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REVIEW ARTICLE

Aspects of insect chemical ecology: exploitation of reception and detection as tools for deception of pests and beneficial insects

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Abstract. Empirical exploitation of insect reception and detection at the peripheral neurosensory level has been extremely valuable for identifying pheromones and other semiochemicals, mainly by electroantennogram or single cell preparations coupled with capillary gas chromatography. Differential sensitivity to semiochemicals at the single-cell level has allowed the identification of some of the most active semiochemicals relating to host location and, more importantly, to the avoidance of nonhosts. However, in terms of molecular recognition, there is still a considerable gap in understanding the detection of particular molecules and their discrimination from closely-related chemical structures. New approaches will be needed to understand the processes of molecular recognition more precisely. Nevertheless, from electrophysiological studies to the most advanced molecular techniques, it has been possible to identify semiochemicals for the deception of pests in their quest to find plant and animal hosts, as well as mates. Even the deception of insects antagonistic to pests, particularly parasitoids, can now be exploited for managing pests in more sustainable systems. Successes in exploiting insect semiochemicals in the interests of better agriculture and animal husbandry are exemplified, and potential new ways of learning more about reception and detection for deception are discussed. This takes the subject beyond the management of pest and beneficial insects to wider commercial and social opportunities.

Key words. Animal/insect interactions, behaviour, chemical ecology, electrophysiology, GM, GMO, insects, mixture recognition, olfaction, plant/insect interactions, semiochemicals, small lipophilic molecules.

Introduction

Insects possess highly sensitive olfactory systems with the capacity for the fine spatiotemporal resolution of olfactory signals having potent effects on their behaviour. The techniques

developed to study the reception and detection of volatile semiochemicals can be exploited to identify tools for the deception of pest insects and to manage, more effectively, beneficial organisms antagonistic to these pests. For example, aphid semiochemicals mediating behaviour at all stages in the development of host-alternating species in the subfamily Aphidinae can be identified. Some have been developed for novel approaches to pest and beneficial insect management, with further opportunities emerging as new discoveries are made. Examples of semiochemicals at each stage of the aphid

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life cycle will be used to exemplify these opportunities. Aphid sex pheromones, employed in mating on the primary (winter) host, also have kairomonal roles for their parasitoids and predators, as does the aphid alarm pheromone. Aphid detection and discrimination of host and nonhost compounds, which can involve responses to specific blends or use of taxonomically-specific semiochemicals (Bruce & Pickett, 2011), facilitate host switching and location of the primary and secondary (summer) hosts in host-alternating species. The induction of nonhost cues on aphid damage is responsible for the recruitment of parasitoids and these induced semiochemicals can also cause neighbouring, intact plants to induce defence strategies.

Many of the semiochemicals that are targets for manipulation to improve management of aphids and other pests are highly volatile and chemically unstable. This presents problems that could be overcome by new plant breeding approaches and the use of genetic modification (GM) of crop plants to release target compounds (Pickett & Poppy, 2001; Bruce & Pickett, 2007). Also, plant species 'attractive' or 'repellent' to pests and beneficial insects have been identified from global plant diversity, particularly in tropical regions such as Africa, where they are grown in companion cropping systems within a push-pull or stimulo-deterrent diversionary strategy (Cook *et al.*, 2007). These plants are useful not only for direct and indirect control of lepidopteran stem borers, but also for providing leads for new plant defence elicitors, particularly in traditional cereal varieties (Bruce *et al.*, 2010; Tamiru *et al.*, 2011).

This review begins with aphid chemical ecology and extends to other phytophagous insects and higher trophic interactions. However, work on carnivorous, particularly haematophagous, insects again demonstrates the value of exploiting reception and detection of volatile semiochemicals in creating new opportunities to manage insects causing nuisance and vectoring pathogens to farmed animals, as well as to human beings.

Insects offer an opportunity for detecting volatile compounds related to food safety and quality, as well as forensic and security issues. However, although the immense sophistication of insect olfaction allows the detection of anthropogenic compounds, as exemplified by use of honeybees in this context (G. I. Aradottir, unpublished data), sensitivity is generally much lower than to volatiles occurring naturally in the environment.

Although it had originally been expected that there would be a greater role for odorant binding proteins in molecular recognition (Field *et al.*, 2000) than has been evidenced so far, there are opportunities for using semiochemical detection measured electrophysiologically; for example, in identifying repellents (Pickett *et al.*, 2008). For the longer term, work on molecular recognition may provide uses for pheromone detection that are more valuable than trapping, which often only impacts male insects responding to such semiochemistry (Birkett & Pickett, 2006). However, in the current absence of absolute knowledge of the molecular recognition principles used by insects in olfaction and, indeed, by other animals, including human beings, it is possible to envisage designing, rationally, semiochemical analogues using the structural biology underpinning their biosynthesis. Analogues that bind more strongly than the

natural ligands could offer a new means for disrupting pest insect behaviour.

Lessons from aphids

Aphids (Aphididae) such as pests in the subfamily Aphidinae have sophisticated life cycles, with crucial stages mediated by semiochemicals. Thus, aphid sex pheromones are employed in mating, which occurs during the autumn on the winter hosts where the aphid is host-alternating, and this activity may also be moderated by host-plant chemistry. The return of the spring alate (winged) generation to the summer hosts is facilitated not only by summer host-derived 'attractants', but also by the 'repellents' effects of winter-host semiochemicals on aphids at this stage of the life cycle, and on alate summer forms generally. Interactions with parasitoids and predators are also mediated naturally by aphid sex and alarm pheromones. For all these stages, volatile semiochemicals have been identified by analytical chemistry methods, guided by electrophysiological and behavioural studies to determine the bioactive compounds (Pickett *et al.*, 1992).

Aphid sex pheromones

By entraining air from around sexual female aphids (oviparae) and analyzing behaviourally active samples by gas chromatography (GC) coupled with electrophysiological preparations, particularly single cell (i.e. olfactory neurone) recordings (SCR), followed by chemical studies, the sex pheromones for many members of the Aphidinae have been identified. These mainly comprise compounds having the cyclopentanoid structure shown in Fig. 1 (I–V) (Dawson *et al.*, 1987; Pickett *et al.*, 1992; Birkett & Pickett, 2003; Pickett & Glinwood, 2007; Dewhurst *et al.*, 2008; Birkett *et al.*, 2010). The SCRs were made with finely-sharpened tungsten electrodes placed,

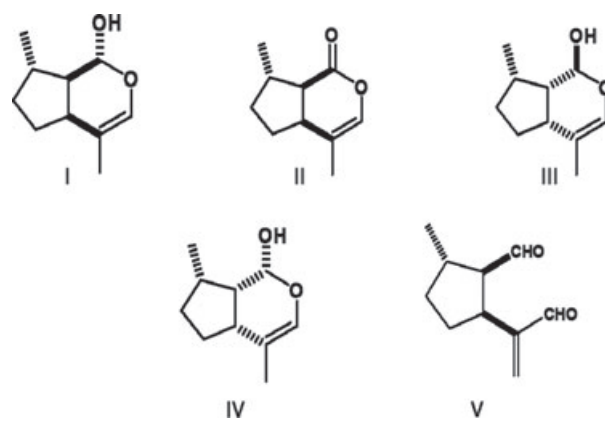


Fig. 1. Chemical structures of sex pheromone components identified for aphids in the subfamily Aphidinae. I, (1R,4aS,7S,7aR)-nepetalactol; II, (4aS,7S,7aR)-nepetalactone; III, (1S,4aR,7S,7aS)-nepetalactol; IV, (1R,4aR,7S,7aS)-nepetalactol; V, (1S,2R,3S)-dolichodial.

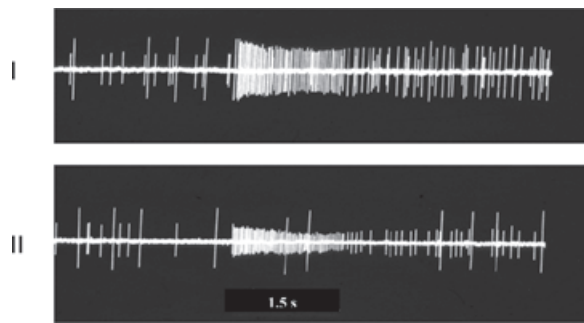


Fig. 2. Responses of two olfactory cells within a secondary rhinarium (third antennal segment) from the male pea aphid *Acyrtosiphon pisum* to sex pheromone components. Upper trace: lactol I; lower trace: lactone II. Bar = 1.5-s stimulation.

using micromanipulators, close to the cell bodies within the secondary rhinaria on the third or fourth segments of the male aphid antenna. Typically, two cell types can be observed, each selectively responding to the lactol (I) or the lactone (II) (Fig. 1). The spike amplitude of the responding cells is usually greater for the lactol (e.g. with the pea aphid *Acyrtosiphon pisum*) (Fig. 2); dose–response curves can be constructed for these cells, which show little or no response to the alternative compound (Dawson *et al.*, 1990). Unexpectedly, for the damson-hop aphid *Phorodon humuli*, the sex pheromone comprises the isomeric lactols (III) and (IV) (Campbell *et al.*, 1990), although an olfactory cell within the rhinarium with smaller spikes also responds to the lactone (II) (Fig. 3). With the full genomic sequence and annotation for *A. pisum* (International Aphid Genomics Consortium, 2010), there is now an opportunity to investigate the nature of isomer recognition by the molecular apparatus associated with olfactory cells responding to sex pheromone components. Genes implicated in the process could be knocked out and electrophysiological responses of the mutant aphids investigated.

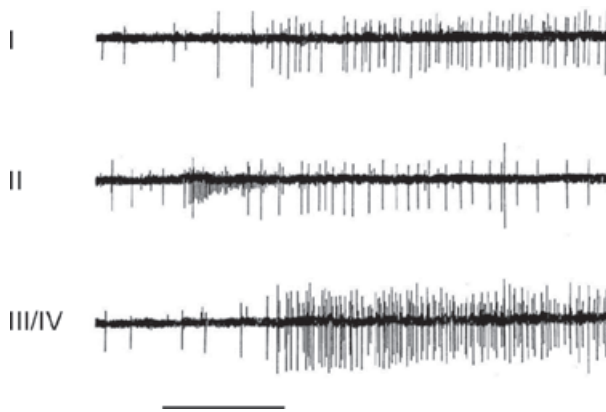


Fig. 3. Responses of several olfactory cells within a secondary rhinarium (third antennal segment) from the male damson-hop aphid *Phorodon humuli* to sex pheromone components. Upper trace: lactol I; middle trace: lactone II; lower trace: lactols III/IV. Bar = 2-s stimulation.

Aphid sex pheromone components influence the behaviour of parasitoids (Powell & Pickett, 2003), acting as ‘attractants’ for these beneficial insects because they are host-associated cues. Interestingly, the parasitoids still respond to these components during the summer, even when aphids are not naturally producing sex pheromones. The behaviour of aphid predators such as lacewings (Chrysopidae) and ladybird beetles (Coccinellidae) is also affected by these sex pheromone components (Boo *et al.*, 2003; Koczor *et al.*, 2010; Leroy *et al.*, 2011), and a particular lacewing, *Peyerimhoffina gracilis*, was discovered for the first time in the U.K. using water traps in the field in association with the lactone (II) (Donato *et al.*, 2001). Ladybird beetles also respond to another aphid semiochemical, the alarm pheromone (Al Abassi *et al.*, 2000), for which the relevant studies are described below. Because these compounds offer an opportunity to control aphids (Campbell *et al.*, 1990), as well as to exploit parasitoids and predators for biological control, an alternative to chemical synthesis, which is too expensive for agricultural use, was developed. Thus, by commercial cultivation of the catmint *Nepeta cataria* (Lamiaceae), the lactone (II) can be isolated by industrial scale steam distillation and converted to the lactol (I) by inexpensive chemical means (Birkett & Pickett, 2003). The large amounts of pure lactone (II), thereby available, allowed further elaboration to fully reduced dihydropetalactols, for which the absolute stereochemistry has been determined (Hooper *et al.*, 2002).

Host location and nonhost avoidance

Regarding the use of semiochemicals for host/nonhost distinction, there are two hypotheses, one involving blend and ratio-specific recognition of mixtures of commonly occurring plant volatiles, and the other involving exploitation of taxonomically characteristic compounds (Bruce & Pickett, 2011). For the first hypothesis, recent work has provided unexpected results. Volatiles entrained from the broad bean *Vicia faba* (Fabaceae) were analyzed by GC coupled to electroantennography (GC-EAG) on the black bean aphid *Aphis fabae*. Fifteen compounds were identified and the complete synthetic mixture, at the relative concentrations found naturally, was shown to be as ‘attractive’ in the Pettersson four-way olfactometer as the entrainment sample, and also the plant itself (Webster *et al.*, 2008a, b, 2010). However, when compounds were tested individually at natural levels in the olfactometer, only (*Z*)-3-hexen-1-ol was ‘attractive’, although less active than the complete mixture. Dose–response measurements in the olfactometer to the individual 15 compounds demonstrated that, at levels close to the natural release rates, each compound could be ‘repellent’. The complete mixture was therefore reassembled using these levels, whereupon it was again significantly ‘attractive’. This example highlights how a combination of semiochemicals, as a blend, can elicit a different behavioural response to individual compounds.

The second hypothesis was tested with the damson-hop aphid *P. humuli*, initially using electrophysiological tools, although no evidence of recognition of compounds specific to its host, the hop *Humulus lupulus* (Cannabiaceae) could

be demonstrated. However, for the mustard aphid *Lipaphis erysimi* and the cabbage aphid *Brevicoryne brassicae*, there was specific recognition, as was expected, of the organic isothiocyanates formed by the catabolism of the glucosinolates typical of their brassicaceous host plants (Nottingham *et al.*, 1991). There were clear dose–response differences, with respect to olfactory cells located in the proximal primary rhinarium on the antenna, from the four isothiocyanates tested, including 3-butenyl isothiocyanate. Interestingly, similar dose–responses were found with cells in the proximal primary rhinarium of the black bean aphid *A. fabae*, which does not colonize plants in the Brassicaceae. At higher levels, 3-butenyl isothiocyanate was ‘repellent’ to *A. fabae* and, at lower levels, when presented with bean volatiles, it significantly interfered with ‘attraction’ to the host odour (Nottingham *et al.*, 1991).

Opportunities for use of genetically-modified crop plants against aphids

By investigating and understanding host location, approaches to deterring pest aphids can be discovered (Bruce & Pickett, 2011). However, rather than using a repellent mixture of compounds applied to the crop, host recognition could be disrupted by altering the composition of mixtures released by the plant, or by adding nonhost specific compounds using GM and even plant breeding, although the latter would probably only apply to changing mixture composition. The biosynthesis of some such semiochemicals is already known, as are the associated genetics, presenting a potential target for this new type of pest resistance in crop plants. Another opportunity for ‘repelling’ aphids by GM was also proposed (Pickett, 1985) and was achieved in the model plant *Arabidopsis thaliana*, genetically transformed with a gene for synthesizing (*E*)- β -farnesene, the alarm pheromone for many pest aphids (Beale *et al.*, 2006). These *A. thaliana* plants expressed a gene for the synthesis of pure (*E*)- β -farnesene, with this being necessary to avoid aphid alarm pheromone inhibitors such as the (1*R*,4*E*,9*S*)-caryophyllene produced naturally by plants (Dawson *et al.*, 1984; Bruce *et al.*, 2005). Transformed plants were found to be ‘repellent’ to the peach-potato aphid *Myzus persicae*, as well as to cause increased foraging by the aphid parasitoid *Diaeretiella rapae* (Beale *et al.*, 2006). Furthermore, transformation with an (*E*)- β -farnesene synthase gene has now been achieved in an elite wheat variety, Cadenza, using more sophisticated molecular methods. The transformed wheat elicits similar aphid ‘repellency’ and increased parasitoid foraging behaviour in the laboratory (T. J. A. Bruce, unpublished data), and permission has now been obtained from the U.K. Government Advisory Committee on Releases to the Environment for field trials commencing in 2012.

Switching on plant defences against pest insects

Another approach to exploiting plant semiochemicals is to ‘switch on’ defence mechanisms by applying naturally existing

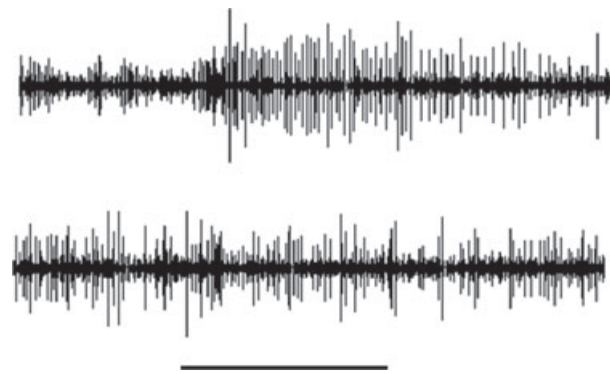


Fig. 4. Response of an olfactory cell on the antenna of an aphid parasitoid *Aphidius ervi* to (*E,E*)-4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT). Upper trace, TMTT; lower trace, hexane control. Bar = 2-s stimulation.

plant-defence activators. Thus, the release of defence compounds that ‘attract’ parasitoids, such as the homo- or tetranorisoprenoids to which many parasitoids, including those of aphids, are highly sensitive (Fig. 4), could be activated by naturally occurring small lipophilic molecules (SLMs) identified from pest-damaged or nonhost plants, as shown in Fig. 5 (A and B, respectively). *cis*-Jasmone has been identified as such an SLM (Birkett *et al.*, 2000; Bruce *et al.*, 2003), causing the release of (*E,E*)-4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT) from cotton, *Gossypium hirsutum* (Malvaceae), that repels the cotton aphid, *Aphis gossypii*, and from soybean *Glycine max* (Fabaceae), which ‘attracts’ parasitoids of the stink bug *Euschistus heros* (Pentatomidae) (Morales *et al.*, 2009). Similar effects occur with *A. thaliana*, including an increase in foraging behaviour by the aphid parasitoid *Aphidius ervi* (Pickett *et al.*, 2007), and this plant enables the genetics associated with *cis*-jasmone defence activation to be investigated. These show substantial differences from those produced by jasmonic acid (Bruce *et al.*, 2008; Matthes *et al.*, 2010, 2011), which not only induces defence but also causes deleterious effects. Eventually, activation with *cis*-jasmone will be used to ‘switch on’ the genes for (*E*)- β -farnesene synthesis in wheat, thereby allowing the genes only to be activated when aphid attack is predicted by decision support systems.

Work in East Africa has led to development of a push–pull system, or stimulo-deterrent diversionary strategy (Cook *et al.*, 2007) for the control of lepidopteran stem borer pests by companion cropping in cereal crops (Poaceae) such as maize (*Zea mays*), sorghum (*Sorghum bicolor*), rice (*Oryza* spp.) and millets (various species) (Khan *et al.*, 2008a, b, 2009; Obura *et al.*, 2009). The release of (*E*)-4,8-dimethyl-1,3,7-nonatriene (DMNT) by intercrop plants ‘repels’ ovipositing stem borer moths and ‘attracts’ their parasitoids (Khan *et al.*, 1997). More recent work has shown that eggs laid on maize by the stem borer moth *Chilo partellus* (Crambidae) cause DMNT and TMTT to be produced, although only with original landraces rather than modern hybrid maize varieties. These compounds ‘attract’ egg parasitoids and also larval parasitoids in anticipation of larval hatching, comprising a truly ‘smart’ natural plant-defence system (Bruce *et al.*, 2010; Tamiru *et al.*,

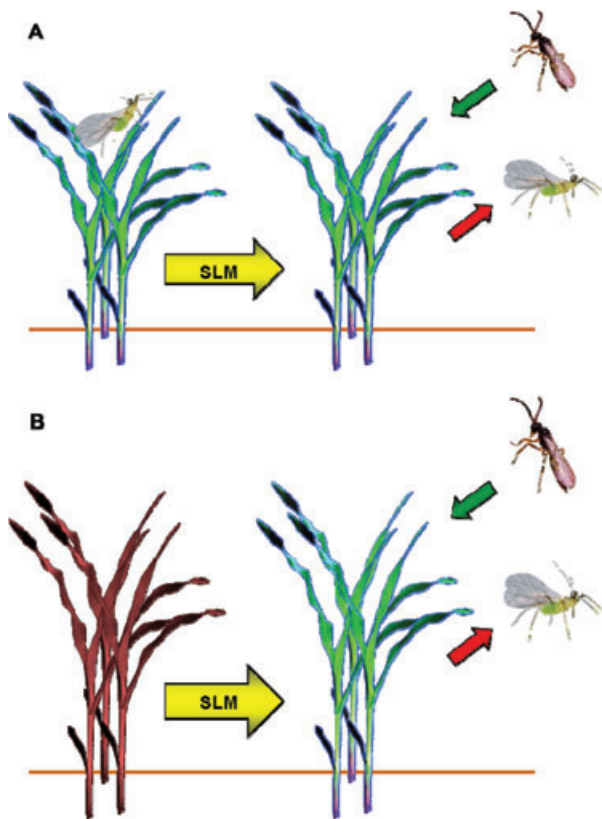


Fig. 5. Plant-defence compounds ‘attracting’ parasitoids and ‘repelling’ aphids could be activated by naturally occurring small lipophilic molecules (SLM) identified from (A) pest-damaged or (B) nonhost plants.

2011). More recently, this effect has been found in farmers’ varieties of open pollinated maize, providing opportunities for exploitation by further breeding for resource-poor farmers who save seed rather than purchasing hybrid seeds (C. A. O. Midega, unpublished data).

Human and livestock disease vectors

Pheromones can be identified for haematophagous insects and affect important stages in their life cycles. For example, the oviposition pheromone of the southern house mosquito *Culex quinquefasciatus*, as well as other nuisance and pathogen vectoring mosquitoes in this genus, ‘attracts’ gravid females to oviposit. The synthetic pheromone (Laurence & Pickett, 1982), now commercialized in the U.S.A., can be used to encourage females to oviposit in water treated with a larvicide (Pickett & Woodcock, 1996) or biological control agents such as the oomycete *Lagenidium giganteum* (Brey & Remaudiere, 1985; Brey *et al.*, 1988). The synthetic pheromone also requires cues for the oviposition site indicating the presence of larval food, and the first example of GC-SCR with mosquitoes identified such semiochemicals (Pickett & Woodcock, 1996). For developing countries, the synthetic pheromone is too expensive,

although this can be solved, as with aphid sex pheromone production, by using a botanical feedstock. In field trials in Nigeria, using the plant-derived-pheromone and the oviposition cue skatole, a synergistic effect between the two agents was demonstrated, leading to a massive deposition of egg rafts (Olagbemi *et al.*, 1999, 2004). A similar approach to developing a plant-based synthesis has been devised for production of potentially useful pheromones for New World sandflies *Lutzomyia longipalpis* (Psychodidae), which are released by males to affect female behaviour (Hooper *et al.*, 2006).

The discovery of the mechanisms by which commercial repellents of haematophagous insects such as *N,N*-diethyl-meta-toluamide act (Pickett *et al.*, 2008; Syed & Leal, 2008; Stanczyk *et al.*, 2010) will provide a more rational route to such agents for insect vector management. Thus, the finding that these compounds act on specific antennal cells naturally responding to plant compounds that mosquitoes, at certain stages of the life cycle, actively avoid, offers a means for screening natural products, and even synthetic compound libraries, by GC-SCR for more active or benign repellents. A more effective repellent from this work could be useful not only against nuisance insects, but also as a component of insect vector management for personal protection in malaria control.

Exploiting molecular recognition by insects

The insect olfactory system has phenomenal sensitivity for certain compounds. Personal experience has shown that electrophysiological responses can be elicited from insects using doses of compounds far below the detection threshold of the GC flame ionization detector. Thus, the molecular recognition power of insects has considerable potential for exploitation beyond the management of pests and beneficial insects, or indeed the conservation of endangered insects and those providing ecosystem services. The company Inscentinel Ltd (U.K.), at present formally associated with Rothamsted, is developing the commercial use of honeybees *Apis mellifera* (Apidae) to detect volatile compounds associated with forensic and security issues. Recently, together with Rothamsted, honeybees were trained, using the odour-conditioned proboscis extension assay, to respond to volatiles associated with early or light infestations of oranges by the Mediterranean fruit fly *Ceratitis capitata* (Tephritidae) for the juicing trade (K. Chamberlain, unpublished data). However, although honeybees were able to detect infestation despite high levels of unrelated volatile compounds produced, field work suggested that the system was insufficiently sensitive for commercial use. It was noted from GC-EAG studies that the Mediterranean fruit fly itself may offer opportunities, although this insect lacks features suitable for commercialization. One aspect may be that the honeybee, although able to recognize completely anthropogenic compounds, may be more sensitive and selective when dealing with compounds for which there is a role in honeybee chemical ecology. Thus, for linalool and 2-phenylethanol, there are substantially greater EAG responses compared with those from the anthropogenic 2,3-dimethyl-2,3-dinitrobutane used in detection of explosives (G. I. Aradottir, unpublished

data). This relates to observations on the single cell acuity of honeybees, with SCR for 2-phenylethanol being two orders of magnitude more sensitive than the EAG responses (C. M. Woodcock, unpublished data). Certainly, in mixture recognition, honeybees use a hierarchy of compounds within a mixture when presented with the individual components (Blight *et al.*, 1997; Le Metayer *et al.*, 1997). All of this argues against the widely expressed views that 'honeybees can smell anything', which may nonetheless be true when using unnaturally high stimulus concentrations from neat compounds or essential oils.

An alternative approach to using whole insects is the use of proteins from the molecular apparatus of insect olfaction itself. The odorant-binding proteins (OBPs), which include the pheromone BPs (PBPs), showed promise because of their robust nature and the genes for these could be identified by searching genome databases; for example, from the fruit fly *Drosophila melanogaster* (Drosophilidae), the African malaria mosquito *Anopheles gambiae* (Culicidae), the yellow fever mosquito *Aedes aegypti* (Culicidae), the silk moth *Bombyx mori* (Bombycidae) and *A. mellifera*. The search uses an algorithm designed to detect the protein structures for OBPs, which, although without unique or common sequence features, have specific configurations of cysteines joined by disulphide bridges (Zhou *et al.*, 2004a, b, 2006, 2008; Li *et al.*, 2005). Over-expressing in *Escherichia coli* and purification provided the recombinant OBPs for ligand binding studies (Zhou *et al.*, 2009; He *et al.*, 2010). Little of the hypothesized molecular recognition could be observed with standard binding studies using displacement of fluorescent ligands such as *N*-phenyl-1-naphthylamine (Zhou *et al.*, 2009). However, with *B. mori*, using mass spectrometry in electrospray mode, it was possible to detect ions from ligand and OBP bound together and, with this technique, it was found that the sex pheromone component bombykol, (*E,Z*)-10,12-hexadecadienol, bound more strongly than other closely-related isomers to the PBP BmorPBP, although the aldehyde component bombykal did not bind at all (Hooper *et al.*, 2009). Nonetheless, to enable future work in this direction, more sophisticated systems that also involve the combined expression of odorant receptor proteins with the OBPs (L. M. Field, personal communication) will be necessary.

A novel approach to determining structure–activity relationships in insect semiochemicals, which so far has not been possible using proteins from the olfactory process, is to provide a range of potential substrates for plant semiochemical biosynthesis to the synthase enzymes involved. Thus, these substrates, recognized and converted into analogues of the semiochemical should, by the very process, have a similar active space and thereby be candidates for having biological activity. This possibility is currently being studied.

Studies on insect molecular recognition, including advances in mass spectrometry that will eventually provide miniaturised systems, could offer new insect monitoring approaches. The semiochemical-releasing stage of the life cycle, i.e. usually adult females for sex pheromones, could be monitored by direct detection of semiochemicals in the environment and thereby offer new insights into chemical ecology.

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