neurons sensitive to them to locate their host plants (Blight et al., 1989) and to feed without competition. However, the interactions between insect herbivores and glucosinolates can be complex (Li et al., 2000; Lambrix et al., 2001). Certain flavonoids can act as stimulants or repellents, dependent on the plant or insect species, with some having a dual role (Matsuda, 1978). Feeding choice appears to depend on small differences in chemical structure (Onyilagha et al., 2004) and glycosides, including those of indole and flavonol, may also function as probing stimulants (Kim et al., 1985; Adjei-Afriyie et al., 2000; Takemura et al., 2002).

Other non dietary compounds have been implicated to have a role in specific host recognition through detection by gustatory neurons (Schoonhoven and van Loon, 2002; van Drongelen, 1979; Rees, 1969; Montgomery and Arn, 1972), although, given the degree of host recognition cues required to explain the attraction of insects to a specific host, the number of gustatory cells identified that can recognise host chemicals remains insufficient.

Rhizosphere Interactions Including Nematode Location of Roots

Many cyst nematode species have been shown to move towards roots by orientation along concentration gradients of root exudates to which they are attracted, and root diffusates have been shown to contain factors that induce phagostimulation (Rolfe et al., 2000), movement or hatching of nematode egg cysts (Devine and Jones, 2000; Devine and Jones, 2003).

Compounds involved in such long distance attraction must be sufficiently stable to enable them to build up concentration gradients within the soil (Perry, 2005). They would also be expected to be hydrophilic, to facilitate movement through aqueous soil media, in contrast to the air borne hydrophobicvolatile compounds that attract insects. However, there is some evidence that volatile compounds may also play an important role in nematode host localisation (Robinson, 2002). *Z. mays*, seedlings release the volatile sesquiterpene (*E*)-caryophyllene, Fig. 3 (17), into the soil from their roots in response to feeding by the root-attacking herbivore, the western corn root worm, *Diabrotica virgifera virgifera*. This compounds attracts the entomopathogenic nematode, *Heterorhabditis megidis* that feeds on the herbivore. *Z. mays* varieties that produce (*E*)-caryophyllene show reduced infestation by the herbivore in field trials (Rasmann et al., 2005; Gershenzon et al., 2005). Testing of the effect of selected monoterpenoids and alkaloids found in roots on chemotaxis, motility, viability and hatch of nematodes with contrasting life styles shows that nematodes respond differently to the individual compounds. Phenolics and flavonols repel to some species and ferulic acid strongly inhibits motility (Wuyts et al., 2006). A hydrophobic fructose related compound, that attracts the beet cyst nematode *Heterodera schachtii* has been purified from white mustard seed, *Sinapis alba*, roots (Rühm et al., 2003).

There is evidence that phytohormones, in particular auxin, may influence nematode invasion of their host and facilitate establishment of feeding sites (Curtis, 2007). These phytohormones may exert their affect by inducing changes in the nematode cuticle (Akhkha et al., 2002), causing alterations in water uptake and cell signalling. Dopamine and salicylic acid have also been shown to attract nematodes (Wuyts et al., 2006).

Solanoeclepin A, Fig. 3 (18), is a complex compound derived from a triterpenoid steroid structure with nine chemical steriocentres. The compound is released from roots of young potato, *Solanum tuberosum*. Biological activity tests demonstrate that synthetic derivatives of the compound induce premature hatching of potato cyst nematode, *Globodera pallida*, juveniles and therefore may have the potential to be used as an environmentally compatible strategy for pest control (Netherlands Organization For Scientific Research, 2001).

Non-host Avoidance and Stress Perception in Hosts

Initial detection by insects and other invertebrates of unsuitable hosts can involve the perception of deterrent volatile compounds released from their leaves. Such emissions benefit the survival of the emitter and are hence known as allomones. The second stage of non host avoidance involves the encountering of unfavourable secondary defence metabolites within plant tissues.

Negative Interactions (e.g. Allomones)

Initially it was assumed that plant derived volatiles acted only as insect attractants but now it is clear that they can also have a repellent effect (Pickett et al., 1999) due to stimulation of specific neurones that detect non-host semiochemicals (Hori, 1996; Hori and Kamatsu, 1997; Guerrero et al., 1997). Highly specific neurones for isothiocyanates that act as repellents have been found in insects for which brassica are non-hosts, for example, the damson-hop aphid, *Phorodon humuli*, and the black bean aphid, *Aphis fabae* (Nottingham et al., 1991). *A. fabae* olfactory neurones respond to the repellent compound (1*R*,5*S*)-myrtenal, Fig. 3 (19), released from the nonhost herb savory, *Satureja montana* (Hardie et al., 1994).

Where an insect requires more than one host to complete its life cycle, its migration from one host to another may be orchestrated by the release of repellent volatiles from the primary host (Pickett and Glinwood, 2007). In aphid species these alterations in host preference may be accompanied by changes in winged or wingless forms that may differ in their response to certain plant semiochemicals. The spring migrant of *R. padi*, is repelled by volatiles from its winter host, the bird-cherry, *Prunus padus*, and here methyl salicylate may be the active component. The winter host for *A. fabae*, the spindle tree, *Euonymus europeaus*, repels the insect species in the spring, but attracts it in the autumn for the sexual colonization stage (Pettersson et al., 1994). The life cycle of the lettuce aphid, *Nasonovia ribis-nigri*, has led to the identification of a further deterrent compound, *cis*-jasmone, Fig. 3 (20). In spring the aphid is repelled by its winter host, the black currant, *Ribes nigrum*, when the volatiles released from the plant contain high concentrations of the compound. Although *cis*-jasmone is a metabolite of methyl jasmonate, it stimulates a specific olfactory neurone and is also repellent to other aphid species (Birkett et al., 2000). There is also evidence that *cis*-jasmone can act as an inducer of plant defence and when applied to *T. aestivum* plants it causes an increase in the concentration phenolic and hydroxamic acids (Moraes et al., 2008).

Stressed or herbivore attacked plants have altered volatile emission profiles and they may then be perceived as non hosts by approaching insects that would normally colonise them (Pickett et al., 2003). This includes the emission of green leaf volatiles, the first stage of the plants response to herbivory (Turlings et al., 1995), frequently followed by the production of terpenoids (Takabayashi and Dicke, 1996; Halitschke et al., 2001), including monoterpenes ((*E*)- ocimene) and sesqueterpenes ((-)-germacrene D), Fig. 3 (21). The plant's response is partly dependent on the nature of the herbivore and although interactions between plants and chewing insects are well documented (Karban and Baldwin, 1997;

Walling, 2000), less is known about plant responses to sucking or piercing insects (Du et al., 1998; Williams III et al., 2005) (see Section on "Regulation of Plant Toxicants by Natural Activators"). A recent study of the interactions between different types of herbivorous insects and plant defence volatiles showed that tobacco, *Nicotiana tabacum*, releases terpenoids and nicotine after caterpillar regurgitate treatment. Colonisation by western flower thrips, *Frankliniella occidentalis*, was reduced on the regurgitate treated plants, possibly due to the production of nicotine (Delphia et al., 2007).

The aphid alarm pheromone, (*E)*-β-farnesene, Fig. 3 (22), is released from aphids in response to predator attack, but it is also produced by some plants in response to herbivory, although its effect may be masked by other volatile emissions. The wild potato, *Solanum berthaultii*, releases sufficiently high and pure levels of the compound from the trichomes to induce avoidance behaviour in *M. persicae* (Gibson and Pickett, 1983). Transgenic *A. thaliana* plants, expressing an (*E)*-β-farnesene synthase gene are also unattractive to these aphids (Beale et al., 2006). Transformation of *A. thaliana* plants with a dual linalool/nerolidol synthase produced plants constitutively containing 40- to 60-fold higher levels of linalool, Fig. 3 (23), and its glycosylated and hydroxylated derivatives and lower levels of nerolidol, Fig. 4 (24). The high expressing transgenic plant significantly repelled *M. persicae* in dual-choice assays (Aharoni et al., 2003).

Contact Action Including Antifeedants

Antifeedants, as the converse of phagostimulants, stimulate deterrent neurones within the insect taste receptor system (Chapman, 2003) and some compounds possess both activities (Onyilagha et al., 2004 and references therein). Plant tissues contain both stimulatory and deterrent compounds and insects select their hosts on the basis of the balance between the two, with the deterrent molecules carrying the most weight. (Chapman, 2003).

Metabolites present in the phloem of coniferous trees (Scots pine, *Pinus sylvestris*, and Norway spruce, *Picea abies*,) can affect the feeding behaviour of the conifer bark beetle, *Ips typographus* (Faccoli et al., 2005). This has been attributed to phenolic compounds and host plant phenolics, including catchetin, Fig. 4 (25), taxifolin, (26), and resveratrol, (27), have been compared to a nonhost compound, *E*-conophthonin, Fig. 4 (28), in *in vitro* feeding experiments. The antifeedant effects of the phenolics was greater in males than in females and the nonhost compound had the greatest antifeedant properties. The authors suggest that females may have developed resistance to the antifeedants by extended feeding on resistant trees at a stage where the tree's hypersensitive response, and hence antifeedant production, is most active. Males, on the other hand, are more sensitive. This may be because, as the pioneers, they have to select the suitable host for colonisation and are therefore more sensitive to repellents. In addition, they spend less time feeding on living trees gaining less opportunity to develop resistance than females (Faccoli and Schlyter, 2007).

The bean aphid, *Megoura crassicauda*, discriminates between its host, *Vicia faba*, and a non-host, the vetch, *Vicia hirsute*, by tasting specific chemicals during stylet penetration. (*E*)-2-methyl-2-butene-1,4-diol 4-*O*-β-D-glucopyranoside, Fig. 4 (29), in the vetch plant is responsible for the observed non-host avoidance by the aphid, and it is present in sufficiently high concentrations to overcome the effect of feeding stimulants (Ohta et al., 2006). Some terpenoids have been shown to be detected by and to deter insects. Using an *in vitro* assay system, Omar et al. (2007) have identified five terpenoid compounds from the bark of a tropical plant, *Lansium domesticum*, that act as antifeedants against the rice weevil, *Sitophilus oryzae*, at very low concentrations.

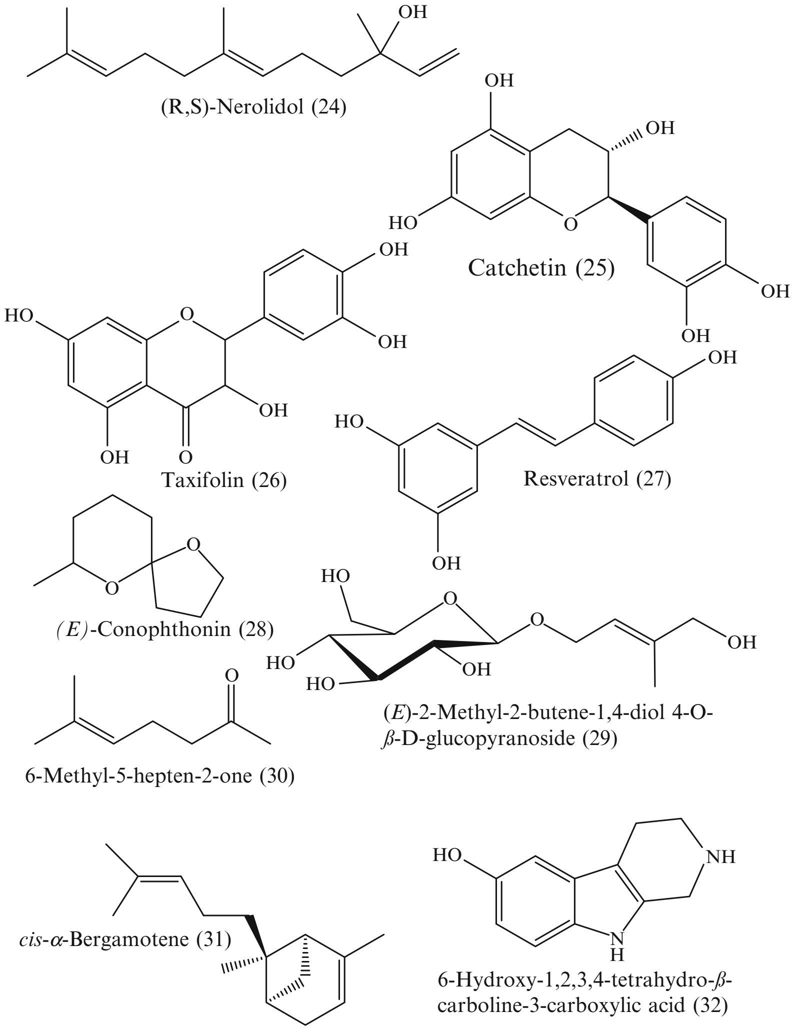


Fig. 4 Chemical structures of compounds 24–32

Higher Trophic Level Interactions

Sequestration of Toxins by Herbivores Against Predators

Some herbivorous insects consume and sequester plant toxins within their tissues to provide protection from predators, either instead of, or in addition to, their own defence mechanisms (Pickett et al., 1999; Macias et al., 2007). This sophisticated strategy frequently leads to highly species specific interactions between host plant and sequestering herbivore. A considerable degree of co-evolutionary development can occur, rendering this phenomenon ideal for the study of the processes underlying natural selection. Pioneering work by Miriam Rothschild

(1972) has led to significant discoveries in more recent years, and it is clear that the sequestration of toxins has been effectively exploited by Lepidoptera and is often associated with aposematic coloration. This can lead to learnt avoidance behaviour by predators or mimicry by other herbivores (Brower, 1969). The chemical structures of the compounds sequestered by moth and butterfly species is posted on the Annual reviews of Entomology web site (www.annualreviews.org) and a review (Nishida, 2002) provides a comprehensive description of many of the intriguing ways that these insects make use of plant compounds to enhance their survival and reproductive capacity.

Some pyrrolizidine alkaloids stored for defence (Bernays et al., 1977), are used to biosynthesise hormones (Nishida et al., 1996), or are converted to other toxic substances (Brown, 1984). The monarch butterfly, *Danaus piexippus*, exploits cardiac glycosides for defence against vertebrate predators (Roeske et al., 1975) and glucosinolates are also favoured by some insects for this type of defence (Aliabadi et al., 2002; Aplin et al., 1975; Müller et al., 2001).

The production of substances that attract herbivores is not of obvious evolutionary benefit to plants. Nonetheless, it is clear that there is a complex interplay between the insects and their hosts and plant induced defence can be converted into a benefit for specialist herbivores by a process of adaptation to toxins that were originally defensive.

Induced Stress Volatiles for Increased Predation and Parasitism (Synomones)

Synomones are semiochemicals that benefit both the emitting and receiving organism. It has been recognised for some time that many plants release volatiles in response to herbivore attack that are capable of attracting insect predators, or parasitoids (parasitic insects that kill their hosts) and this process represents an efficient form of indirect defence for the host plant (Du et al., 1996; Dicke et al., 2003; Turlings and Wäckers, 2004). Wind tunnel bioassays that demonstrate that *A. ervi*, is equally deterred by *V. faba* plants infested by the pea aphid herbivore, *Acyrthosiphon pisum*, as by those that have been infested but have had the aphids removed, demonstrate existence of emissions that function in this way (Du et al., 1996). Many plants exploit this form of indirect defence, including legumes, brassicas and a range of cereal species (Dicke et al., 1998; Takabayashi and Dicke, 1996; Heil, 2008). Several species of spiders, caterpillars and aphids have been shown to induce their host plants to attract their predators or parasitoids (Turlings et al., 1995; Pickett and Glinwood, 2007; De Moraes et al., 1998).

Green leaf volatiles and terpenoids are released from healthy and mechanically damaged plants (Mattiacci et al., 1994; Shiojiri et al., 2001) but their emissions increase upon herbivory and these compounds are one of the herbivore-induced synomones that attract carnivores (Takabayashi and Dicke, 1996; Takabayashi et al., 1994). An intriguing aspect of this tritrophic phenomenon is that the predatory insects can identify the precise nature of the herbivore feeding upon the same host. Female *A. ervi* are more attracted to *V. faba* plants previously infested with host than non host aphids (Du et al., 1996). *Cardiochiles nigriceps*, a parasitic wasp, can distinguish *N. tabacum*, cotton, *Gossypium* spp, and *Z. mays* plants infestated by its host aphid, *Heliothis virescens*, from plants infested by the closely related non-host aphid, *Helicoverpa zea*. (De Moraes et al., 1998). The diamond back moth, *Cotesia plutellae*, discriminates between cabbage plants, *Brassica oleracea*, infested with *Plutella xylostella* (host) and plants infested with *Pieris rapae* (nonhost) aphids (Shiojiri et al., 2000). Analysis of the volatiles released showed both qualitative and quantitative differences in the compounds produced in response to the two aphids (Agelopoulos and Keller, 1994; Shiojiri et al., 2001). Compounds released from these plants in differing amounts included (*Z*)-3-hexen-1-ol, linalool, *cis*-jasmone, humulene, (*E*,*E*)-α-farnesene, (*E*)-ocimene and (*E*)-caryophyllene. Similar compounds, but in different ratios, are released by apple plants, *Malus* spp, infested by two different spider mites, *Panonychus ulmi* and *Tetranychus urticae* (Takabayashi and Dicke, 1996) enabling the predatory mite, *Phytoseiulus persimilis*, to distinguish between the two species. *V. faba*, plants produce higher levels of similar compounds in response to the aphid host of *A. ervi* than its non host, but one compound, 6-methyl-5-hepten-2-one, Fig. 4 (30), appears to have a particularly profound effect on the wasp's behavior (Guerrieri et al., 1999; Pickett and Glinwood, 2007)

The release of volatiles from plant leaves that attract third trophic level insects can be systemic (Dicke et al., 1990). The upper leaves of *V. faba* plants infested with *A. pisum*, become attractive to the parasitoid, *A. ervi*, at least 2 days later than infested leaves (Guerrieri et al., 1999; Pickett and Glinwood, 2007). This suggests that a mobile signal, possibly transported through the vascular system is responsible although more rapid volatile signalling may also occur (See Fig. 5 and the following section).

The production by phylogenetically diverse plant species and the exploitation by parasitoids

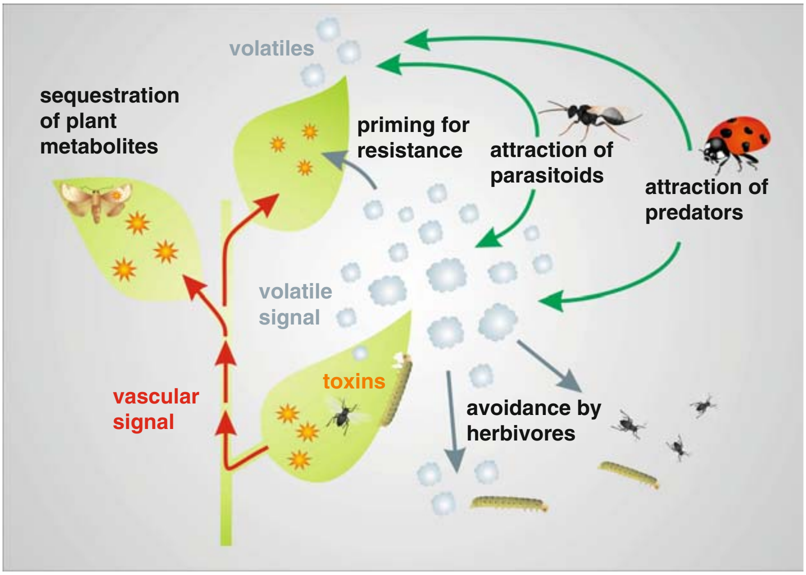


Fig. 5 A diagrammatical representation of the above ground interactions between plants and insects. Feeding by both sucking and chewing insects induces the accumulation of compounds, including those that are directly toxic (basal leaf, orange stars), to defend themselves against the herbivorous insects. The release of volatile emissions is also induced and these cause approaching herbivores to avoid the plant (*grey arrows*) but attract parasitoids and predators (*green arrows*). Volatile emissions also prime neighbouring parts of the plant (upper leaf) for resistance so that when these leaves are challenged herbivores they respond more rapidly to attack. Signals are released into the plants vascular system from insect infested leave that induce the production of defence compounds, including volatiles, from neighbouring, uninfected leaves (*red arrows*). However, some insects consume these compounds and store them within their tissues to deter their own predators (second leaf)

of highly specific chemical signals, keyed to individual herbivore species, indicate that the interaction between plants and the natural enemies of the herbivores that attack them is a highly sophisticated process.

Plant: Plant Interactions

Induction of Direct and Indirect Defence (Parasitoid or Predator Attraction) by External Signals, Both Aerially and Through the Rhizosphere

In addition to their role in defence against herbivores, both directly and involving the third trophic level, it has been believed for some time that plant derived volatiles released upon herbivore attack can induce insect resistance in neighbouring plants (Baldwin and Schultz, 1983; Karban and Baldwin, 1997; Tscharntke et al., 2001). In view of the fact that volatile compounds released from herbivore attacked plants include recognised plant defence signalling compounds, such as methyl jasmonate, methyl salicylate, and ethylene (Farmer, 2001), this is perhaps unsurprising. The rapid release of herbivory induced green leaf volatiles can also affect the expression of genes involved in defence pathways in neighbouring plants and can alter their secondary metabolite profiles including the induction of the release of terpenoids (Bate and Rothstein, 1998; Arimura et al., 2002; Farag and Pare, 2002; Ruther and Kleier, 2005). These effects can be between plants of the same or different species (Karban et al., 2003) and can involve both deterrence of feeding by herbivores and attraction of their predators or parasitoids (see Fig. 5).

The concept has been received with some scepticism as on occasions the observed effect has required unrealistically high levels of compounds, which are often synthetic or purified rather than applied in the ratios released from the plant. Frequently, methods have tested effects in sealed containers (bell jars) which may cause a depletion of CO_2 resulting in non-specific stress responses. The responses in the receiver plants are consider too weak to be of any physiological significance, sufficient replication or reproducibility is often lacking and evidence of the robustness of the phenomenon under field conditions is limited. Furthermore, receiver plants located more than 20 cm away from the emitter plant cease to respond (Karban et al., 2003). The relative merits and short comings of the experimental approaches and the conclusions drawn from them have been the subject of a comprehensive review (Dicke and Bruin, 2001).

The phenomenon continues to be the focus of scientific interest (Baldwin et al., 2006) and has involved the study of a wide range of plant/insect systems. Recent investigations have included analysis of the relationship between the release of converted exogenously applied volatiles (green leaf volatiles) and their *de novo* biosynthesis by the receiving plant (Yan and Wang, 2006) and synergistic effects (Ruther and Kleier, 2005). Transgenic approaches are also now being applied (Paschold et al., 2006) and this has revealed that green leaf volatiles or *cis*-alpha-bergamotene, Fig. 4 (31), may suppress induced defence in neighbouring plants under certain circumstances.

Communication between damaged and healthy plants can also take place below ground, leading to affects on above ground herbivory and parasitoid attraction in neighbouring plants. *V. faba*, and lima bean, *Phaseolus lunatus*, plants exposed to root exudates from plants damaged by *A. pisum*, or *T. urticae*, were more attractive to carnivorous enemies of the herbivores (Dicke and Dijkman, 2001; Guerrieri et al., 2002). Also, root exudates from *V. faba* plants infested by *A. pisum*, cause intact neighbouring plants to become more attractive to parasitoids (Chamberlain et al., 2002). Plant-plant communication affecting herbivore resistance has also been demonstrated between healthy plants. Barley, *Hordeum vulgare*, cultivars experience less aphid settling when exposed to volatiles from other barley cultivars (Pettersson et al., 1999). Root exudate collected from couch grass, *Elytrigia repens*, a pernicious weed known to release a number of biologically active compounds from its roots (see references in Glinwood et al., 2003) induces resistance to *R. padi* when added to *H. vulgare*, roots. The most active ingredient in the exudate was found to be 6-hydroxy-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid, Fig. 4 (32). Root colonisation of *Z. mays*, plants by the parasitic weed, *Striga hermatothica*, reduces susceptibility of the maize plant to infestation by the stem borer, *Chilo partellus* (Khan et al., 2007).

Because neighbouring plants compete for resources, it is not clear how the emitting plant can benefit from this form of plant-plant communication. Possibly, the volatile signals are really intended for other leaves on the same plant, rather than leaves on neighbouring plants. The transmission of an air borne signal would be faster than one transmitted through the plant's vascular system and the latter route would be too slow to provide a defence response in time to protect adjacent leaves effectively from attack by chewing insects (Heil and Ton, 2008). Further more, if the release of volatiles by damaged leaves was intended for leaves of the same plant, this would address the anomaly that the plant to plant effects require the plants to be very close (Karban et al., 2003). Leaves of hybrid poplar, *Populus deltoides* × *nigra*, damaged by the gypsy moth, *Lymantria dispar*, larvae have been shown to release volatiles that enhance defense against the larvae in neighbouring leaves. This has confirmed that damaged leaves can transmit resistance to leaves of the same plant (Frost et al., 2007).

Priming Effects

The benefits to the plant of inducible as opposed to constitutive defence have already been discussed in this chapter with respect to conservation of the plant's energy resources and the reduction of the likelihood of the development of resistance within the insect population. The ability of damaged or herbivore infested plants to induce direct or indirect defence in neighbouring plants has been described above. However, a further novel aspect of plant defence involves the ability of plants that have received prior exposure to certain signals to respond more rapidly to a subsequent encounter by a insect pest (Conrath et al., 2006). The existence of this phenomenon, known as "priming", would indicate that plants have the capacity for memory, better described as "stress imprinting" as the latter definition would not imply that plants are cognisant (Bruce et al., 2007). The advantage to the plant of such a mechanism would be obvious as resources would not be expended but the plant would be on guard to respond more effectively. The initial priming event would be related to the subsequent attacking agent as it would be volatile blends released from damaged plants that would indicate a likelihood of damage in the near future to the receiving plant by a pest known to be in the vicinity.

Definitive evidence for the existence of such defence mechanisms in plants was first provided by Engelberth et al. (2004). These authors observed that the effects of green leaf volatiles on the defence responses of neighbouring plants are weaker, more transient and involve the induction of a limited selection of defence genes in the receiving plant compared to direct exposure to methyl jasmonate or herbivory. However, they demonstrate that *Z. mays* seedlings treated with green leaf volatiles respond both more rapidly and more strongly to a subsequent challenge by mechanical damage or induction with *S. exigua*, regurgitant. This enhanced response involves production of increased amounts of jasmonic acid and volatile sesquiterpenes. By studying the effects on gene expression, volatile emission and insect behaviour Ton et al. (2007) have also shown that green leaf volatiles released from the Mediterranean brocade caterpillar, *Spodoptera littoralis*, infested plants prime neighbouring plants for defence against the same insects. The volatile emissions induced faster and greater enhancement of expression of several defence genes on caterpillar attack, but did not induce the gene expression directly. The volatile profile was enhanced, caterpillar growth negatively effected and there were positive effects on the third trophic level. Priming has also been demonstrated with other plant species, for example volatile compounds released from detached sagebrush, *Artemisia tridentate*, leaves increase the defence response of *N. tobacum* plants to *M. sexta* attack (Kessler et al., 2006). The within plants effects described above in poplar are also described as priming, and here the advantage to the plant of the speed of the transmission of the wound signal are self evident (Frost et al., 2007; Heil and Ton, 2008).

The underlying mechanisms responsible for priming are currently speculative but are the focus of much scientific investigation. It has been suggested that signalling metabolites or transcription factors may be increased upon exposure to the priming agent. Potentially this could represent the increased accumulation of an inactive precursor (glycoside for example) that could be converted to an active defence compound more rapidly than the production of the defence compound by *de novo* biosynthesis. Epigenetic modifications could also occur, such that after priming a genetic change is instigated that enables the transcriptional events involved in defence to proceed more rapidly upon induction (Bruce et al., 2007).

Conclusions

The interactions between plants and insects are highly complex and are subject to continuing co-evolutionary changes and developments (Wheat et al., 2007). Plants have successfully exploited the wide range of natural secondary metabolites that they produce to defend themselves against insects. Although these strategies include the accumulation or release of compounds that are directly toxic or repellent to herbivores, there are also many examples of the ability of plants to further enhance their defensive capacity by the attraction of natural enemies of herbivorous insects. In turn, however, pest populations have managed to circumvent, or even benefit from, many plant defence products by detoxification or sequestration, enabling some specialist feeders to develop their own independent ecological niche.

The important challenge for the future is to establish to what extent these interactions can be extended or manipulated to develop environmentally compatible pest control. This could involve either traditional breeding or genetic engineering to introduce defence enhancing traits into plants. Such traits could include spatially advantageous enhanced constitutive or induced expression of defence compounds or more rapid, sensitive priming responses. At this stage field studies to test the feasibility of such approaches are at preliminary stages but there is clear evidence that plant released compounds can influence pest behaviour in natural situations (De Moraes et al., 1998; Rasmann et al., 2005; Steppuhn et al., 2004; Thaler, 1999). Fast through-put molecular techniques, genome mapping and both plant and insect whole genome sequence information are now becoming available. It can be anticipated that with the application of these technologies the regulatory mechanisms underlying plant defence responses will be unraveled enabling progress towards this goal to be achieved. However, it remains to be established whether the pressures of co-evolution leading to pest resistance can be overcome.

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