Pure Appl. Chem., Vol. 79, No. 12, pp. 2129–2136, 2007.
doi:10.1351/pac200779122129

Semiochemicals for insect pest management*

Torbjörn Norin‡

Organic Chemistry, Department of Chemistry, Royal Institute of Technology, SE-10044 Stockholm, Sweden

Abstract: Methods for crop protection based on semiochemicals show advantages over methods based on conventional insecticides. Applications of semiochemicals for insect pest management have, however, been limited. Some recent studies carried out in an interdisciplinary research program by five research groups in Sweden are presented. In spite of the chemodiversity in nature, it is striking that many simple and common compounds are important as chemical signals. This paper focuses on some examples of such simple signals, which are now used for monitoring and suppression of pest insects.

Keywords: pheromones; allelochemicals; allomones; kairomones; antifeedants; SPME technique.

INTRODUCTION

Semiochemicals determine insect life situations such as feeding, mating, and egg-laying (ovipositing). Semiochemicals are thus potential agents for selective control of pest insects (for definitions of terms used for various chemical signals, see Fig. 1). Biological control with pheromones or kairomones can be used for detection and monitoring of insect populations. Monitoring is important for the efficient use of conventional insecticides. Mating disruption by use of pheromones is a promising and, in many cases, a successful strategy for control (confusion strategy). The use of semiochemicals as feeding deterrents is another strategy. The most common strategy for control by the use of semiochemicals is to attract, trap, and kill the pest insects.

Since the first identification of a pheromone over 40 years ago, chemical signals have received much attention from scientists in biology, chemistry, and agriculture/forestry. Many of the findings have come into practical use for monitoring or suppression of insect pests. Crop protection based on semiochemicals has advantages over conventional insecticides, but is not yet widely used. We need more efficient technology transfer for those who will benefit by applications of control methods based on semiochemicals. We also need to learn more about the chemical language of insects and plants. The olfactory system of insects is very sensitive, and limited amounts of semiochemicals are needed for control. This is demonstrated by the current application of pheromones for control (mating disruption by confusion strategy) of codling moth (*Cydia pomonella*) in apple orchards [1]. A dispenser for insect control emits about 1 μg/ha, and the amounts of pheromone needed for control using confusion strategy are only about 1 g/ha. On the other hand, the amount of insecticide needed for a conventional treatment is in this case about 1 kg/ha. Furthermore, the use of nonselective insecticides is questioned because of ecological and environmental reasons.

This account is a presentation of some results from a current research program carried out in close collaboration between several research groups in Sweden (see: <http://www.biosignal.org>). The ulti-

*Paper based on a presentation at the 9th Eurasia Conference on Chemical Sciences, 9–13 September 2006, Antalya, Turkey. Other presentations are published in this issue, pp. 2101–2177.

‡E-mail: tnorin@kth.se

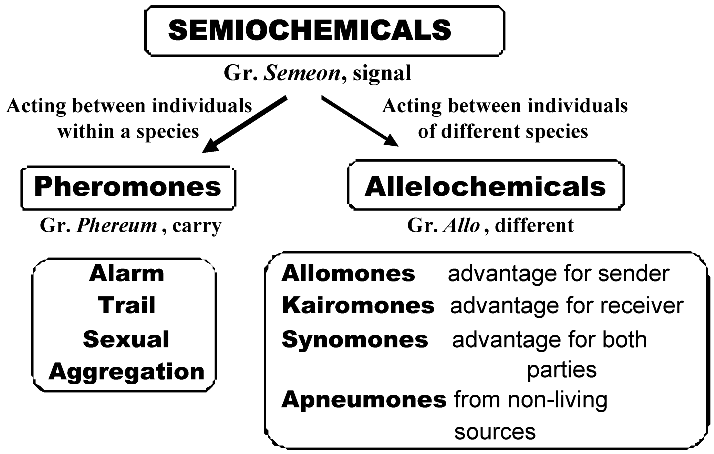


Fig. 1 Terms commonly used for various semiochemicals (chemical signals).

mate aim of the program is to develop methods for control of pest insects. The interdisciplinary research is most stimulating and is carried out in collaboration between specialists in biology, ecology, ecological chemistry, and organic chemistry. This paper is dedicated to the memory of the late Prof. Jan Löfqvist (1935–2004), professor of chemical ecology of the Swedish Agricultural University. Jan has been a stimulating partner and coworker as well as an efficient coordinator of the research program.

DISCUSSION

Chemistry plays a central role in an interdisciplinary research of this type. Sensitive analytical techniques and advanced organic synthesis are essential for successful research. Advanced tools are needed such as sensitive spectroscopic equipment (e.g., NMR, GC-MS, HPLC-MS), as well as equipment for electrophysiological recordings.

An important tool is the solid-phase micro extraction (SPME) technique, which is used for collection and enrichment of the signals [2,3]. The advantage of using the SPME technique is clearly shown in our study of the pheromone constituents of the Brazilian leafroller, *Bonagota cranoides* (Fig. 2) [4].

Important contributions in research on semiochemicals and their applications for control of pest insects can also be achieved in rather simply equipped chemical laboratories. Collaboration with biologists is essential. In particular, biological tests are needed for the detection and evaluation of chemical interactions between organisms.

Synthetic organic chemistry is important for successful identification of active compounds. Synthesis is also important for preparing compounds for biological tests in order to confirm the chromatographic and spectroscopic identification of a chemical signal and for field tests.

The chemical signals are either one single compound or a mixture of compounds in specific proportions. The signal may be a rather common and structurally simple compound. Very often, such a common compound can have different biological functions on different species. In this presentation, you will find examples of such simple chemical signals.

We have recently found that water is an aggregation signal for the almond moth, *Ephestia cautella*, an insect that may cause problems in chocolate and candy production units [5]. Water seems also useful for the aggregation of other pest insects (the pyralid moths *Ephestia kuehniella* and *Plodia interpunctella*) that cause damage in the food industry and on stored food products. Water traps in combination with pheromones for mating disruption seem to be an efficient method for control [5,6]. This control method is at the moment under further investigation for practical applications.

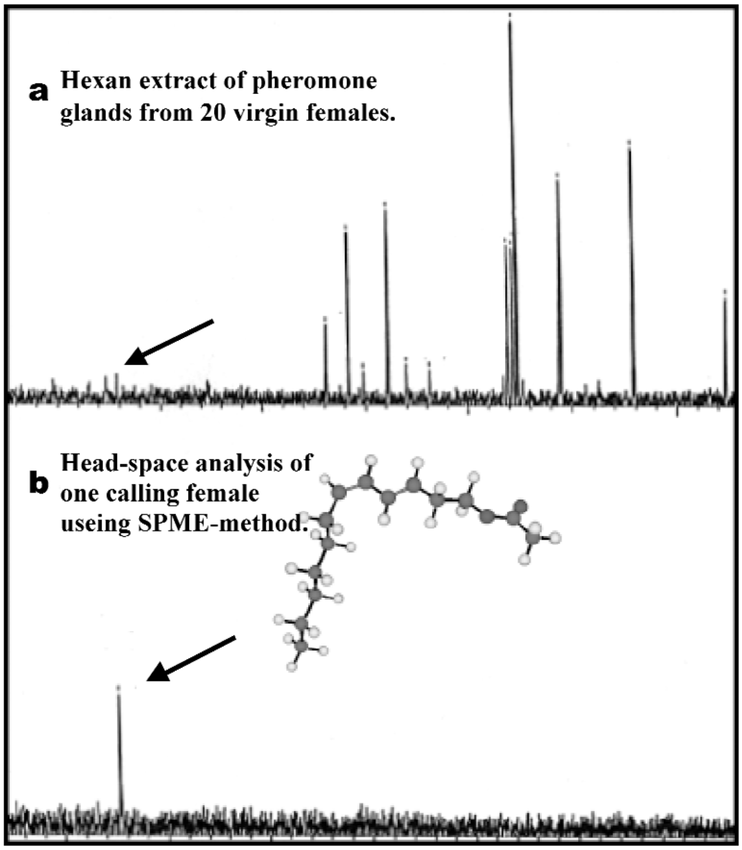


Fig. 2 SPME technique for collection and enrichment of volatiles. Pheromone analysis of the Brazilian leafroller, *B. cranoides* [5]. (a) GC of a hexane extract of the pheromone glands from 20 virgin females; (b) GC from a head space analysis of one virgin female using SPME technique. Note the very weak GC peak from the pheromone component (3*E*,5*Z*)-dodeca-3,5-dienyl acetate in the GC recording from the hexane extract.

Chocolate volatiles are powerful attractants for both sexes of *E. cautella* and *P. interpunctella*. Important volatile constituents are ethyl vanillin, nonanal, and phenylacetaldehyde (Fig. 3) [7]. Control methods based on these findings are under investigation.

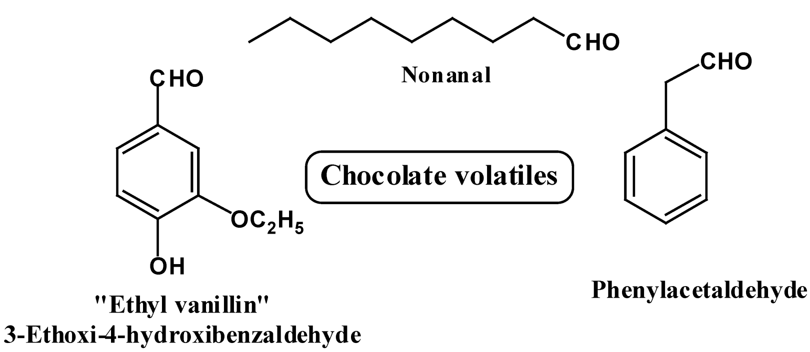


Fig. 3 Chocolate flavors are attractants for *E. cautella* and *P. interpunctella.*

Impurities of isomeric compounds may completely change the biological response. Selective synthetic methods are therefore essential for successful work. This is clearly demonstrated in our work on the pheromone constituents of the pine saw-fly, the larvae of which feed on fresh pine needles. The active pheromone composition was shown to be an intricate mixture of diastereomers of diprinyl acetate (Fig. 4) [8]. The presence of very small amounts of one minor component is essential for biological activity. The development of selective asymmetric synthetic methods was essential and led to samples of more than 99.9 % isomeric and enantiomeric purity [8].

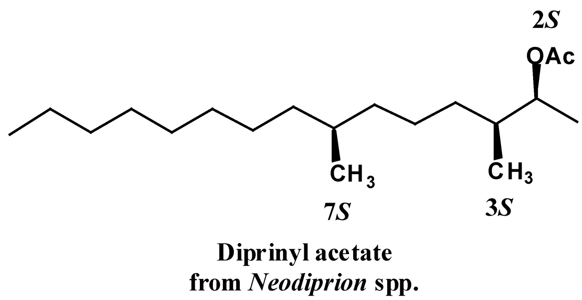


Fig. 4 Diprinyl acetate, (2*S*,3*S*,7*S*)-3,7-dimethylpentadecanyl acetate—one of several isomeric sex pheromone constituents of pine saw-flies, Diprinoide family.

Synthesis has also been essential for the development of pheromone-based control methods of many Lepidopteran insect pests. Common Lepidopteran pheromone constituents are long-chain saturated or unsaturated alcohols and their derivatives (acetates and aldehydes) [9]. The double bonds are conjugated or nonconjugated. The positions and configurations of the double bonds are important. Efficient and selective syntheses of such compounds have been part of the development of pheromone-based control methods such as in our study of the pheromone communication of the codling moth, *Cydia pomonella* [1,10]. The importance of the composition of the pheromone blend is clearly shown by a comparative study involving some closely related species [10].

Host volatiles are of importance for the aggregation of many insects. A combination of host plant volatiles and pheromones has been shown to be efficient for the control of the apple fruit moth, *Argyresthia conjugella*. The preferred hosts for this moth are the fruits of mountain ash (rowan), *Sorbus aucuaria*, and apple (*Malus domestica*) with a slight preference for the fruits of mountain ash. We investigated the volatile constituents of apple and rowan berries and found some similarities. Some simple and common compounds were found to be particularly attractive to both males and females as shown by electrophysiological recordings in combination with gas chromatography (GC) [11]. The compounds are now used in a field test in Norway for a strategy based on attract and kill. An advantage is that both males and females are trapped.

A common ecological observation is that many pest organisms detect dead or weakened host plants for feeding or egg-laying. At an early stage of our research on chemical signals, we were involved in a study of some forest pest insects that exhibit this behavior. To our surprise, some simple compounds were responsible for the aggregation of these pest insects. In fact, the mixture of ethanol and (–)-α-pinene is now used for monitoring of these and some other forest pest insects.

One serious forest pest insect in Scandinavian and North European forests is the pine weevil, *Hylobios abietis* (L.). This insect feeds on pine and spruce seedlings in forest plantations and therefore causes considerable economic damage for the forest owners. The pine weevil is polyphag and can feed on a number of woody species. Since the feeding on these seedlings in a plantation constitutes only about 10 % of its food resource, it may be anticipated that an antifeedant on the seedlings will be efficient for protection. The weevil will easily find other food resources.

Today the seedlings are treated with an insecticide (synthetic pyrethroids) before plantation. However, the use of this insecticide will be prohibited for this purpose in the near future. New methods for saving the forest plantations from pine weevil attack are urgently needed. We have screened a considerable number of compounds for their antifeedant activity using a micro feeding assay. An antifeedant for practical use needs to be active for at least two to three years. Some of the compounds, which we have tested, are constituents of non-host plants and exhibited strong positive effects, however, there are also drawbacks either because they are too volatile or not stable enough for practical use [12]. Furthermore, some of the compounds were phytotoxic. Some of the tested compounds are shown in Fig. 5.

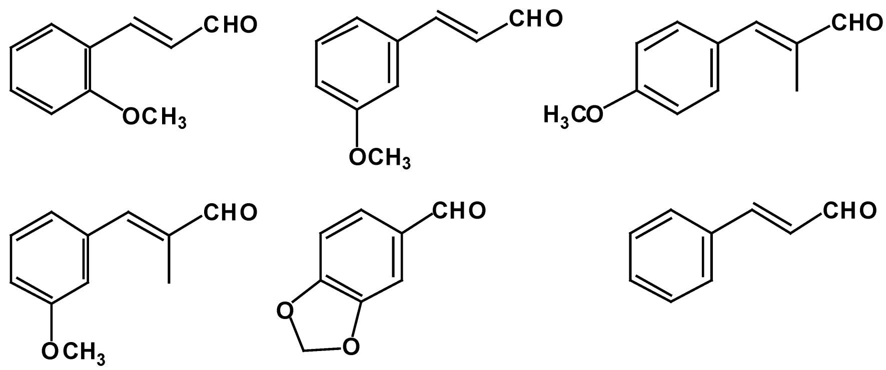


Fig. 5 Some compounds with antifeedant actvity for pine weevil, *Hylobius abietis.*

The pine weevils oviposit on root stumps of host trees. An observation by the forest entomologists is that female weevils never oviposit near a part of the stump which is previously occupied by an egg nest of another female. The female weevil bores a hole, lays an egg at the bottom, then deposits her feces over the egg. We have found that this excrement acts as a deterrent, and that the active constituents are simple phenolic compounds (Fig. 6)—probably degradation products from the digestion of wood constituents [13].

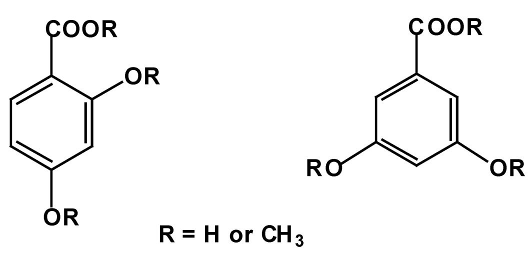
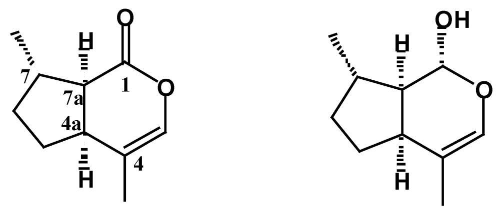


Fig. 6 Antifeedants produced by the female pine weevil, *H. abietis*, in connection with egg-laying.

An important part of our research program deals with aphids, which are small insects living on the juice of plants. There are about 4000 species around the world. Some species are serious pest insects. Many aphids are living on specific host plants, monophagus, but some are polyphagus and accept several different host plants. Aphids reproduce "explosively" by giving birth to living offsprings (viviparous) by parthenogenic (asexual) reproduction. A new-born aphid starts to reproduce within six to eight days, producing three to six offsprings daily over about 20 days. All these aphids are females, but at the end of the season the females become ovoviviparous and start to produce eggs which give birth to males and females, which mate and the mated females start a new generation. Usually, the egg-laying is late in the autumn on a specific winter host.

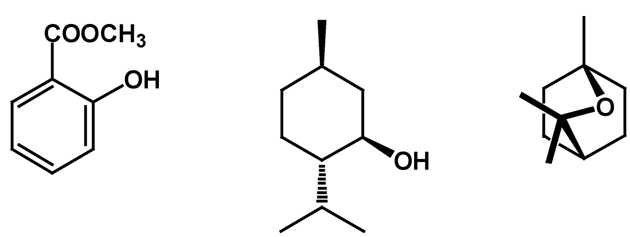
Female aphids release sex pheromones to attract males, and many of these pheromones have been identified [14]. Important pheromone constituents are various stereoisomers of nepetalactone or the nepetalactol (Fig. 7) either as single compounds or as species-specific blends. Ladybird beetles are aphid predators and are attracted by these pheromone constituents. In order to have access to reference compounds for field studies on the predator behavior, we have developed a synthesis of some iridoides, among them the gastrolactyl acetate and gastrolactol in almost enantiomerically pure form [15]. The gastrolactol was transformed to the gastrolactone, which was transformed to nepetalactol by catalytic hydrogenation. Nepetalactone has also been isolated from a natural source by a new efficient simple chromatographic procedure [16].



(4a*S*,7*S*,7a*R*)-Nepetalactone **(1*R*,4a*S*,7*S*,7a*R*)-Nepetalactol**

Fig. 7 Nepetalactone and nepetalactol, pheromone constituents of aphids.

The bird cherry oat aphid, *Rhopalosiphym padi*, has been a model insect in our studies. During the summer season, this aphid is polyphagus and can live on many different grasses and commercially important crops. It is thus a serious pest insect. It is specific for its winter host, which is the bird cherry tree, *Prunus padus* L. In an investigation of the volatile compounds from this host, it was found that methyl salicylate is an active compound for host identification but seems also to block the aggregation pheromones, which are important for keeping the aphid colonies together [17]. Methyl salicylate in parafin pellets were applied in fields of barley. The number of aphids feeding on the cereals was reduced by 25–50 %. Similar successful treatments with methyl salicylate together with menthol and 1,8-cineol have more recently been applied for aphid control in greenhouses (Fig. 8).



Methyl salicylate **(1*R*,2*S*,5*R*)-(–)-Menthol** **1,8-Cineol**

Fig. 8 Active compounds for aphid control.

Methyl salicylate has also been found to be an important chemical signal for the green-veined white, *Pieres napi*, which is a pest on rape (*Brassica napus*) an important oil seed in Europe. The entomologists had observed that a calling but already mated female deterred a courting male. We became interested in identifying this "anti-aphrodisiac" [18]. We used our SPME technique to collect and enrich the volatile constituents from mated females. There was a significant difference between virgin and mated females. The mated females emit methyl salicylate, which is also the main volatile constituent of the male spermatophore. Labeling experiments also show that the biosynthesis of methyl salicylate in males originates from phenylalanine.

CONCLUSIONS

Our research on semiochemicals and their applications for control of pest insects has shown that even rather common and structurally simple compounds can act as important chemical signals and exhibit biological activity on many different species and that one single compound can have different functions on different species. Methyl salicylate is a good representative of this type of semiochemical. Furthermore, it is clear that multidisciplinary research work in the area of ecological chemistry is successful and will provide tools for sustainable methods for control of many pest insects and other pest organisms.

ACKNOWLEDGMENTS

I gratefully acknowledge the work of my colleagues and coworkers, who have participated in the interdisciplinary research program "Biosignal–Pheromones and Kairomones for Control of Pest Insects," on which this brief survey is founded. They are named as coauthors in the references. Financial support for the research from the Foundation for Strategic Environmental Research (MISTRA), Swedish Natural Science Research Council (VR), The Swedish Council for Forestry and Agricultural Research (FORMAS), and some private foundations as well as Swedish forest industries and the Swedish Farmers Organisation (LRF) are gratefully acknowledged.

REFERENCES

1. P. Witzgall, A.-C. Bäckman, M. Svensson, U. T. Koch, F. Rama, A. El-Sayed, J. Brauchli, H. Arn, M. Bengtsson, J. Löfqvist. *BioControl* **44**, 211 (1999).
2. Z. Zang, J. Pawliszyn. *Anal. Chem.* **65**, 1843 (1993).
3. A.-K. Borg-Karlson, R. Mozuraitis. *Z. Naturforsch., C: Biosci.* **51**, 599 (1996).
4. C. Ryne, M. Ekeberg, P.-O. C. Olsson, P. G. Valeur, C. Löfstedt. *Entomol. Exp. Appl.* **103**, 99 (2002).
5. (a) C. Ryne, M. Ekeberg, N. Jonzén, C. Oehlschlager, C. Löfstedt, O. Anderbrandt. *Pest Management Science* **62**, 912 (2006); (b) J. Zhu, C. Ryne, R. C. Unelius, P. G. Valeur, C. Löfstedt. *Entomol. Exp. Appl.* **92**, 137 (1999).
6 A. E. Eiras, C. R. Unelius, A. Kovaleski, I. Liblikas, R. Mozuraitis, E. F. Vilela, A. K. Borg-Karlson, J. P. Chambon, P. Witzgall. *Z. Naturforsch.* **54**, 595 (1999).
7. (a) P.-O. C. Olsson, O. Anderbrandt, C. Löfstedt, A.-K. Borg-Karlson, I. Liblikas. *J. Chem. Ecol.* **31**, 2947 (2005); (b) P.-O. C. Olsson, O. Anderbrandt, C. Löfstedt. *Entomol. Exp. Appl.* **119**, 137 (2006).
8. (a) D. M. Jewette, F. Matsumura, H. C. Copple. *Science* **192**, 51 (1976); (b) F. Matsumura, A. Tai, H. C. Copple. *J. Chem. Ecol*. **5**, 237 (1979); (c) H.-E. Högberg, E. Hedenström, A.-B. Wassgren, M. Hjalmarsson, G. Bergström, J. Löfqvist, T. Norin. *Tetrahedron* **46**, 3007 (1990); for further refs., see (d) M. Larsson, B.-V. Nguyen, H.-E. Högberg, E. Hedenström. *Eur. J. Org. Chem.* 353 (2001); (e) M. Larsson, J. Andersson, R. Liu, H.-E. Högberg. *Tetrahedron: Asymmetry* **15**, 2907 (2004).
9. P. Witzgall, T. Lindblom, M. Bengtsson, M. Tóth. *The Pherolist* (2004); on-line version: <http://www-pherolist.slu.se>.

10. (a) A. El-Sayed, R. C. Unelius, I. Liblikas, J. Löfquist, M. Bengtsson, P. Witzgall. *Environ. Entomol.* **27**, 1250 (1998); (b) R. C. Unelius, I. Liblikas, R. Mozuraitis. *Acta Chem. Scand.* **52**, 930 (1998); (c) A. El-Sayed, M. Bengtsson, S. Rauscher, J. Löfqvist, P. Witzgall. *Environ. Entomol.* **28**, 775 (1999); (d) P. Witzgall, M. Bengtsson, A. El-Sayed, A.-C. Bäckman, S. Rauscher, A.-K. Borg-Karlson, R. Unelius, J. Löfqvist. *IOBC wprs Bull.* **22**, 1 (1999); (e) A. El-Sayed, I. Liblikas, R. C. Unelius. *Naturforsch., C: Biosci.* **55**, 1011 (2001); (f) P. Witzgall, M. Bengtsson, S. Rauscher, I. Liblikas, A.-C. Bäckman, A.-C. Coracini, P. Andersson, J. Löfquist. *J. Ent. Exp. Appl.* **101**, 131 (2001); (g) Z. Yang, M. Bengtsson, P. Witzgall. *J. Chem. Ecol.* **30**, 619 (2004).
11. (a) G. Jaastad, M. Bengtsson, P. Andersson, S. Kobro, G. Knudssen, P. Witzgall. *Agric. Forest Entomol.* **4**, 223 (2002); (b) S. Kobro, L. Søreide, E. Djønne, T. Rafoss, G. Jaastad, P. Witzgall. *Population Ecol.* **45**, 25 (2003); (c) M. Bengtsson, G. Jaastad, G. Knudsen, S. Kobro, A. C. Backman, E. Petterson, P. Witzgall. *Entomol. Exp. Appl.* **118**, 77 (2006).
12. C. Eriksson. *Isolation, Synthesis and Structure–Activity Relationships of Antifeedants against the Pine Weevil*, Hylobius abietis, Ph.D. thesis, Royal Institute of Technology, Stockholm, Sweden (2006). The thesis is available online: <http://www.diva-portal.org/kth/theses/fulltext.xsql>.
13. (a) A.-K. Borg-Karlson, G. Nordlander, A. Mudalige, H. Nordenhem, R. C. Unelius. *J. Chem. Ecol.* **32**, 943 (2006); (b) S. Legrand, G. Nordlander, H. Nordenhem, A.-K. Borg-Karlson, C. R. Unelius. *Z. Naturforsch., B: Chem. Sci.* **59**, 829 (2004).
14. (a) M. A. Birkett, S. Al Abassi, J. Petterson, J. A. Pickett, L. J. Wadhams, C. M. Woodcock. *Cell. Mol. Life Sci.* **54**, 876 (1998); (b) G. W. Dawson, N. F. Janes, A. Mudd, J. A. Pickett, A. M. Z. Slawin, L. J. Wadhams, D. J. Williams. *Pure Appl. Chem.* **61**, 555 (1989).
15. E. M. Santangelo, D. Rotticci, I. Liblikas, T. Norin, R. C. Unelius. *J. Org. Chem.* **66**, 5384 (2001).
16. I. Liblikas, E. M. Santangelo, J. Sandell, P. Baeckstrom, M. Svensson, U. Jacobsson, C. R. Unelius. *J. Nat. Prod.* **68**, 886 (2005).
17. (a) V. Ninkovic, R. Glinwood, E. Ahmed, J. Pettersson. *Agric. Forest Entomol.* **5**, 27 (2003); (b) J. Petterson, R. Glinwood. *Entomol. Exp. Appl.* **94**, 325 (2000); (c) A. Quiroz, J. Petterson, J. A. Pickett, L. J. Wadhams, H. M. Niemeyer. *J. Chem. Ecol.* **23**, 2599 (1997).
18. (a) J. Pettersson. Personal communication (2006); (b) O. Anderbrant, M. Bengtsson, H.-E. Högberg, C. Löfstedt, T. Norin, J. Pettersson, F. Schlyter, P. Witzgall. *Feromoner och kairomoner för bekämpning av skadeinsekter*, Slutrapport 1996–2005, Institutionen för Växtvetenskap, SLU, for information in English, see <www.biosignal.org>.
19. J. Andersson, A.-K. Borg-Karlson, C. Wiklund. *Proc. R. Soc. London, Ser. B* **267**, 1271 (2000).