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Chemical ecology = chemistry + ecology!*

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Abstract: Chemical ecology (CE) is an active, interdisciplinary field between chemistry and biology, which, stimulated by natural curiosity and possible applied aspects, has grown to its present position during the last 40-odd years. This area has now achieved a degree of maturity with its own journals, its own international society with annual meetings, and many enthusiastic scientists in laboratories around the world. The focus is on chemical communication and other chemical interactions between organisms, including volatile chemical signals, which guide behaviors linked to various vital needs. It reflects both biodiversity and chemodiversity. All living organisms have these important signal systems, which go back to the origins of life. Successful work in this area has called for close collaboration between chemists and biologists of different descriptions. It is thus a good example of chemistry for biology.

The aim of the article is to give a short introduction to the field, with an emphasis on the role of chemistry in a biological context by

- giving an overview of the development of the area;
- showing some examples of studies of chemical communication in insects and plants, basically from our own work; and
- describing some current trends and tendencies and possible future developments.

Keywords: chemical ecology; chemistry; ecology; interdisciplinary field; insects; plants; behaviors; pheromones; chemical signals; semiochemicals.

CHEMICAL ECOLOGY—AN INTERDISCIPLINARY SCIENCE: HOW DID IT COME ABOUT?

Females of the great peacock moth, *Saturnia pyri*, attract males from far away, several hundred meters. This discovery was made by Jean-Henri Fabre (1823–1915), a school teacher from Avignon, France, in his classic studies performed at the beginning of the last century [1]. Fabre speculated that this phenomenon was mediated by electromagnetic waves.

Chemists and biologists at laboratories of the U.S. Department of Agriculture struggled, from the 1930s onwards, with attempts to identify the female sex attractant of different species of moths by the techniques available then. One was the gypsy moth, *Lymantria dispar*, an introduced tree defoliator in northeastern United States and elsewhere. Its pheromone was eventually identified as (7*R*,8*S*)-7,8-epoxy-2-methyloctadecane ("disparlure") [2]. Biological observations and experiments had already been performed at the end of the earlier century. H. von Zehmen and others were active in this area in Germany in the 1940s. Stressing the high sensitivity of these odor signals (far beyond the capacity of

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Fig. 1 Great peacock moth, *Saturnia pyri*, males gathering at lamplight. Photo from Fabre [1].

the human nose), in analogy with ultrasound and ultraviolet/infrared, he used the term "ultrasmell" (German: ultrageruch).

In 1959, Adolf Butenandt (1903–1995), chemist and Nobel laureate (for his pioneering work on hormones), from Munich, published the identification, by classical organic chemical methods and large amounts (>500 000 specimens per batch) of insects, of the female sex attractant of the silk moth, *Bombyx mori* [3]. This work had then been going on for 20 years. It turned out to be a doubly unsaturated long-chain alcohol, named bombykol, (*E*,*Z*)-10,12-hexadecadien-1-ol. Synthesis of its four geometrical isomers, behavioral experiments, and electrophysiological recordings proved the chemical structure. Butenandt et al. demonstrated the very high activity and specificity of the right isomer. The silk moth is interesting chemically also because of its strong binding, by chemical means, to its host plant, the mulberry tree.

Based on these findings, Karlson and Lüscher [4] later the same year (1959) proposed the term "pheromone" (Greek pherein = carry, transfer, and Arab horman = excite, effect) for compounds which are given off by an organism and in another individual of the same species elicit or prepare for a certain behavior or (more general) reaction.

The long-chain fatty acid derivatives are typical for the structures of moth female sex pheromones. They have now been identified in a great many species, many of them of economic importance as pest insects, which are important to control. With modern chemical and biological methods and techniques, much less material is needed than before; analyses can often be performed now on single individuals. These studies demonstrate a large variation of chemical structures based on the fundamental long-chain framework. Species specificity is achieved by varying chain lengths, number, position and geometry of unsaturations, functional groups, sometimes chirality/enantiomeric composition, and the combination of two (or more) compounds. Most "classic" moth pheromones are nonchiral. There are now lists (such as Pherolist) of most identified moth pheromones. It is a bit like a jukebox. You press a certain code, say E35, and out comes the pheromone of a certain species. Referring to the varied and repetitive patterns, one could see moth pheromones as the blues of chemical ecology (CE).

Other early studies included defense compounds, e.g., in beetles, and pheromones of social insects. They showed not only many different active volatile compounds, but also many examples of biological/behavioral variability.

These singular activities and achievements mark the beginning of collaborative studies on the guiding of behavior in insects by natural chemical signals. The efforts grew into a new interdisciplinary research area which was to develop, with improved methods and techniques, into the discipline of chemical ecology:

> "Chemical Ecology came to be recognized as a distinct interdisciplinary research area about three decades ago. It deals with the intriguing chemical mechanisms which help control intra- and interspecific interactions among living beings. All organisms use chemical signals to transmit information; "chemical languages" are the oldest forms of communication. Research in the field of Chemical Ecology is concerned with the identification and synthesis of the substances which carry information, with the elucidation of receptor and transduction systems which recognize and pass on these "semiochemicals", and with the developmental, behavioral, and ecological consequences of chemical signals."

This statement and definition is from the International Society of Chemical Ecology (ISCE) Web page, see also below.

Among stimulating factors for the establishment of this new field was the growth of ecology (the term had already been introduced by Ernst Haeckel in Jena in 1866), where one asked how the liaisons between organisms and populations were maintained. One answer to this question is precisely through chemical signals. In ethology, likewise, the question was raised as to how behaviors, linked to various vital needs such as development, feeding, nesting, mating, and defense, were guided. Once again, the explanation lies to a large extent in chemical signals. From the applied side, there was the urge to come up with selective and nontoxic control measures as positive alternatives to different types of biocides (pesticides). Species-specific volatile compounds seemed to meet these criteria. Improved chemical and biological methods and new techniques represented another important factor. Research groups sprung up at universities and at research institutes, some of them linked to agriculture or forestry. Most of the work on chemical signals has been done on plants and insects, from which the examples in this article will be taken, but some studies, and they are increasing in numbers, have been made on mammalians, aquatic organisms, and microorganisms.

Over time it became more of hand-in-hand cooperation and less of "sending samples to the chemists" as in many earlier collaborations. One of the pioneers in the field, the late Prof. Milt Silverstein, chemist (originally a coffee aroma specialist) at the State University of New York in Syracuse, had a standard positive question to potential biology partners before collaborations started: "What's your bioassay"? It underlines the importance of behavioral tests to find the active chemical compounds. The strong links between the chemical and the biological levels of studies of natural chemical signals can be summarized by Scheme 1.

| Biology --- Organisms |

Genetics | ------------------------------ | Evolution

| Chemistry --- Molecules |

Scheme 1

To put some figures on it, one can give an estimate of the number of known, described, and named species according to Wilson [5], and likewise an approximate, very rough, number of potential chemicals which could act as volatile chemical signals, Scheme 2:

Organisms: > 1.5 million

Chemicals: > 1 million

Scheme 2

It should be noted that insects make up about half of the number of known species of multicellular organisms (>750 000)—the real number is in all likelihood considerably larger—and that flowering plants contribute by 1/6 (>250 000). This puts a quantitative meaning to the concept of biodiversity. In the same way, one can talk about chemodiversity! The number of orders, a higher systematic category of insects, is defined as 30, and the number of plant orders, which varies more according to authors, has in one taxonomy been given as 58. The numbers of organisms and of chemicals are certainly tricky to define because of our lack of knowledge. For the chemicals, the estimated number refers to compounds of sufficient volatility. It is still an open question as to how many of them are used as signals.

A simple model, Scheme 3, of a chemical signalling system can be helpful in discussing chemical signals. It consists of the sender (S), the chemical signal (CS), the medium, which can be air, water, or direct contact, and the receiver (R):

Behaviors/Vital Needs

Sender --- Chemical Signals --- Receiver

Medium

Scheme 3

An important aspect is how the sender and the receiver are coupled, or attuned, through the chemical signals; genetically, by learning, or by a combination of them. It must be realized that the three components of the system (S-CS-R) in principle are under strong selection pressure in order to adapt to changing conditions. They really represent dynamic equilibria. Sometimes, the chemical signalling systems seem very resistant to change and they can be constant over a long time. Sometimes—in fruit flies adapting to new hosts and in moths with separating populations, for instance—they can evolve rather quickly. When we look at a group of systematically related species, like a genus or a family, the basic traits seem to be resilience and conservatism. Dobzhansky [6] formulated the principle:

> “Nothing in biology makes sense except in the light of evolution.”

This statement is equally true for the chemical level and must serve as a guiding star for our scientific efforts.

Behavior-releasing and other chemical signals have been designated different terms depending on how they function and what behavior they guide. They are often termed semiochemicals (from Greek semeion = sign), divided into pheromones (acting between members of the same species), allelochemicals (between individuals of different species), and juvenile hormones (which influence the development of organisms). Pheromones are given prefixes according to their function, e.g., marking, trail, aggregation, sexual, and alarm (in defense). Allelochemicals are separated with reference to their advantage to the sender (allomones), to the receiver (kairomones), or both (synomones). Another important group of semiochemicals are *pollination stimulants*, which can attract, excite, or otherwise guide pollinators. Semiochemicals are thus natural products that by acting as signals can regulate interactions between organisms.

Before exemplifying the state of affairs in this area, and as a stepping stone for trying to look into the future, it is necessary to find out more about the development of the research on chemical signals. This will throw light on how the productive relations between chemistry and biology (i.e., between chemists and biologists) have progressed. By looking at history, we should be able to extrapolate into the future.

Lincoln Brower—the monarch butterfly specialist—used the term “ecological chemistry” for a review article in *Scientific American* in February 1969 [7]. The term also appeared on the front page of that issue. In the year before, a series of lectures were held at Syracuse, NY under the title *Chemical Ecology*. It produced a book with this title in 1970 [8]. These events marked the end of the first 10-year period, since 1959, during which several groups studying insect olfaction had been set up in many countries.

Some important dates for CE worldwide can be summarized as follows:

1959	Butenandt et al. publishes on bombykol. The term “pheromone” is introduced.
1975	The publication of the *Journal of Chemical Ecology* (*JCE*) is initiated.
1979	20 years since 1959, we (Prof. Torbjörn Norin and myself) arranged the first international meeting in Borgholm, Öland, Southern Sweden, on “Chemistry of Insects”. It was sponsored by IUPAC and the Swedish Chemical Society.
1984	25 years since 1959, the International Society of Chemical Ecology is formed and since then a series of annual meetings has been held in different countries. The ISCE forms a nucleus for worldwide interdisciplinary cooperation between biologists and chemists. Its membership directory currently lists more than 600 scientists from 35 countries.
1990	The journal *Chemoecology* is started, edited in Belgium. Adoption of “The Göteborg Resolution”, see below.
1997	The Max Planck Institute for Chemical Ecology is created in Jena, Germany.
2009	50-year anniversary of CE, considering 1959 as the starting year.

As in most sciences, the success of the work stands and falls with the availability of suitable techniques and methods; in CE, both on the chemical and the biological side. This means specifically instrumentation which combines adequate information with high sensitivity. On the chemical side, it implies a great success for further developed gas chromatography/mass spectrometry, a prerequisite for analyzing mixtures. We have ourselves been engaged in improving the analytical techniques; for a selection of reports on this, see refs. [53–61]. It is now, in principle, possible to bring the instrumentation directly into the field. Improved methods of organic synthesis, including the synthesis of chiral compounds of high purity, represent another important achievement. On the biological side, methods to study behaviors induced by chemical signals (like flight chambers), and electrophysiological recordings of the effect of olfactory stimuli, have proved to be most valuable. A combination of chemical separation and electrophysiological recording is the GC/EAD technique (gas chromatography/electro-antennal detection), which has proved to be very helpful in order to identify active compounds. Figure 2 summarizes the analytical challenge. Ideally, one would have liked to have an analytical tool, which could be carried in the field and could momentarily identify emitted volatiles in very small amounts. Of course, this “good cigar” does not exist, and we have to stick to our stepwise procedures in the lab, plus behavioral observations and experiments in the field and in the lab. This calls for close collaboration between chemists and biologists!

Experience has shown that it is a large advantage if the collaborative work is carried out in close cooperation between chemists and biologists. Much of the work in CE has been carried out in this fashion. Ideally, the collaborations could be carried out “under the same roof”. An example of this kind of work is the studies carried out at the Ecological Research Station of Uppsala University on the island

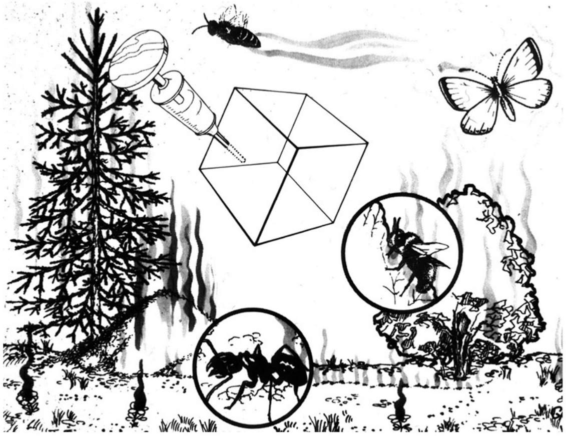


Fig. 2 The analytical challenge: identification of potentially active volatile compounds given off by insects and plants, or other organisms. An isolation/concentration step is needed in most cases. The complete, perfect analytical tool has still to be invented!

of Öland (southeast of the Swedish mainland). But there is one risk of which one must be aware! The animals, and I am thinking primarily of the insects, are very sensitive toward minimal amounts of active compounds, so that the air, and all exposed surfaces like walls, tables etc., are easily contaminated. This caused great problems for some laboratories, especially in the first years of this kind of work, and particularly for work with moth pheromones, until one learned to separate the chemical and the behavioral activities. They often have to be carried out in separate localities.

In 1997, the new Max Planck Institute for Chemical Ecology was built in Jena, Germany. This institute, which hosted the 2007 annual meeting of the ISCE, has five different departments: molecular ecology, bioorganic chemistry, biochemistry, evolutionary neuroethology, and entomology, each with its own director/head professor. They are very well equipped with scientists, technicians, and fine instrumentation. Furthermore, there are also three special research groups: genetics and evolution, biosynthesis/NMR, and mass spectrometry. It has good chances to be an important Center for CE, and thereby foster and further develop interdisciplinary collaboration, but it must be emphasized that today there are in the world other very active groups in the area, some of which warrant the title Center, based on their size, equipment, funding, activity, etc. (no names given since it is difficult, and maybe unfair, to single out some).

The members of ISCE are concerned about the rapid rate of species extinction. This led to a unanimously adopted resolution at the 6th Annual Meeting in Göteborg, Sweden, in 1989 [cf. *Journal of Chemical Ecology* **16**, 643 (1990) “The Göteborg Resolution”]:

> “Natural products constitute a treasure of immense value to humankind. The current alarming rate of species extinction is rapidly depleting this treasure with potentially disastrous consequences. The ISCE urges that conservation measures be mounted worldwide to stem the tide of species extinction, and that vastly increased biorational studies be undertaken aimed at discovering new chemicals of use to medicine, agriculture and industry. These exploratory efforts should be pursued by partnership of developing and developed nations in such fashion that the financial benefits flow in fair measure to all participants.”

It can be pointed out that CE has connections to several applied fields such as environmental chemistry, agriculture and forestry, flavors and fragrances (perfumery), food chemistry, pharmaceutical chemistry, forensic science, sports chemistry, and aspects of military (defense) analysis. If the capacities of a person trained in CE should be summed up in one sentence, it would be: An ability to work with small amounts of compounds of biological importance, often in complex mixtures.

FURTHER READING

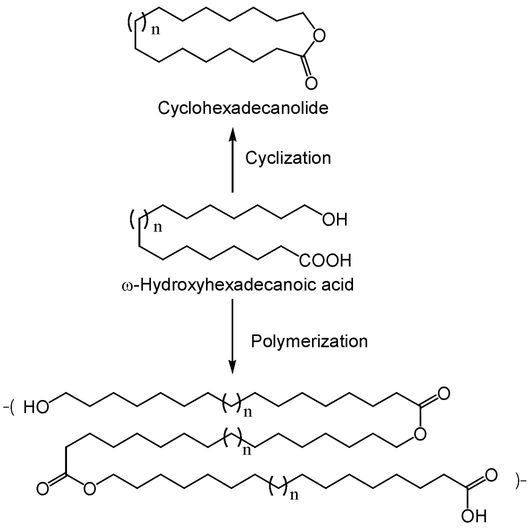
Today, there are many books, authored or edited, in the field of CE, and in neighboring areas. To suggest just a few, a comprehensive, recent, multi-authored one, in two volumes, is edited by Stephan Schulz [10]. It contains current information on many of the basic groups of insects. A good classic book, in its 4th edition, is *Introduction to Ecological Biochemistry* (another label for this area) written by the late Jeffrey Harborne [11]. He also published a Millenium Review, entitled “Twenty-five years of chemical ecology”, which focuses on plant–animal interactions. Thomas Eisner (biologist) and Jerrold Meinwald (chemist) edited one text in CE [12]. Bell and Cardé edited another comprehensive text, *Chemical Ecology of Insects*, which appeared in two volumes [13]. Two important books on methods in chemical ecology are edited by J. G. Millar and K. F. Haynes [14]. For a good summary of our understanding of insect olfaction, we recommend to the reader the book with this title edited by Bill Hansson [15]. Two texts on behavior-guiding volatile signals in mammals are the edited one by Vandenbergh [16] and the authored book by Albone [17]. A third comprehensive book on this subject, in two volumes, is edited by Brown and Macdonald [18]. On the subject of allelochemicals, the edited text by Waller [19] is still valuable. A recent edited text by M. Dicke and W. Takken [20] contains many good contributions.

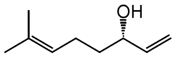
For general texts on insects, the books by E. O. Wilson [21] and Grimaldi and Engel [22] are recommended. For bee behavior, C. D. Michener`s book [23] is a must, and on ants “everything” is included in the text by B. Hölldobler and E. O. Wilson [24].

CHEMICAL COMMUNICATION IN BEES

The insect order Hymenoptera includes bees, bumblebees, ants, and sawflies. It is one of the most successful and numerous orders of insects (there are about 30), both for the number of species and for the estimated number of individuals. The first three groups show different degrees of social organization; some of them are highly social with overlap of generations, worker castes, division of labor, advanced construction of nests, etc. This level of development is also reflected in their communication systems, which rely to a large degree on exocrine chemical signals. Most of the chemical signalling compounds are produced in special cells. Insects can have up to around 10 different glands for this purpose, located on various parts of the body. The secretions are often complex; they contain many components, which are often members of homologous series.

We have studied the main volatile compounds from the Dufour gland, located in the abdomen of females of species belonging to the four genera: *Halictus*, *Lasioglossum*, *Colletes*, and *Evylaeus* (34 species altogether). They produce ω-hydroxy acids and their corresponding macrocyclic lactones. The ω-hydroxy acids are converted either to polymers for making a hydrophobic layer on the inner walls of the nest or to the musk-smelling lactones, C16–C24, which are used, in different combinations, for producing species-, kin-, and individual-specific blends for marking the nest entrance and the flying territory, thereby serving species recognition, see Figs. 3 and 4. This dual function of compounds with the same biogenetic origin represents a good example of the economy of Nature! (cf. refs. [25–30]).





(*S*)-Linalool

Fig. 3 (left) ω-OH-acid (center) with macrocyclic (musk-smelling) lactone (above) and polymer (used for nest-wall coating) (below).

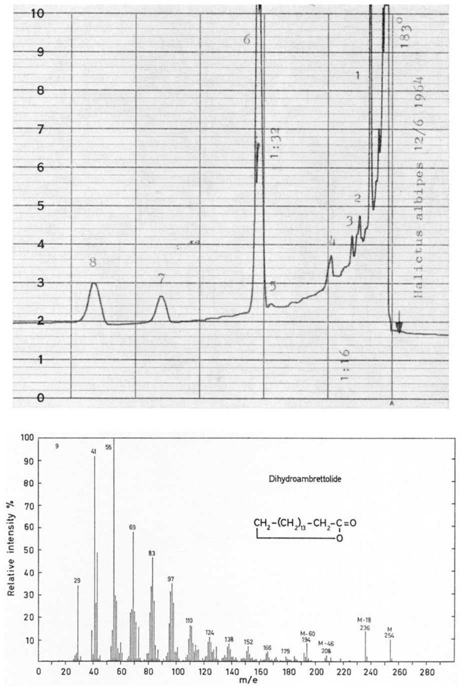


Fig. 4 (right) Early (1964) gas chromatogram and mass spectrum for identification of the C16 macrocyclic lactone as main component.

The lactones are stable compounds, not too volatile, and therefore work well as marking pheromones. They are well known in this capacity also in mammals, as in the musk deer and in the civet cat. They have been used for a long time in perfumery, both as agreeable scents and as keepers in blends for more volatile components. Their composition in each species was used as a basis for describing the phylogenetic relationships between a number of them. (*S*)-(+)-Linalool, see Fig. 3, is produced in the mandibular glands (located in the head) of many *Colletes* species, both in males and females, see Fig. A for an *en face* presentation of this musk bee. A distinct increase in flight activity is observed when it is released in an area of nest aggregation, where males patrol. Some other species instead emit geranial and neral. The analysis of *H. calceatus* and *H. albipes* (initially 19 and 9 individuals of each) represents our first published work, in 1964. Analyses of single individuals followed.

Many other species and genera of bees have been studied. One reason is that they represent different degrees of social organization, which leads to needs for communication between individuals, often by chemical communication. The excellent text by Michener [23] summarizes much of this research. Secondly, bees (and bumblebees) are of great economic importance as effective pollinators of flowering plants, including various crops. The long-lasting studies by Karl von Frisch (Nobel laureate, together with Konrad Lorenz and Niko Tinbergen, for physiology or medicine in 1973), his collaborators and successors, revealed much also about the remarkable information in the bee dance—about direction, distance, and quality of food sources. Through combined chemical analyses and behavioral studies, we have learned a lot about alarm and defense in bees, about male and female pheromones, the queen substance in honeybees and related species, and about trail pheromones, which mark the way to food sources.

In some genera of bees, viz. *Andrena*, *Melitta*, and *Nomada*, we discovered the phenomenon of chemical mimetism to occur between host and nest-parasites, i.e., that one organism (the parasite) mimics major volatile compounds from the other (the host).

Bumblebees are also bees (superfamily Apoidea) that employ male marking secretion as flying territory beacons. We have found that each species (38 species in Scandinavia and a few North American species have been studied) has a characteristic composition and that females will only mate with males of their own species. In two bumblebee species, we found two distinctly different chemical forms. These bumblebees are now discerned as separate species.

Further substantial work on the many varieties of chemical structures and biological activities of volatile compounds in bees and bumblebees has been carried out by W. Francke and his group in Hamburg in collaborations with several biologists. Among many other findings, Prof. Francke and collaborators have shown that spiroacetals (including dioxa-spiroacetals), and bicyclic acetals in general, are a widespread new group of active volatile compounds, occurring also in many bee species. For reviews, see ref. [62].

CHEMICAL COMMUNICATION IN FORMICINE ANTS

There are two major ant families: Formicinae and Myrmicinae. The Formicine group includes *Formica*, *Polyergus*, *Lasius*, *Camponotus*, and other genera, which we have investigated [31–33]. Volatile, pheromonal secretions have been studied, emanating from Dufour and mandibular glands, in worker ants of 9 species of *Formica*, 1 species of *Polyergus*, 4 species of *Lasius*, and 2 species of *Camponotus*. In addition, the Dufour gland components of virgin females and old queens of *F. polyctena* were analyzed. The secretions possess a part, common to all the species, consisting of straight-chain hydrocarbons and another part, characteristic for each species and made up of fatty acid derivatives and/or isoprenoids, see Fig. 5. It is typical for these secretions that they occur in multicomponent bouquets and likely that the complex blends serve as both defense and alarm and recognition pheromones. Through these compounds of different volatilities, it is possible that gradients are formed, both in space and time, which could carry important information.

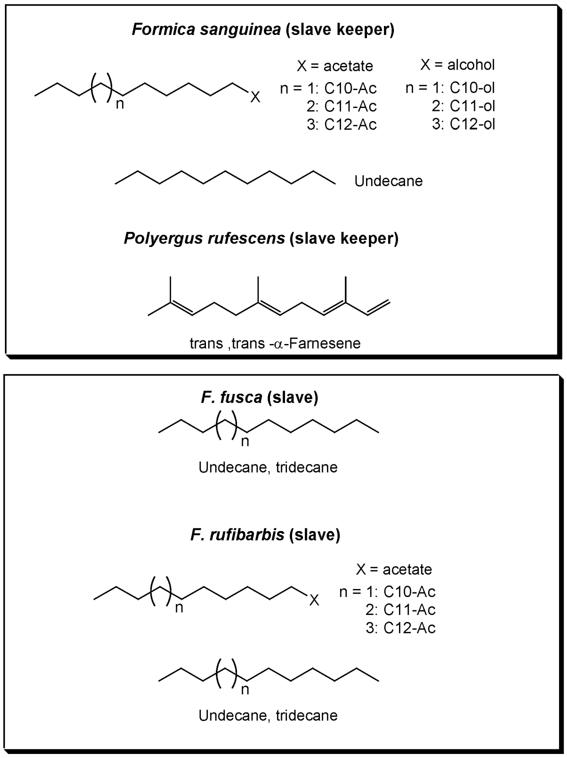


Fig. 5 Typical components of Formicine ant secretions, *Formica* and *Polyergus* genera (left).

One major alarm pheromone component is undecane (hendecane), which is present in all Formicine ant species studied. This serves communication inside each species, and primarily in or outside the nests, see Fig. B, which shows a nest hive of *Formica rufa*, and there is obviously no selection pressure for producing different alarm pheromones for different species.

The two slave-keepers *F. sanguinea* and *P. rufescens* keep the same species, *F. fusca* and *F. rufibarbis*, as slaves. The slave species *F. rufibarbis* seems to mimic the scent of *F. sanguinea*, whereas the slave *F. fusca* seems chemically "naked", apart from defense hydrocarbons.

The four *Lasius* species studied are very similar in the hydrocarbon part, but distinctly different, species-specific, in the set-up of polar components, Fig. 6.

A group of ants of considerable medical importance is the fire ants, genus *Solenopsis*. The major venom compounds of these ants, which cause severe skin burns, are a series of 2,6-dialkylpiperidines, related to the poisonous plant alkaloid coniine (occurring in hemlock). Ants are, like the bees, very rich in chemicals, which most often emanate from special cuticular glands and represent a great variability in chemical structures and functions. The comprehensive text by Hölldobler and Wilson [24] tells a good many of these stories.

Fig. A (left) Male head of *Colletes cunicularius*—one of many musk-smelling bee species, belonging to several different genera.
Fig. B (right) Nest (anthill) of *Formica rufa* ants. Volatile chemical signals, perceived through the olfactory sense, are particularly common among social insects.

Fig. C (left) *Neodiprion sertifer*, one of the pine sawfly species studied. Male and female, observe the large antenna of the male (left in the picture). This is an example of antennal sexual dimorphism. The male insect has a large number of receptors specialized for detecting the female sexual attractant.
Fig. D (right) *Linnaea borealis* L., Linnaeus's "planta nostra" in bloom.

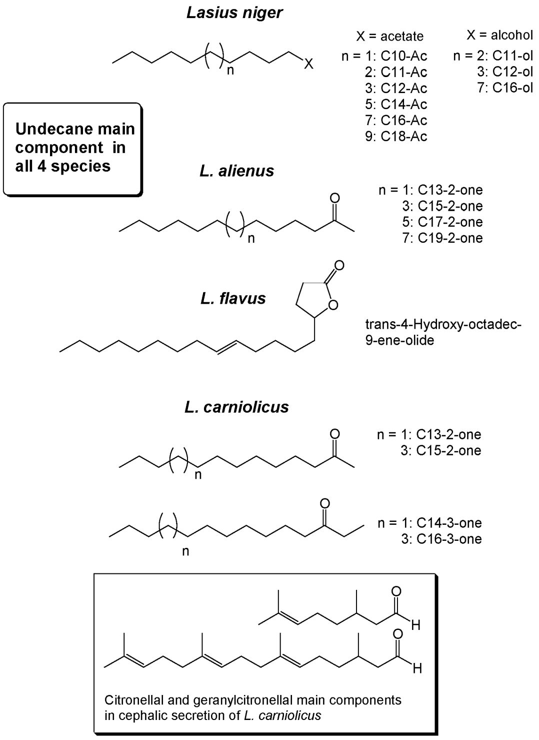


Fig. 6 Multicomponent and multifunctional secretions of *Lasius* ants (right).

CHEMICAL COMMUNICATION IN PINE SAWFLIES

There are about 128 species of Diprionidae sawflies worldwide. We have so far studied 10 of them. This example shows the female sex pheromones of pine sawflies (Hymenoptera, Diprionidae) to be esters of long-chain, methylated secondary alcohols (precursors), mainly acetates and propionates, see Fig. 7 right. Up to 4 chiral centra have been found (one carbon carrying the OH-group and 3 carbon atoms bearing methyl groups) giving 16 possible stereoisomers in *Mi. pallipes* and *Ma. nemoralis*. The identification of stereoisomers in 1 ng or sub-ng amounts per female represents an analytical challenge, see Fig. 7 left, and the results pose interesting evolutionary questions regarding production and sensory reception. As can be seen from the molecular formulas, they all represent variation on a theme: methyl-branched secondary alcohols as precursors, and their acetates and/or proprionates as the active pheromones. What varies in the 10 different species studied, and one could assume that this pattern repeats itself in other pine sawfly species, is the chain length, the position and number of methyl groups, and the stereochemistry of the stereogenic centra. This pattern, variation of a basic chemical structure among a number of related species, is very common in large groups of insects.

In *Neodiprion sertifer*, inhibitors/antagonistic compounds, structurally similar to the pheromone, were demonstrated. Of three species of *Gilpinia* one, *G. frutetorum*, produces a pheromone with just two chiral centers [34–42].

The sawflies are sometimes of direct economical importance through occasional outbreaks. Control measures can be applied through sex pheromones, either by a limited number of traps for monitoring, or by a larger number of traps for population control. See Fig. C for a photo of *Neodiprion sertifer* (the “red pine-sawfly”).

Hilker et al. (ref. in [10]: I, p. 149) studied hymenopteran parasitoids on sawfly eggs and found that two species responded to the sex pheromones of their hosts, *Neodiprion sertifer* and *Dipion pini.*

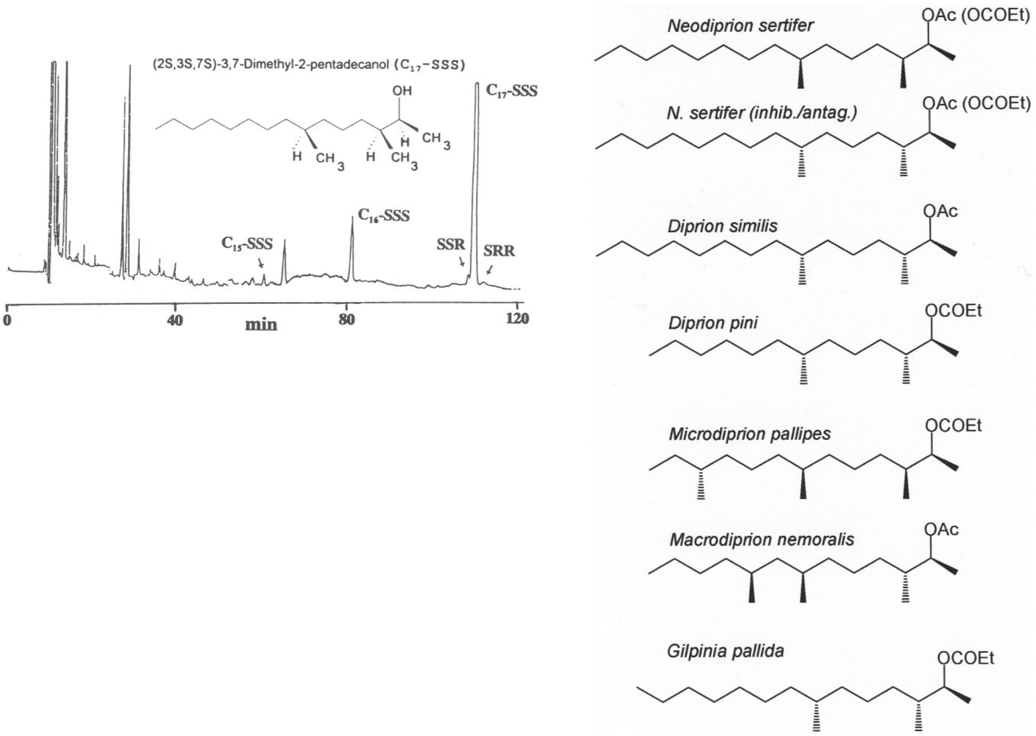


Fig. 7 Analysis of pheromonal secretion from a single *Neodiprion sertifer* female (left). Main female sex pheromones from six different species of pine sawflies (right).

From the parasitoid point of view, they are called kairomones, meaning that they have an advantage for the receiving part in a biological relationship.

SCENTS OF FLOWERING PLANTS

Volatile compounds given off by flowering plants are thought to have evolved as defensive compounds, acting between plants as allelopatic compounds, and secondarily as insect attractants/stimulants. They represent all the major types of volatiles: fatty acid derivatives, isoprenoids, aromatic compounds, and, in addition, some phenylpropanoid products. Most flowers give off complex bouquets of scent compounds. In many groups of flowering plants, the flowers possess elaborate mechanisms for facilitating pollination by insects. The flower scents, together with color and form, act to optimize attraction and stimulation of pollinators, which sometimes represent a great variety of species, and in other cases are highly specialized.

In orchids, this scent is very pronounced. In the genus *Ophrys*, which occurs with 20–30 species and forms, mainly in the Mediterranean region, males of certain species of bees and sphecid wasps are attracted to and sexually stimulated for pseudocopulation with the labella of the flowers, causing pollinia to attach to the insect. This is a highly specific pollination strategy on the part of the plant, which does not produce any nectar as a reward for the pollinating species, see Fig. 8. We studied volatiles from flowers of several *Ophrys* species in order to find specific pollination attractants/stimulants, which might be identical to sex attractants of the female bees and wasps. Our first candidates were cyclic sesquiterpenes, alcohols, and hydrocarbons, which occurred in patterns that seemed to coincide with the different types of pollinators. Today, the combined chemical/biological technique of gas chromatographic separation and electrophysiological recording (GC/EAD) has proved very helpful, and

Fig. 8 *Ophrys insectiphera* being visited, and pollinated (see pollinia on the head of the insect) by a male *Gorytes* sp.

some of our colleagues have succeeded in identifying active compounds. Much of this work was done with *O. sphecodes* [63]. *O. exaltata* and the *O. fusca* group have also been analyzed. Hydrocarbons are an important group of active compounds.

Linnaea borealis is another flowering plant that we have studied, partly for sentimental reasons, (G. Bergström, unpublished). Carl Linnaeus called this circumpolar plant "planta (or herba) nostra" and the Latin name was suggested by a Dutch colleague. Linnaeus noted "a weak scent of almond" from it, see Fig. D for a stand of *L. borealis*. It forms the single member of this genus. We decided to make an analysis of its odor, partly to honor the 300th anniversary of Linnaeus' birth, and studied it in three populations in western, central, and northern Sweden. The scent is composed of five benzenoid (aromatic) compounds as main components, with rather small variation between the populations, which should fit the original description of its odor by Linnaeus. Benzaldehyde is the compound mainly responsible for the almond-like smell, see Fig. 9.

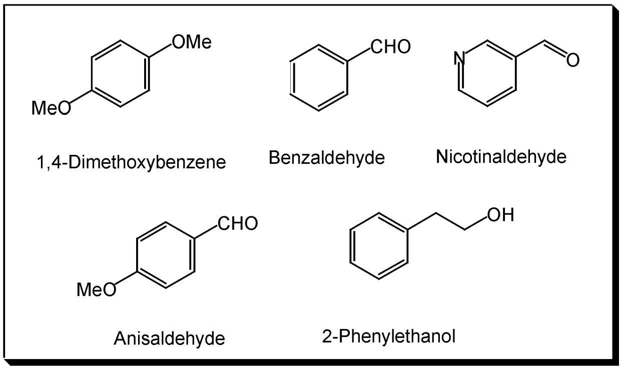


Fig. 9 The odor bouquet of *L. borealis*: five aromatic compounds.

We have also studied volatile compounds given off by flowers of *Cannabis sativa*, and we found that the petals give off a blend of monoterpenes, see Fig. 10. The pollen was found to emit characteristic scent compounds, which are not found in the other parts of the flower. This phenomenon is common in many flowering plants [45–52].

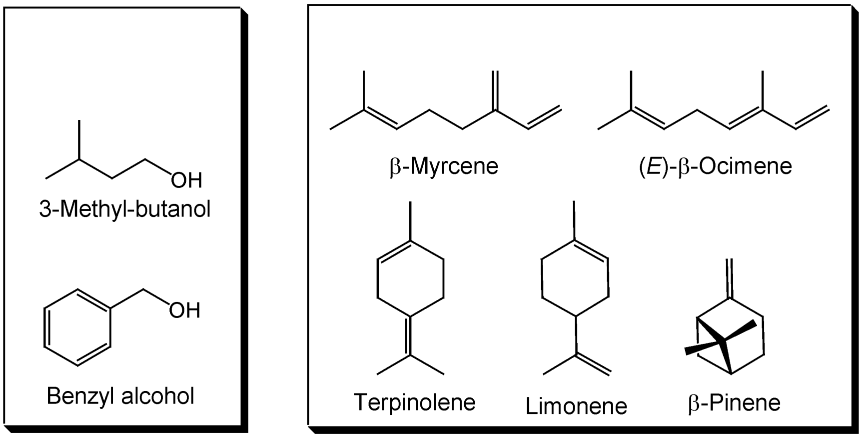


Fig. 10 Characteristic components of the volatile secretions from pollen (left) and sepals/petals (right) of *C. sativa*.

CHEMICAL ECOLOGY: SOME TRENDS, TENDENCIES, AND THE FUTURE

Analytical work on various aspects of behavior-releasing chemical signals—essentially the new area of CE—has indeed come a long way since the first studies some 40 years ago. There is still much work going on with insects and plants, aimed at deepening the understanding of chemical communication in these organisms, and of the evolutionary relationship between them. Further work on means of controlling insects using natural chemical signals is another active sub-area. Many studies are focused on chemical compounds in plant–plant and plant–microorganism interactions. But there is also a widening of the area to groups of organisms that have hitherto received comparatively little attention: mammals, aquatic organisms, and microorganisms. Major new lines of research, which bear great promise, are various studies employing genetic methods and techniques. This almost new aspect of CE will probably uncover "large secrets" and will probably mean nothing less than a new dimension.

Continued and enforced studies on the neurophysiological mechanisms of the reception of chemical signals, via both the peripheral and central nervous system, will most certainly contribute a lot to our overall understanding. Especially interesting and promising is neuroethology, the combination of neurophysiology and behavioral studies, particularly when these efforts will have a genetic basis. Looking into field studies, the time is ripe for intensified studies of the role of chemical signals in ecological relationships. Such studies may be facilitated, or indeed made possible, by the development of techniques and methods for use directly in the field.

The further development of methods and techniques is essential. We rely to some degree on commercially available instrumentation, but there is also room for and need of new innovations for improvements.

CURRENT HIGHLIGHTS

After a look into the 24 latest issues of the *Journal of Chemical Ecology*—the last two years, comprising over 200 articles—some areas of special interest and actuality can be singled out. They are complemented below through work reported at the recently held 24th Annual Meeting of the ISCE, in Jena, Germany (July 2007).

Induced defense, tritrophic interactions

Studies on insect chemical communication dominated the first decades in the development of CE. With a continued interest in that subfield, there is now a strong interest in plant chemistry. The focus is on allelopathy (interactions between plants, and between microorganisms and plants), herbivory (plants attacked for food), and direct or induced defense. Jasmonic and salicylic acids (JAs and SAs) are important for defensive responses of plants to attacks by herbivores and pathogens, both in chewing and nonchewing insects. They are often found in high concentrations in eggs, which may be attacked by insect parasites. De Moraes et al. have recently made further contributions to the information about these relationships [64a,b]. Volatile emissions in rice induced by JA and the effect on egg parasitism was reported by Turlings et al. [64c], and allelochemicals release, also in rice, was studied by a Chinese group [64d]. Volatile emission induced by methyl jasmonate in *Iva frutescens* was studied by Degenhardt and Lincoln [64e]. Hilker et al. found [64f] anthraquinones and anthrones as protective compounds in eggs and larva of some insects. These few examples reflect phenomena of plant–insect relationships with both theoretical and applied interest. It can be noted that there is not always a strict difference between hormone and pheromone, and between volatile and nonvolatile. This is the situation, for instance, with some of the chemical signals that honeybees use.

R. Mumm and M. Dicke presented recent data [64g] on the effects of genotypic and phenotypic manipulation of plant volatile emission and the effects on herbivorous and carnivorous arthropods. Induced by herbivory, infochemicals are produced, which form information webs overlapping the food webs.

The 15 talks presented on this topic at the three-day ISCE meeting are a measure of the activity of the area of induced plant defenses. Active compounds described include salicylates, jasmonates, glucosinolates, green leaf volatiles (GLVs, some simple C6 compounds), 2,3-butanediol, and so-called caeliferins (unusual saturated and monounsaturated α- and ω-substituted fatty acids). In a related field, animal responses to plant secondary metabolites (concept/term secondary seems to have a renaissence), there were another 10 presentations. In addition, there were no less than 144 poster presentations, many of them dealing with various aspects of these topics.

Odor reception

Work on pheromone binding proteins (PBPs) and their encoding by two new cDNAs are important as steps to understand the mechanism and high selectivity in the olfactory process. Further studies along this line have been carried out by E. Jacquin-Joly et al. on male antennae of the corn stemborer, *Sesamia nonagrioides* [65a]. Possible binding properties and their homologies with other known PBPs are discussed. W.-M. Xiu and S.-L. Dong cloned two PBP genes from antennal cDNA of the beet armyworm, *Spodoptera exigua* [65b]. Another Chinese group, Lu et al., identified and cloned two putative OBPs and a CSP (chemosensory protein) from females of a wasp, *Scleroderma guani*, which is an ectoparasitoid on the pine sawyer beetle, *Monochamus alter* [65c]. The idea is to attempt to control the pinewood nematode *Bursaphelenchus xylophilus* through its beetle vector by the wasp.

In contrast to releaser pheromones, which cause immediate and short-term responses in organisms, primer pheromones exert their effect in part by causing changes in brain gene expression. Alaux and Robinson have shown [65d] that isopentyl acetate, which acts as an alarm pheromone in honeybees, also influences behavior for a longer time by affecting brain gene expression.

Krieger et al. have identified candidate pheromone receptors of several moth species and found that they form a relatively conserved group, in contrast to the typical high diversity of insect olfactory receptors. They found the receptor cells to be surrounded by cells expressing PBPs and suggest that both a distinct PBP and receptor contribute to the specific recognition of a pheromone component.

Hansson et al. have studied the primary olfactory relay center of two strains (one has the proportion 99:1 between E11:Z11 tetradecenyl acetates, the other 3:97) of the corn borer, *Ostrinia nubilalis*. They put forward the interesting explanation of a single gene mediated reversed sensitivity swap of olfactory receptors that could be evolutionary unique to insects.

Guerrero et al. have earlier shown the antagonistic effect of some trifluoromethyl ketone pheromone analogs of the Mediterranean and European corn borers. This is due to inhibition of the crucial rapid esterase degradation of pheromones on the antenna. Practical utilization of this effect in the field showed remarkably high efficacy.

One genetic study, by C. Wicker-Thomas and T. Chertemps [65e], concerns two genes, desatF and eloF, responsible for female pheromone biosynthesis in *Drosophila melanogaster* and *D. sechellia*, which both produce C27 and C29 dienes (males produce C23 and C25 monoenes). The proteins they control are crucial enzymes for courtship behavior and responsible for sexual isolation that leads to speciation.

As the research field of CE proliferates, both as regards types of organisms and different chemical and biological specialties, it is important to keep it together so that the complex phenomena can be studied from all angles. In this way, we have the best chance to understand not only chemical signalling in all its aspects, but also to make our contributions to the insight into evolutionary mechanisms—which is our ultimate goal.

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