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Pheromones and kairomones for control of pest insects. Some current results from a Swedish research program*

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Abstract: Some recent results from a research program dealing with the isolation, identification, and synthesis of biologically active compounds for applications in agriculture and forestry will be reported. The solid-phase micro extraction (SPME) technique has been successfully used for identification of the main sex pheromone components of *Cydia* and *Bonagota* species (Lepidoptera, Tortricidae). Synthesis of a series of dodecadienols, tetradecadienols, and their corresponding aldehydes and acetates have been performed to be used for testing inhibitory and synergistic effects on pest insects of these species. Behaviorally active volatile compounds emitted from aphids and aphid-infested plants have been identified by SPME-technique, synthesized, and used in olfactometer tests. Methyl salicylate is shown to act in interplant communication released by plants infested by insects. In the presence of the compound, the colonization density of aphids in crop is reduced. Methyl salicylate is a common multifunctional compound, which is active in several biological systems. The action of this compound as an anti-aphrodisiac will be presented. The compound is transferred at mating from the male pierid butterfly *Pieris napi* to the female and makes the female unattractive for mating.

The chemodiversity in Nature is most fascinating. There are more than 100 000 different low-molecular compounds described in the literature. Many more are to come since there is a rapid development in the field of organic natural product chemistry and ecological chemistry. A compound in a living organism is produced (biosynthesized) because it serves a specific function or several functions. Some compounds have functions, which are common to all living organisms or to certain groups of organisms. They are essential and are directly involved in the life processes (e.g., hormones and cofactors). A compound may also occur because once in the earlier evolution of the organism, it served a specific function but now remains as a "metabolic fossil" with potential for a function.

Most of the organic natural products have functions that are species specific or specific to certain classes or groups of living organisms. They have evolved because they play part in biological interactions such as defense, protection, signal transduction, or other specific functions essential for the life processes or beneficial for the organism.

In order to obtain selectivity, Nature has applied different strategies for the evolution of chemicals (signals) for specific functions. Either a very specific and unique chemical signal has evolved or, more commonly, Nature has used a combinatorial approach using a mixture of compound with a unique composition. When considering these evolutionary aspects, one has also to take into account the parallel evolution of suitable and selective receptors for the signals.

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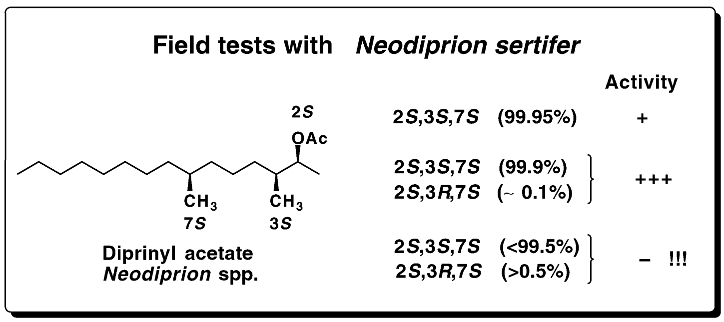
Chemodiversity is essential for chemical communication between organisms in Nature and is demonstrated by research on volatile compounds, which are active in insect–insect, insect–plants relationships (semiochemicals such as pheromones and allomones). The biological effects of the complex insect and plant scents are evaluated by tests in the field and in the laboratory. The identified insect behavior releasing compounds may find or have found applications in the monitoring and control of insect pest populations. Part of the research in this field in our laboratory is organized in a research program on “Pheromones and Kairomones for Control of Pest Insects”. This program is sponsored by the Foundation for Strategic Environmental Research (MISTRA) in Stockholm, Sweden.



Scheme 1

The chemodiversity in Nature very often rests on stereochemistry. Most of the asymmetric natural products occur in an optically active form. The pheromone field offers excellent examples where chirality and stereochemistry plays an important role for the bioactivity. In this context I wish to bring forward a particular case, which has been studied in our laboratories. It deals with the very active sex pheromones of sawflies, *Neodiprion* and *Diprion* species [1]. There is a very delicate tuning of the diastereomeric and chiral compositions of the sex pheromone components released by these insects (for one example, see Scheme 1). This tuning provides species specificity and proper biological effect among sympatric species. Minor alterations of the composition inhibit the pheromonal effect. This case also demonstrates the importance of having access to enantiomerically and diastereomerically pure compounds for biological studies.

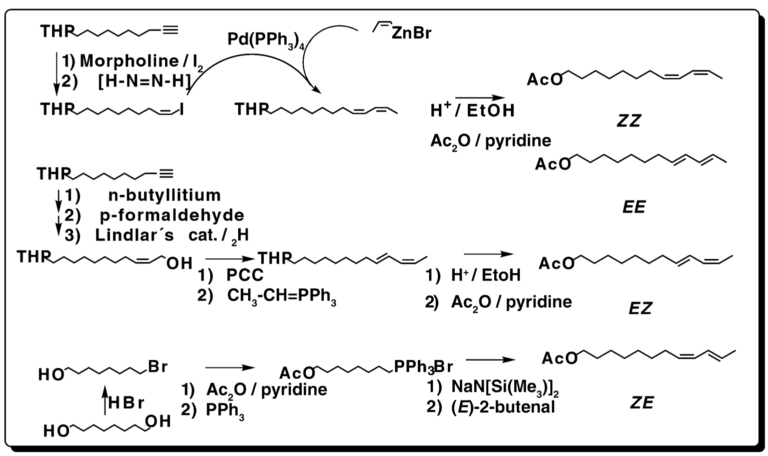
The pheromones emitted from a number of lepidopteran pest insects are currently investigated. Solid-phase micro extraction (SPME) techniques [2,3] in combination with electro antennographic (EAG) measurements are most useful for such studies. Lepidoptera pheromone constituents are usually long-chain (C_{10}–C_{18}) saturated or unsaturated alcohols, aldehydes, or esters, and the active signal is usually a mixture of constituents of narrowly defined composition.

Insects from the genus *Cydia* (Lepidoptera, Tortricidae) cause problems in fruit orchards. The pheromone constituents of *Cydia* species (Lepidoptera, Tortricidae) have been investigated by several groups [e.g., 4–6]. The main pheromone constituent of *C. pomonella* is codlemone [(*E*8,*E*10)-8.10-dodecdienol] and has been used for control of this pest insect. The importance of a correct composition of the lure for control applications is clearly shown by the fact that the components may act both as an attractant and as an antagonist depending on the composition of the lure. This is shown in Table 1, which is a brief compilation of a field study performed in our research program [7,8]. The strategy for the synthesis of the isomeric pheromone constituents is outlined in Scheme 2.

Extracts of the female pheromone gland of a Brazilian pest on apples (*Bonagota cranaodes*, Lepidoptera, Tortricidae) have been analyzed by gas chromatography mass spectrometry (GC-MS) [9]. One component elicited very strong activity in an EAG study and appeared to be a dodecadienyl acetate. The SPME technique provided an excellent tool for the identification of this pheromone constituent

Table 1 Compilation of a field study [18,19] of attractive and antagonistic activities of pheromone components of some *Cydia* species (Lepidoptera, Tortricidae). The proportions of the two pheromone components, (*E*8,*E*10)-8,10-dodecadienyl acetate and its corresponding alcohol, varies between 10 / 0, 10 / 2, 10/10, 2 / 10, and 0 / 10 (+ = attraction; – = antagonistic activity).

***E*8,*E*10-12OAc**	**10**	**10**	**10**	**2**	**0**	
***E*8,*E*10-12OH**		**0**	**2**	**10**	**10**	**10**
C. nigiriana		+++	+	(+)	–	–
C. pyrivora		+++	+	–	–	–
C. fagiglandana	+	+++	+	(+)	–	
C. pomonella		–	–	–	+	+++



Scheme 2

(Fig. 1). The exact configuration was determined to be (3*E*,5*Z*)-3,5-dodecadienyl acetate by comparison with synthetic samples. The geometrical isomers of this pheromone have now been synthesized, and their biological effect will be studied in the field. Synergistic or inhibitory effects are important to investigate in order to find the economic and efficient trap-lures for future insect pest control program.

Aphids are ubiquitous on earth, and there are 500–600 different species in Sweden alone. They cause considerable losses in agricultural production of many different crops and products. It is supposed that nepetalactones and other terpenoids with the iridoid skeleton are general chemical messengers among the aphids, and there is a need for pure samples of nepetalactones and -lactols for the interpretation of the chemical language of aphids. The strategy for the syntheses of the compounds is shown in Scheme 3. For the preparation of some of the chiral compounds, we have used biocatalytic methods [10].

A current project regarding semiochemicals for control of aphids deals with aphid/host plant relationships and we study an apparent tri-trophic interaction (plant–aphid–predator). Plants under aphid attack emit volatile compounds that initiate the production of the chemical defence mechanisms in neighboring plants. The emitted volatile compounds attract aphid predators and some of the compounds also aphids [11]. One important compound in these interactions is methyl salicylate, which seems to be a common multifunctional bioactive compound involved in different natural chemical signalling systems.

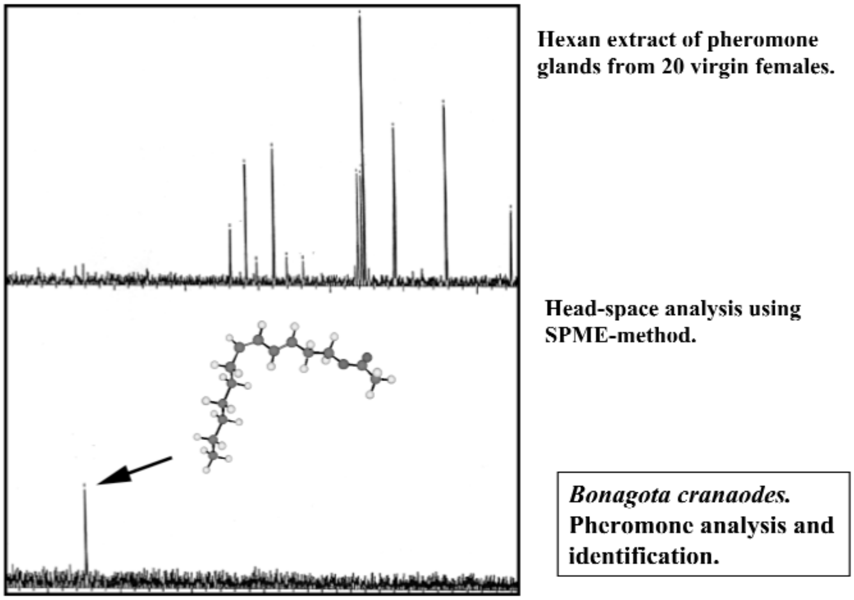
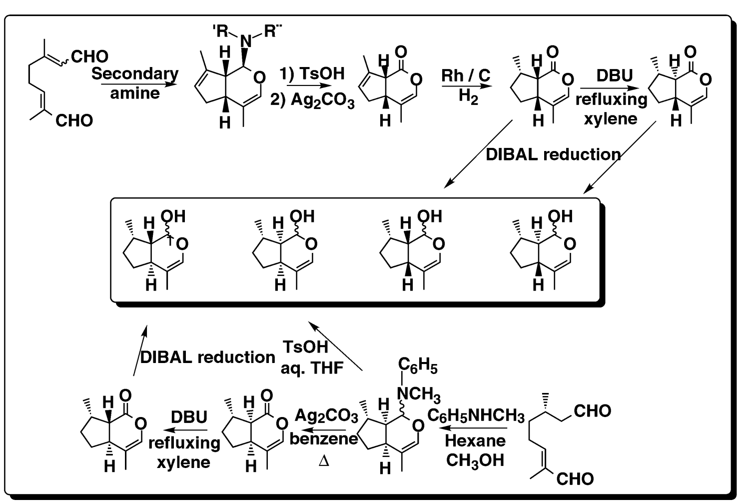


Fig. 1 GC analysis of pheromone constituents of *Bonagota cranaodes* (Lepidoptera, Tortricidae) (20). The active pheromone constituent is not detectable by GC in the hexane extract of the pheromone gland but appears as a strong signal by using the SPME technique.

The action of methyl salicylate as an anti-aphrodisiac has also been demonstrated [12]. The compound is present in the spermatophore of the pierid butterfly *Pieris napi*. It is transferred at mating from the male to the female and makes the female unattractive for mating. Methyl salicylate is a very potent anti-aphrodisiac. Males refrain from mating virgin females to whom extremely small amounts (20 ng/female) of the compound have been artificially applied. A ^{13}C-labeling experiment demonstrated that the biosynthesis of methyl salicylate by the male proceeds via L-phenylalanine [12].



Scheme 3

This short review on some current work on semiochemicals demonstrates the importance of fundamental and interdisciplinary research dealing with the chemistry of biologically active compounds in combination with biological studies on their action. Such studies provide tools for future applications of the compounds for the benefit of mankind. Research efforts in organic chemistry, both analytical and synthetic, play an essential role in such research efforts.

ACKNOWLEDGMENTS

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