

Chemical sorcery for sociality: Exocrine secretions of ants (Hymenoptera: Formicidae)

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Abstract

Insects make great use of chemicals in communication, attack and defense. Social insects make still greater use of them in communication. Ants, particularly, make extensive use of communication chemicals, and have received the attention of chemists in discovery of these substances. These chemicals are produced in, and often stored by exocrine glands. The wide range of chemical compounds in exocrine glands of ants are illustrated here with examples. They extend over a broad spectrum of volatile organic compounds, most of them used in communication, as part of the social organisation of species. Illustrative examples of their chemical abilities are found among trail pheromones, defensive secretions, alkaloidal venoms, antibiotics, alarm pheromones, territorial marking and others. In many, but by no means all, examples, we know the function of these compounds, although we still know very little about how they may act together to convey more information. This review is written for a broad audience of entomologists to show the great diversity of substances used by ants. Compounds are grouped by the glands in which they have been found.

Key words: Chemical communication, pheromone, defense, alarm, antibiotic, exocrine glands, metapleural gland, Dufour gland, mandibular gland, venom gland, hindgut, postpharyngeal gland, pygidial gland, Pavan's gland, tibial gland, review.

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Introduction

Murray Blum, a doyen of insect chemical ecology, said that the road to insect sociality was paved with pheromones (BLUM 1974). He also said, in another place, that the glands of ants were a veritable chemical factory. His early investigations of ant secretions and the great variety of compounds he discovered prompted him to make these statements. The chemicals found in ants have been reviewed at various times, and in different ways. This review is intended for the entomologist who would like to know more about the kinds of chemicals made by ants, and where they are frequently found, but is not a specialist in this study. But why are ants the source of so many and so varied compounds?

Communication

For a tiny non-flying creature in a world of giant grasses, plants, stones and trees, sight is of little use. Light travels in straight lines and is instantaneous. A moment later the image is gone. But scents can filter around objects, and can linger at a spot. Depending upon the odour used, it can linger for a shorter or longer time. It can be detected rapidly in the total darkness of an underground nest. With air movement, it can tell direction. LE MANGEN (1970) has perceptively noted that "Nature is more a world of scents than a source of noise." For a non-flying, underground-nesting insect, odour is the obvious choice for communication. For social organisation, communication is essential.

Pheromone communication is most elaborate and much more advanced in ants compared to solitary insects, and

even more than in other social insects (GRONENBERG 2008), and ants rely particularly strongly on olfaction (where other insects rely more on vision). It is therefore remarkable how the resulting information is processed by their tiny brains to give meaning to their social organisation. DARWIN (1871: 145), knowing nothing of pheromones, was impressed by the minute size of the ant brain. The combination of exocrine glands, antennae and brain are the internet world of ants.

In a few cases we have knowledge of two or more of these chemicals being used together to convey a more complex signal, or rather, one that gives more information to the recipient. The writer attempted to explore the complexity of the language that could be conveyed by use of more than one signal by social insects in a meeting on *Insect Communication* a quarter of a century ago (MORGAN 1984), and the theme has been further developed by HÖLLDOBLER & WILSON (1990: 252), and HÖLLDOBLER (1995), who points out that the chemical signals can also be combined with vibrations or tactile stimuli to further modulate the message. We have only begun to decode a fragment of their language. Oh that we had a Rosetta stone to help us with this one!

It is evident that the same compound can be found in different glands in different species, and serve different functions. That is an example of what is called pheromone parsimony. The alkylpyrazines and methyl 6-methylsilylate can be found in the mandibular, venom or pygidial glands in different species and for different purposes (see

later). Mellein can be found in the metapleural, Dufour and mandibular glands, and in the hindgut.

Other functions

Communication is but one, though important chemical function. Ants also need chemicals for attack and defense, and protection from their environment and from infection. It would be good if we could arrange the chemicals that have been identified by the message they convey, or the function they perform, but there are too many substances identified where we do not know their purpose. Another way would be by their chemical type, but many compounds do not fit neatly into one category. An expedient, until more is known about the subject, is to arrange them by the glands that secrete them. The subject of this review then, is the diversity of substances that are produced, and sometimes stored, in the exocrine glands, i.e., those that secrete to the outside. Whether ants are unique in the number of chemicals they employ, we cannot yet know, but the collaborative efforts they have received have revealed a number and diversity that is not matched within the Hymenoptera, or by any other order. The exocrine glands of ants that can be sources of external chemicals are described by HÖLLDOBLER & WILSON (1990: chapter 7), and by BILLEN & MORGAN (1998).

Metapleural glands

SCHOETERS & BILLEN (1993) have shown that the metapleural gland does not have a sphincter or muscles, it secretes continually so the secretion is spread over the cuticle. MASCHWITZ & al. (1970) showed that the metapleural glands of *Atta sexdens* contained 3-hydroxydecanoic acid **1** (Fig. 1), which they called myrmicacin, and lesser amounts of 3-hydroxyoctanoic acid and 3-hydroxyhexanoic acid. These were accompanied by indole-3-acetic acid **2** and phenylacetic acid **3**. *Myrmica rubra* (as "*M. laevinodis*") also contained **1**, **2** and **3**, *Messor barbarus* **1** and **2**, and *Acromyrmex subterraneus* **1** and **2**. SCHILDKNECHT & KOOB (1971) showed that **1** prevented the germination of fungal spores, **2** promotes the growth of the mycelium that *Atta* and *Acromyrmex* cultivate, and **3** acts as an antibiotic. BEATTIE & al. (1986) showed with *Myrmecia* that antibiotic substances in the gland prevent infection, while NASCIMENTO & al. (1996) confirmed the antibiotic nature of substances from leaf-cutting species. More detailed analysis discovered a range of fatty acids from acetic acid, pentanoic, heptanoic, nonanoic and decanoic acids, palmitic and stearic acids, 4-oxo-octanoic acid **4**, γ -octalactone **5**, and 4-oxodecanoic acid **6** (MAILE & al. 1998, ORTIUS-LECHNER & al. 2000), all of which showed some activity against nest fungi (BOT & al. 2002).

It is not beyond possibility that a secretion could serve a protective and a communicative function at the same time, or part of the secretion was protective and another part communicative. *Crematogaster difformis sewardi* (as "*C. deformis*") has hypertrophied metapleural glands. According to ATTYGALLE & al. (1989) it contains a mixture of four phenols and mellein **7** which act as a repellent when released in the presence of attacking ants, but small amounts are released regularly, serving as an antiseptic. Recently JONES & al. (2005) found that these compounds were minor components in *C. difformis* and 6-propyl-, 6-pentyl- and 6-heptyl-salicylic acids **8 - 10** were the main

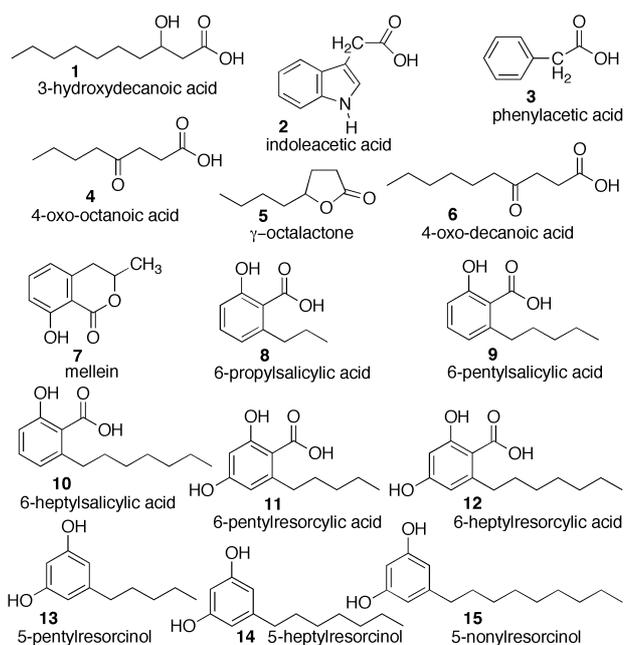


Fig. 1: Some antibacterial compounds from the metapleural glands of ants.

components and in *C. inflata* the major compounds were 6-pentyl- and 6-heptyl-resorcylic acids **11**, **12** while pentyl-, heptyl- and nonyl-resorcinols **13 - 15** were minor components.

Dufour glands

The Dufour gland occurs in all species of ant, and yet its function is perhaps the least understood of all these exocrine glands. In a few species it contains the trail pheromone; in a few others it has been shown to have a homemarking effect (CAMMAERTS & al. 1981), in *Pogonomyrmex* species it provides longer-lasting trunk route markers (HÖLLDOBLER & al. 2004), and its secretion confuses or repels potential slaves of slave-making species. The Dufour glands of at least some myrmicine, formicine, poneromorph, myrmeciine, pseudomyrmecine and dolichoderine ants contains a mixture of straight-chain hydrocarbons from about C₉ to C₂₇. Pentadecane or heptadecane are often the most abundant alkanes in myrmicines, and undecane or tridecane the most abundant alkanes in formicines. Some formicine species contain very few hydrocarbons, e.g., over 95 % of the secretion of *Camponotus japonicus* and *C. obscuripes* is undecane (HAYASHI & KOMAE 1980), while *Lasius fuliginosus* contains sixteen components of which eight are 2-ketones, while undecane comprises 77 % of the total (ALI & al. 1988a), and *Camponotus aegyptiacus* contains 52 % undecane and 28 % dodecyl acetate **16** (Fig. 2) with small amounts of many other acetates (ALI & al. 1988b). *Lasius flavus* is unique in containing 4-hydroxyoctadec-9-enolide **17**, a lactone derived from a hydroxy-fatty acid (BERGSTRÖM & LÖFQVIST 1970).

The shorter chain hydrocarbons are mostly saturated (alkanes) with an increasing proportion of alkenes at longer chains. This has a specific purpose, because alkanes of 16 carbon atoms (hexadecane) and more are solids at room temperature, while similar chain-length alkenes are liquids, and mixtures of substances usually have lower melting

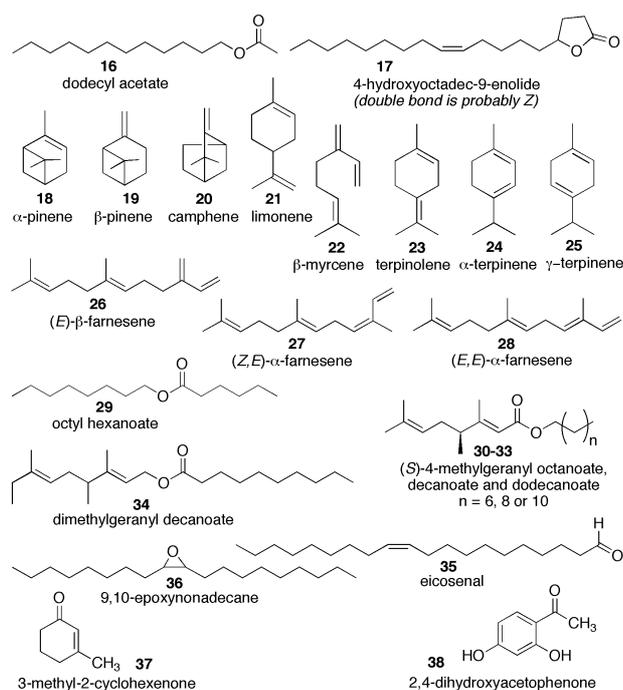


Fig. 2: Some examples of compounds from the Dufour glands.

points (or rather melting ranges) than either component. If the ant is to produce a secretion of hydrocarbons with longer chains and keep its secretion fluid, it must produce a rising proportion of alkenes or a more complex mixture to maintain the resultant secretion in a liquid state. The general statement that the gland contains hydrocarbons was immediately modified by noting that there are many species that contain in addition, alcohols, ketones and esters. These can be described as oxygenated derivatives of the straight-chain alkanes and alkenes. There are also in some species terpenes, exemplified by farnesene, which is usually accompanied by related compounds with one to three extra carbon atoms. These compounds have the same carbon skeleton as the various isomers of insect juvenile hormone (GOODMAN & GRANGER 2004). *Pristomyrmex* species differ from the general rule for myrmecines in having species-specific mixtures of very volatile monoterpenes (α - and β -pinene, camphene, limonene, β -myrcene, terpinolene and α - and γ -terpinene **18 - 25**) in their Dufour glands (BILLEN & al. 2000). *Cephalotes* (as "*Zacryptocerus*") *pusillus* has a mixture of 13 aldehydes from C₉ to C₁₈ (MORGAN & al. 2006a). *Manica rubida* stands out as a fertile chemical synthesiser, producing three isomers of farnesene **26 - 28** and seven homologues in its Dufour gland, that is, ten compounds close in structure to farnesene, but some with one or two more carbon atoms (JACKSON & al. 1990). *Manica rubida* is equally versatile with its mandibular gland chemistry (see below). *Camponotus balzani* is different from other *Camponotus* species. It has hypertrophied Dufour glands, with 97 % of its contents being octyl hexanoate **29** (KOHL & al. 2003).

We have reviewed the chemicals that have been identified in the Dufour glands of poneromorph and ectatommine ants (MORGAN & al. 2003). They frequently contain a long list of straight-chain alkanes, alkenes and alkadienes with some methyl-branched alkanes with C₁₅ to C₁₇ car-

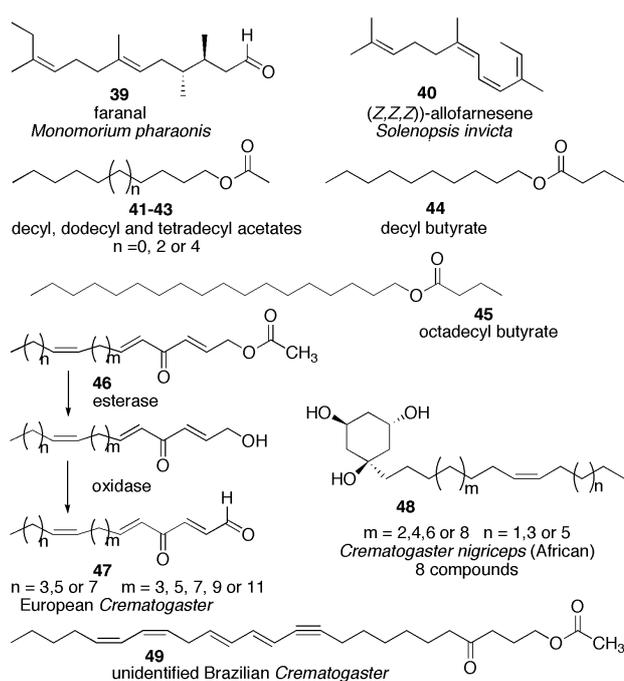


Fig. 3: Trail pheromones found in Dufour glands, and Dufour gland substances peculiar to *Crematogaster*.

bon chains most abundant. They also occasionally, as in *Ectatomma ruidum*, *Gnamptogenys menadensis*, *Odontomachus bauri*, *Odontoponera transversa*, *Pachycondyla striata*, and *Rhytidoponera metallica* contain terpenes, not always fully identified. In *Gnamptogenys striatula* are three aliphatic esters of a methylgeraniol **30 - 33** (SCHULZ & al. 2002) and a decyl ester of a dimethylgeraniol **34**. It is surprising to note that there is only one (unpublished) report on the contents of Dufour glands for dolichoderine ants (hydrocarbons in *Dolichoderus bispinosus* [as "*Monacis bispinosus*"] and four *Azteca* species, BLUM & WHEELER 1975). There is also a report of hydrocarbons in the gasters of *Linepithema humile* (as "*Iridomyrmex humilis*"), but the Dufour glands alone were not analysed (CAVILL & HOUGHTON 1974). We have recently examined some species of the small and rare Cerapachyinae subfamily (MORGAN & al. 2008). Dufour glands of *Cerapachys jacobsoni* contain tetradecyl acetate, tetradecanal, some other alcohols, aldehydes, and esters accompanied by hydrocarbons. *Cylindromyrmex whymperi* contained eicosanal **35**, epoxynonadecane **36**, and small amounts of hydrocarbons, while another *Cerapachys* species contained nothing volatile in its Dufour glands.

The hydrocarbons of the Dufour gland stand at the involatile end of exocrine substances, and therefore should persist in the environment longer, although they are more volatile than the cuticular hydrocarbons. It is possible that sometimes the hydrocarbons are not themselves an important part of communication, but act as "keepers" (in the language of perfumery) by reducing the rate of evaporation of more volatile components, such as 3-methyl-2-cyclohexenone **37** (found in the Dufour glands of *Rhytidoponera chalybaea*, along with 2,4-dihydroxyacetophenone **38**) (BROPHY & al. 1981), or lowering the rate of decomposition of unsaturated compounds like α -farnesene that are rapidly oxidised in air.

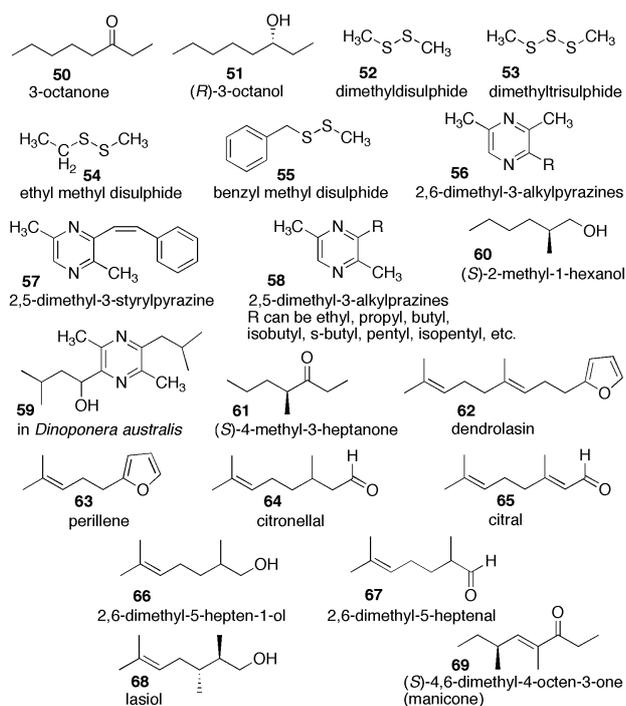


Fig. 4: Compounds from mandibular glands.

In a few examples the Dufour gland is the source of the trail pheromone. Faranal **39** (Fig. 3) is the trail pheromone of *Monomorium pharaonis* (RITTER & al. 1977) and a mixture of farnesene compounds in *Solenopsis invicta*, but writers disagree about which compounds. According to WILLIAMS & al. (1981) the most active compound is (*Z,Z,Z*)-allofarnesene **40**, but VANDER MEER (1983) and VANDER MEER & al. (1988) showed it is chiefly (*Z,E*)- α -farnesene **27** (Fig. 2) and another terpene, probably a methylclove, but as yet of unknown structure.

In slave-making species the Dufour gland is often enlarged and its contents are sprayed in the invaded nest to confuse the residents while captures are made. Some raiding *Formica* species contain large amounts of decyl, dodecyl and tetradecyl acetates **41** - **43** (REGNIER & WILSON 1971). In *F. subintegra* each worker has about 700 μg of these esters, or about 10 % of its body weight, and in *F. pergandei* about 40 μg . It appears that these acetates from the Dufour gland perform three functions, as defensive and offensive chemical weapons, as alarm pheromones within the colony, and as offensive "propaganda substances" when on a slave raid (REGNIER & WILSON 1971). The Dufour glands of queens of *Rossomyrmex minuchae*, before a slavering raid, contain large quantities of tetradecanal, and minor quantities of dodecanal to hexadecanal, and the glands have discharged all of this after the queen was adopted by a colony of *Proformica longiseta* (RUANO & al. 2005). The repellent effect of tetradecanal was tested by adding a little to a droplet of honey and noting how much time elapsed before the ants would take it. It was highly repellent to the host workers of *P. longiseta* and to the non-host *Formica selysi* (RUANO & al. 2005). In the obligate slave-maker *Polyergus rufescens* the gland of queens contains a number of esters of which decyl butyrate **44** forms more than 80 % (D'ETTORRE & al. 2000). This compound was not present in its potential slave *Formica cuni-*

cularia, and acts as a repellent to the *F. cunicularia*. Workers of *P. rufescens* have chiefly octadecyl butyrate **45** in their glands, but it is not a repellent (D'ETTORRE & al. 2000). The Dufour glands of *Harpogoxenus sublaevis*, which enslaves *Leptothorax* ants contains large quantities of (*E*)- β -farnesene **26** (Fig. 2) (also an alarm pheromone in some aphid species) and a homofarnesene (a related compound with one more carbon atom, in an unknown position) in addition to the usual hydrocarbons (OLLETT & al. 1987), but the proof that this confuses or subdues the *Leptothorax* workers has not been made.

The Dufour glands of *Crematogaster* ants produce unique substances. The anatomy of this genus does not permit them to bring the tips of their gasters to the ground, as many species do. When alarmed, they raise the gaster and extend their spatulate sting lance, exuding unusual compounds from the Dufour gland. In three European species these are unsaturated keto-acetates **46**. In the presence of an esterase and an oxidase from the venom gland the acetates are cleaved and the alcohols oxidized to aldehydes **47**. The resulting products (Fig. 3) act as alarm pheromones and contact poisons (DALOZE & al. 1991). In African and Brazilian *Crematogaster*, the gland contains different substances **48** and **49**, of unknown function (DALOZE & al. 1998, LECLERCQ & al. 2000a, LAURENT & al. 2003), and furanocembrenes (structures not shown), some of which are as toxic to ants as nicotine. Defensive compounds of ants have been reviewed by LECLERCQ & al. (2000b).

Mandibular glands

The range of compounds found in mandibular glands is equally broad, but they tend to be more volatile than Dufour gland compounds. Mandibular gland compounds are frequently identified as alarm pheromones. HÖLLDOBLER & WILSON (1990: 263-264) list all the alarm pheromones then known. Ethyl ketones and 3-alkanols, as well as terpene aldehydes, ketones and alcohols are often found in the mandibular glands of myrmicine and formicine ants. 3-Octanol and 3-octanone **50** (Fig. 4) are the principal constituents of the mandibular glands of a number of species of *Myrmica* (CREWE & BLUM 1970). One or both of these compounds are active as attractants, depending upon species (CAMMAERTS & al. 1983). (*R*)-3-Octanol **51** is the only or predominant enantiomer in many *Myrmica* species, but *M. scabrinodis* responds best to a 9 : 1 blend of (*3R*)- and (*3S*)-3-octanol (CAMMAERTS & MORI 1987). In *Crematogaster castanea* and *C. liengmei* it is (*R*)-3-octanol (BRAND 1985).

Poneromorph ants have a wide range of compounds, perhaps because of their greater diversity of foraging habits. *Pachycondyla analis* (as "*Megaponera foetens*") uses dimethyl disulphide **52** and dimethyl trisulphide **53** from its mandibular glands when raiding termite nests to attract sister workers to the attack (LONGHURST & al. 1979). For *Paltothyreus tarsatus* these compounds provide a mandibular alarm pheromone (PAVAN & VALCURONE DAZZINI 1971). The same compounds, together with ethyl methyl disulphide **54** and benzyl methyl sulphide **55** were found in *P. analis* (LONGHURST & al. 1979). Alkylpyrazines are more common in the mandibular glands of poneromorph ants, although not confined to that subfamily, that gland or even to ants. Of thirty three poneromorph species reviewed, twenty three of them contained alkylpyrazines (e.g., **56** -

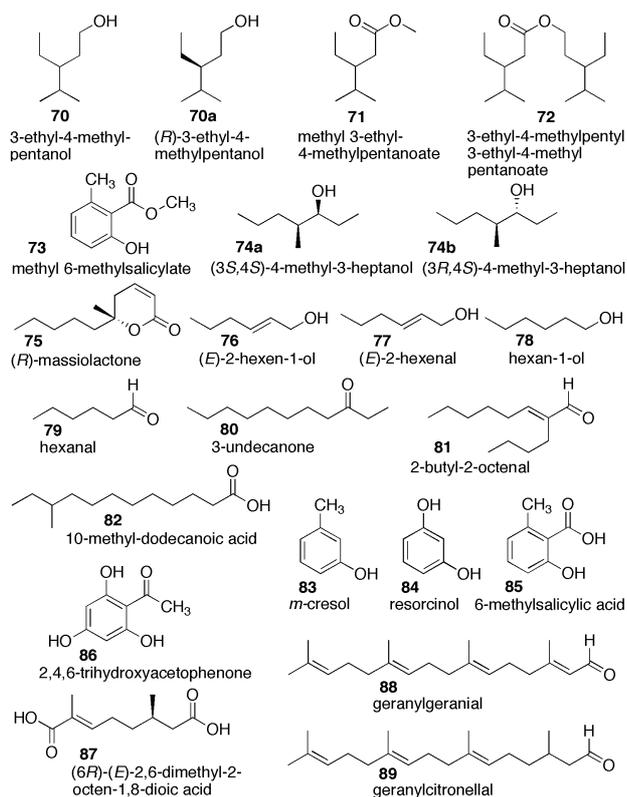


Fig. 5: Further compounds from mandibular glands.

58) in their mandibular glands (MORGAN & al. 1999). This group of compounds is found in other insects, and a number of foods. They are very interesting as odour chemicals. Not only can insects detect them at very low concentrations but so can humans, down to part per billion in the air. For us, they are important constituents of the flavours of coffee, chocolate, cheese, and cooked meat and even some wines. Eighteen alkylpyrazines were identified in the mandibular glands of *Pachycondyla striata* (MORGAN & al. 1999), and five trisubstituted alkylpyrazines (the major one being 58, where R is isopentyl) and six tetrasubstituted pyrazines (59 the major one) in *Dinoponera australis* (OLDHAM & MORGAN 1993).

(S)-2-Methyl-1-hexanol 60 seems to be a characteristic mandibular gland compound of a number of North African desert *Cataglyphis* species, and 4-methyl-3-heptanone is found in a number of *Pogonomyrmex* and *Atta* species. (S)-(+)-4-Methyl-3-heptanone 61 is found in *Atta texana*, and it produces a threshold response at 100 times lower concentration than the unnatural (R)-enantiomer (RILEY & al. 1974). Dendrolasin 62, a terpene compound, was an early discovery in the mandibular glands of *Lasius fuliginosus*, along with perillene 63 (QUILICO & al. 1956). Its presence also in the hindgut of *L. fuliginosus* is possibly a contaminant there (KERN & al 1997). Citronellal 64 and citral 65 are present in *Acanthomyops claviger* together with 2,6-dimethyl-5-hepten-1-ol 66 and 2,6-dimethyl-5-heptenal 67, which can be considered as derived from citronellal or citral (PAVAN & VALCURONE DAZZINI 1971). 2,6-Dimethylhepten-1-ol is also found in the mandibular glands of *Acanthomyops claviger* (LLOYD & al. 1975). A related compound with an extra carbon atom (compare with faranal

39, Fig. 3), is lasiol 68, from *Lasius meridionalis* (LLOYD & al. 1990). The ketone manicone 69 is the principal component of the mandibular glands of *Manica rubida*, *M. mutica* and *M. hunteri*, accompanied by some homologues with one less, one more or two more carbon atoms (BESTMANN & al. 1988). The so-called "wine-glass alcohol" 3-ethyl-4-methylpentanol 70 (Fig. 5) (FRANCKE & al. 1980, 1985) is found in many species of *Formica*, sometimes accompanied by methyl 3-ethyl-4-methylpentanoate 71 an ester of the corresponding acid, and another ester made from the "wineglass alcohol" and its acid 72. The alcohol 70, together with methyl 6-methylsalicylate 73, in the ratio 1 : 6, form the sexual attractant pheromone of virgin queens of the North American slavemaker *Polyergus breviceps* (GREENBERG & al. 2007), and the same compounds in a ratio somewhere between 1:50 and 1:90 in the European species *P. rufescens* (CASTRACANI & al. 2008). In the case of *P. breviceps* it has been shown to be (R)-3-ethyl-4-methylpentanol 70a.

There are a few reports that show that the exocrine glands fill rather slowly after the adult workers emerge from the pupa. In a study of *Formica sanguinea* it was found that the mandibular glands fill slowly with 70 and 71 from near zero at emergence from the pupa, to about 50 ng per gland after six months (MOENS & al. 1990).

Most of these reports refer to workers, but the mandibular glands of males and females can have quite different substances, and different castes of workers can have different secretions. For example, the mandibular glands of small workers of *Atta sexdens rubripilosa* contain 4-methyl-3-heptanone 61, and larger workers contain a mixture dominated by citral 65 (NASCIMENTO & al. 1993). Virgin and mated queens of this species also contain 4-methyl-3-heptanone (5 µg in virgins, 9 µg in mated queens) but unmated males contain an equimolar mixture of 4-methyl-3-heptanol 74 and 4-methyl-3-heptanone (11 µg of mixture) (NASCIMENTO & al. 1993). Glands of mated males are empty. Moreover only (S)-4-methyl-3-heptanone 61 is present in queens and males while the alcohol consists of both (3S,4S)-4-methyl-3-heptanol 74a and (3R,4S)-4-methyl-3-heptanol 74b (NASCIMENTO & al. 1997). The male secretion causes excitement and aggression in workers outside the nest at the time of sexual swarming (BENTO & al. 2007). There have been a number of investigations of the mandibular glands of sexuals of *Camponotus* species, summarised in TORRES & al. (2001). It is pointed out there that the finding of mellein 7 and methyl 6-methylsalicylate 73 in mandibular glands of males and rectal glands of workers (see later) is a recent discovery the significance of which as yet is unexplained.

A chemical curiosity is massiolactone 75 found in the mandibular glands of two Australian *Camponotus* species (CAVILL & al. 1968). It was said to be a powerful skin irritant and had an effect on vertebrate heart muscle. The compound had originally been discovered in the bark oil of *Cryptocaria massoia*, a traditional medicine in Papua-New Guinea. It was also found to be a flavour component of cane molasses, tuberose flowers and in *Hierochloa* (sweetgrass) plants, used in making vodka. It is now being used in butter and milk flavour. Nature sometimes seems to play games with us.

"Green leaf volatiles" are C₆ alcohols and their esters and aldehydes, given off by damaged or attacked plants. They

are important for signalling between plants and other organisms in their surroundings. (*E*)-2-Hexen-1-ol **76** and (*E*)-2-hexenal **77** are green leaf volatiles, found in the mandibular glands of *Crematogaster africana* and *C. buchneri* (CREWE & al. 1972). Hexan-1-ol **78** is an attractant for major workers of *Oecophylla longinoda* and they are alerted by hexanal **79**; the less volatile compounds 3-undecanone **80** and 2-butyl-2-octenal **81** release biting behaviour (BRADSHAW & al. 1979).

Phenols are frequently found in insects, particularly Coleoptera as defensive secretions. Simple phenols are relatively rare in ants. Quinones, common as defensive secretions in other insect orders, seem not to be used by ants. The phenols of the metapleural glands of *Crematogaster difformis* have been described above. Mellein **7** (Fig. 1) already described in *C. difformis* is also found in the mandibular glands of *Camponotus herculeanus*, *C. ligniperda* and *C. pennsylvanicus*, together with methyl 6-methylsalicylate **73** and 10-methyldodecanoic acid **82** (BRAND & al. 1973). The large mandibular glands of the bizarre exploding ants of some *Camponotus* species (*C. cylindricus* complex) also contain phenols. The glands stretch from the head through the thorax and into the abdomen. When attacked by predatory ants, some of the workers break the gland and the cuticle of the gaster and spray the contents over the attackers. JONES & al. (2004) have shown the hypertrophied glands contain a mixture of *m*-cresol **83**, resorcinol **84**, 6-methylsalicylic acid **85**, 2,4-dihydroxyacetophenone **38** (Fig. 2) and 2,4,6-trihydroxyacetophenone **86**, and others. In some species the unusual (6*R*)-(*E*)-2,6-dimethyl-2-octen-1,8-dioic acid **87** (JONES & al. 2004) is also found in quantity, evidently an oxidation product of a terpene like citronellal **64** (Fig. 4). A further example of less volatile compound in mandibular glands are geranylgeranial **88** and geranylcitronellal **89** in *Lasius carnolicus* (BERGSTRÖM & LÖFQVIST 1970).

Pseudomyrmex ants occupying acacia trees in Costa Rica produce complex blends of ketones, alcohols, aldehydes and carboxylic acids, all of which, except for the carboxylic acids, have already been described (WOOD 2005).

Venom glands

Where the sting is functional in Hymenoptera, the venom gland usually contains a mixture of proteins and peptides that form the venom. Ant venoms have received relatively little attention and are outside the subject of this review (see SCHMIDT 1986). It is interesting that while many other insects (even arachnids) have the ability to use formic acid, it does not appear anywhere among ants except among the Formicinae. The formic acid can be as concentrated as 60 % of the secretion, and workers can contain as much as 2 mg each. Formic acid also acts as the major recruitment signal in some species of *Camponotus* (KOHL & al. 2003) and other formicines.

While the venom usually contains proteins and peptides, there are nevertheless some examples of species where the venom consists of nitrogen-containing small molecules. Five- and six-membered ring nitrogen compounds are found in venom reservoirs of the Myrmicinae in the genera *Megalomyrmex*, *Monomorium*, *Myrmicaria* and *Solenopsis* (fire ants) (JONES & al. 2007). The compounds can be considered as straight alkyl chains cyclized by a nitrogen atom to form monocyclic piperidines **90** (Fig. 6),

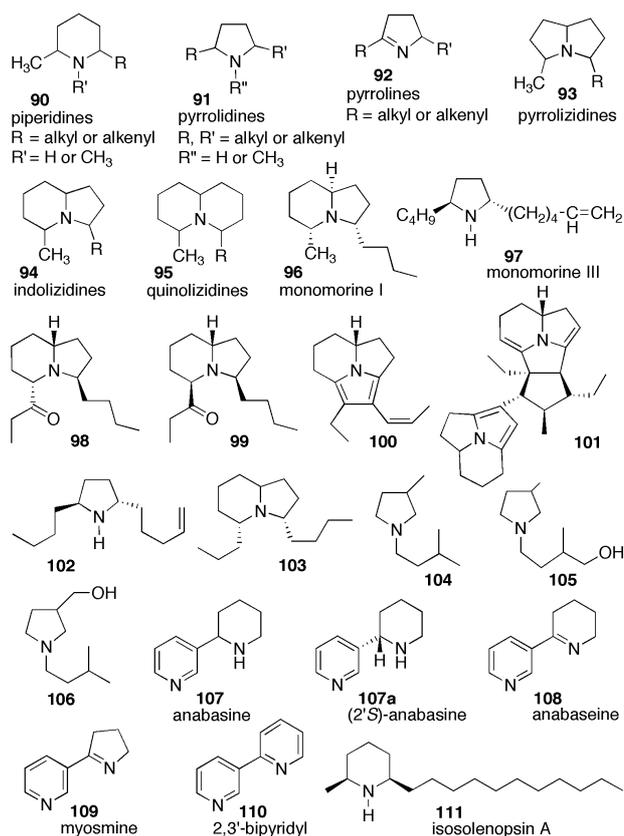


Fig. 6: Substances from venom glands.

pyrrolidines **91**, and pyrrolines **92**, or they can be cyclized again to give bicyclic pyrrolizidines **93**, indolizidines **94** and quinolizidines **95** (JONES & al. 2007). All those known at the time of writing were listed with species by ATTYGALLE & MORGAN (1984). Such compounds are called alkaloids, although the term originally referred to basic nitrogen compounds from plants. *Monomorium pharaonis* typically contains the compounds monomorine I **96**, an indolizidine, and monomorine III **97**, a pyrrolidine, which were once suggested as the trail pheromone of that species before the discovery of faranal **39** because they showed some attraction for workers (RITTER & al. 1973). In *Myrmicaria natalensis eumenoidea* (+)-limonene **21** (Fig. 2) is present in the venom gland and acts as a solvent and spreading agent for the alkaloidal venom and also as a long-range recruiting pheromone (KAIB & DITTEBRAND 1990). The principal alkaloids are **98** and **99** (FRANCKE & al. 1995). More complex alkaloids of the same type have been found in other *Myrmicaria* species. *Myrmicaria opaciventris* collected in East and West Africa have different secretions. In Kenya, as well as α -pinene **18**, β -pinene **19** and limonene **21**, they contain nine alkaloids, of which the major one is **100**, which can be seen as a further cyclized indolizidine (SCHRÖDER & al. 1996). The same species from Cameroon contains the same volatile terpenes plus terpinolene **23** and a still more complex alkaloid in which two indolizidine molecules are fused together **101** (SCHRÖDER & al. 1996) and another with three indolizidines joined to give a C₄₅ compound with ten rings (SCHRÖDER & al. 1996). *Myrmicaria melanogaster* from Brunei contains β -pinene **19**, myrcene **22** and limonene **21** and fourteen

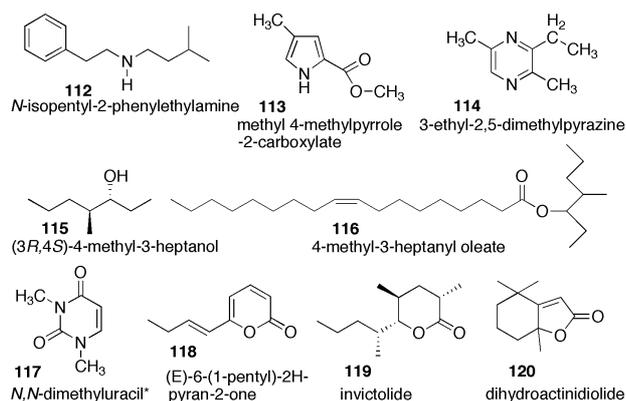


Fig. 7: More examples of compounds from venom glands.

alkaloids, including isomers, of which **102** and **103** are the most abundant (JONES & al. 2007).

A different use for venom alkaloids has been found in the social parasites *Harpagoxenus sublaevis* and *Leptothorax goesswaldi*, but also in *Leptothorax acervorum* and *L. muscorum*. The females produce a male-attractant pheromone in their poison glands which consists of up to six *N*-alkyl-3-methylpyrrolines (REDER & al. 1995). The major components are **104**, **105** and **106** in *H. sublaevis*; **105** and **106** in *L. acervorum*, and **105** in *L. muscorum* and *L. goesswaldi* (REDER & al. 1995).

Pheidole and *Messor* species have mixtures of nicotine alkaloids, particularly anabasine **107**, anabaseine **108**, myosmine **109** and 3,2'-bipyridyl **110** (CRUZ-LÓPEZ & al. 2006). These are all known to have strong physiological effects on higher animals, and are no doubt equally effective in insect attack and defense. The pharmacological effects of the *Solenopsis* (fire ant) venoms have been studied, both the mixture and the pure compound isosolenopsin A **111** (YI & al. 2003).

The venom gland has been identified as the source of a trail pheromone in a number of species. In some it is a trace of nitrogen-containing substance in the venom. In *Aphaenogaster rudis* four compounds were identified: *N*-isopentyl-2-phenylethylamine **112** (Fig. 7), anabasine **107**, anabaseine **108** and 3,2'-bipyridyl **110**, all of which were necessary to reproduce its trail pheromone (ATTYGALLE & al. 1998a). Anabasine was detected in three other species, and shown to be pure (2'*S*)-anabasine **107a** (Fig. 6) in *Messor sanctus* and predominantly that enantiomer in *Aphaenogaster subterranea* and *A. miamiana* (LECLERCQ & al. 2001). Anabaseine **108** (Fig. 6) was found in *A. subterranea* and *A. senilis* (LECLERCQ & al. 2001). In *Atta texana* and *A. cephalotes* the trail pheromone is the non-basic compound methyl 4-methylpyrrole-2-carboxylate **113**; in all twelve species of *Myrmica* studied and in *Atta sexdens* and *Acromyrmex octospinosus* the pheromone is 3-ethyl-2,5-dimethylpyrazine **114**. *Atta sexdens sexdens* contains both the pyrrole and pyrazine compounds, but the pyrazine is much more effective for trail-following.

The trail pheromone of *Leptogenys diminuta*, contained in the venom gland is (3*R*,4*S*)-4-methyl-3-heptanol **115** (ATTYGALLE & al. 1988). It is accompanied there by larger amounts of long-chain esters of the alcohol, e.g., 4-methyl-3-heptanyl oleate **116** and 4-methyl-3-heptanyl stearate, which probably serve to reduce the volatility of

this very small molecule (MAILE & al. 2000). *Tetramorium* cf. *impurum* is one species known to use methyl 6-methylsalicylate **73** (Fig. 5) as its trail pheromone (MORGAN & OLLETT 1987).

The ponerine ant *Pachycondyla analis* (as "*Megaponera foetens*") uses *N,N*-dimethyluracil **117**, a quite different compound, in its poison gland as trail pheromone (JANSSEN & al. 1995).

The preponderance of nitrogen-containing substances in the venom gland is noticeable, and unsurprising for a gland otherwise used for producing peptides and proteins.

Further secondary functions are known for the venom gland. In the glands of mated queens of *Solenopsis invicta* there are three compounds that comprise a queen recognition pheromone (ROCCA & al. 1983). The three compounds are (E)-6-(1-pentyl)-2*H*-pyran-2-one **118**, first identified in soil fungi, another pyranone named invictolide **119**, and the already known dihydroactinidiolide **120**, also found in tobacco and other plants. Materials marked with these compounds are carried into the nest by workers.

Hindgut

The hindgut (or rectal sac) is found throughout the Formicinae and also in *Eciton* and *Neivamyrmex* of the Ecitoninae and *Diacamma* in the Ponerinae. At the present state of knowledge, it is the only source of trail pheromones in the Formicinae. It was formerly claimed that six fatty acids (hexanoic to decanoic acid and dodecanoic acid) were the trail pheromone of *Lasius fuliginosus* (HUWYLER & al. 1973), which seemed unlikely. Later KERN & al. (1997) showed that it was mellein **7** (Fig. 1), a substance already identified serving other functions in the metapleural and Dufour glands, and also serving as a trail substance in *Formica rufa*. The mellein is accompanied in *L. fuliginosus* by 2,3-dihydro-3,5-dihydroxy-6-methyl-2*H*-pyran-4-one **121** (Fig. 8), which has much less trail activity. But even these two compounds do not equate to the activity of the natural secretion (KERN & al. 1997). It is interesting that this pyranone **121** occurs in the aphid honeydew which forms part of the normal diet of this species. It is possible that the ants do not synthesise the compound but sequester it from their food, as happens with many plant substances eaten by insects (MORGAN 2004). In *Lasius niger* the same group identified a dimethylmellein, (R)-8-hydroxy-3,5,7-trimethylisocoumarin **122**, but although they found mellein and this dimethylmellein in *Formica fusca* and *F. sanguinea*, the compounds were not active trail substances in these species. *Camponotus herculeanus* uses 2,4-dimethyl-5-hexanolide **123** as a component of its pheromone (BESTMANN & al. 1995). There are further examples where only a component of a formicine trail pheromone has been identified. KOHL & al. (2003) also identified the trail pheromone of *Camponotus castaneus* as 6-sec-butyl-2,5-dimethyltetrahydro-2*H*-pyran-2-one **124** (compare with invictolide **119**, but here the stereochemistry is not known) while for *C. balzani* and *C. sericeiventris* it is again the dimethylmellein **122** identified in *Lasius niger*.

Postpharyngeal gland

This gland lies on the borderline of our subject. It has a smooth endoplasmic reticulum and surface microvilli, which are consistent with a non-protein secretor, but also consistent with digestive tissue. It has been shown for several

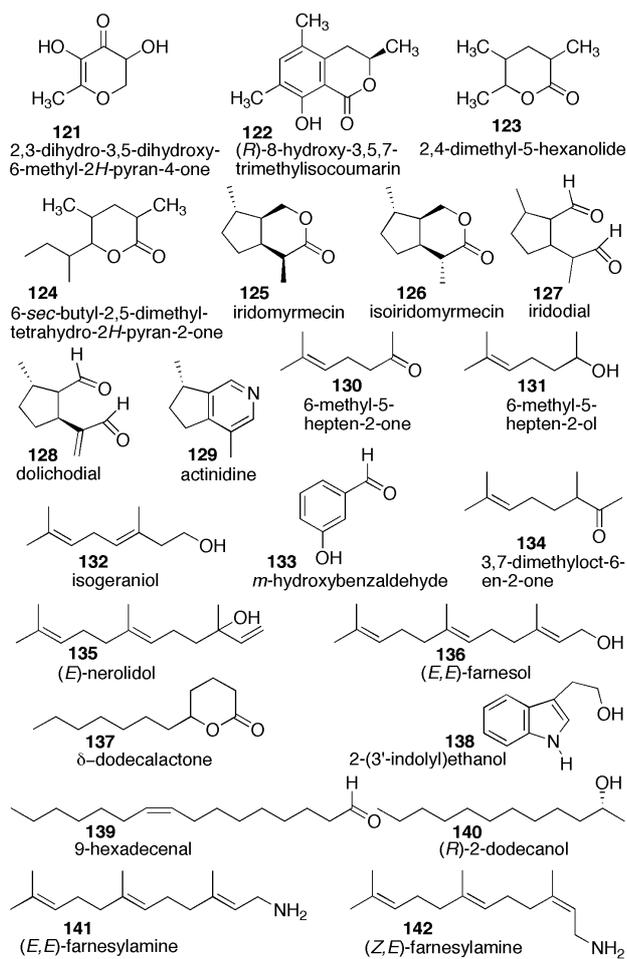


Fig. 8: Compounds from the hind gut and pygidial glands.

species that it contains the same substances as are found on the cuticle (BAGNÈRES & MORGAN 1991), that is, chiefly long chain hydrocarbons with some long chain acids and esters. A study of biosynthesis of hydrocarbons in *Cataglyphis niger* (SOROKER & HEFETZ 2000) has shown that some lipids are synthesized in the gland but not hydrocarbons (SOROKER & HEFETZ 2000). The gland can acquire the hydrocarbons from the cuticle by grooming and the contents can be regurgitated. The question of the function of the gland as an exocrine secretor remains.

Pygidial gland

The pygidial gland can be found in all subfamilies except the Formicinae. In the Dolichoderinae it is usually very large and there it is also known as the anal gland. In the Dolichoderinae the gland is used in defense and alarm, and is the source of iridoids, a group of monoterpene compounds now recognised to be widely distributed in insects (for example, in aphids, leaf beetles and stick insects) and plants. The first of these, iridomyrmecin **125**, was discovered by Pavan in *Linepithema humile* (as "*Iridomyrmex humilis*") (PAVAN 1949) and claimed as an antibiotic, but the function of iridoids are chiefly deterrent and immobilising to other insects. Other examples of iridoids are isoiridomyrmecin **126**, iridodial (six isomers) **127**, and dolichodial **128**. The iridoids are often accompanied by the

nitrogen derivative, actinidine **129**. *Tapinoma simrothi* uses its pygidial gland secretion for both alarm and trail following. At higher concentrations from a point source the workers display alarm. At lower concentrations the iridodial **127** and iridomyrmecin **125** from the gland when drawn in a line are followed by the workers calmly (SIMON & HEFETZ 1991).

The iridoids are often accompanied by actinidine **129**. 6-Methyl-5-hepten-2-one **130** and 6-methyl-5-hepten-2-ol **131** have also been isolated from a number of species of *Iridomyrmex* (e.g., *I. near pruinosus*, in CREWE & BLUM 1971) and *Tapinoma*.

In other subfamilies, in roughly half the cases where it has been studied the gland contains nothing volatile. *Pachycondyla analis* (as "*Megaponera foetens*") uses the secretion as a possible alarm pheromone because it stimulates the workers to leave the nest. The principal components are actinidine **129** and the six isomers of iridodial **127** (JANSSEN & al. 1995). Another ponerine, *Pachycondyla marginata* employs citronellal **64** (Fig. 4) from the gland in predatory raids on termites and in nest emigration (HÖLLDOBLER & al. 1996). *Rhytidoponera metallica* workers contain isogeraniol **132** and *m*-hydroxybenzaldehyde **133** (MEINWALD & al. 1983). *Leptogenys diminuta* also contains isogeraniol, which provokes recruitment behaviour (ATTYGALLE & al. 1988).

The pygidial gland of the primitive ant *Nothomyrmecia macrops* contains 3,7-dimethyloct-6-en-2-one **134** and a variety of other compounds (BILLEN & al. 1988). In *Myrmecia nigriceps* the major compounds are (E)-nerolidol **135**, (E,E)-farnesol **136** and δ-dodecalactone **137** (JACKSON & al. 1990b).

The first myrmecinae studied, *Pheidole biconstricta* has hypertrophied pygidial glands, that, too, are filled with iridoids with alarm and repellent properties (DAVIDSON & al. 2005). Unusually, the myrmecine species *Ocymyrmex laticeps* uses its pygidial gland to lay trails of 2-(3'-indolyl)ethanol **138** (MORGAN & al. 2006b).

Pavan's glands

Pavan's gland, an abdominal source of trail pheromones is found in the Dolichoderinae and Aneureinae. It is reported as the source of the trail pheromone in *Aneuretus*, *Iridomyrmex*, *Tapinoma* (but see above), *Liometopum*, and *Dolichoderus* (as "*Monacis*"). The Pavan's gland of *Dolichoderus thoracicus* contains a mixture of eighteen long-chain aldehydes all of which contribute to the trail pheromone. The most active single compounds are 9-hexadecenal **139** and 9-octadecenal but others contribute and the effect of the mixture is greater than any component or pair of components (ATTYGALLE & al. 1998b). (Z)-9-hexadecenal is a component of the trail pheromone in *Linepithema humile* (CAVILL & al. 1979).

Tibial glands

The anatomy of the gaster of *Crematogaster* ants prevents them from laying trails from abdominal glands, so they have adopted another system, using glands in the hind tibia with a duct to the tarsi to lay the secretion by the feet (LEUTHOLD 1968). 2-Alkanols and methyl ketones from C₁₁ to C₁₅ have been identified in several species (OLLETT 1989). As yet, the pheromone has been identified in only one species, *C. castanea*. The major compound is (R)-2-dodecanol **140** (MORGAN & al. 2004).

Conclusion

Finally we should add two more compounds, (*E,E*)- and (*Z,E*)-farnesylamine **141**, **142** for which no gland has been identified but found in whole body extracts of *Monomorium fieldi* (JONES & al. 2003). Though this pair of compounds has been extensively studied, and they are known to inhibit arthropod moulting and reproduction and have other physiological effects, this is the first time they have been identified in nature.

We see many compounds are used in the same roles by different species, and some in different roles in different species, and produced in different glands; some compounds are unique to a species, and many groups of compounds are found in blends of different proportions to create species-specific odours. Different compounds, e.g., terpenes and alkaloids produced in the same gland can be used together for greater effect and for different purposes.

Chemists can, without too much difficulty, separate and identify nanogram quantities of compounds that the entomologist can provide. More difficult is the designing of behavioural tests to learn the function they perform in the insect life. More and better bioassays are the technique that will greatly advance our knowledge of the chemical language of ants.

Zusammenfassung

Insekten setzen generell häufig chemische Stoffe in Kommunikation, Angriff und Verteidigung ein. Für soziale Insekten ist die Bedeutung in der Kommunikation besonders groß, und Ameisen weisen eine ganz herausragend reiche chemische Kommunikation auf. Chemiker haben der Erforschung dieser Substanzen dementsprechend besondere Aufmerksamkeit gewidmet. Diese chemischen Substanzen werden in exokrinen Drüsen produziert oder aufbewahrt. Das breite Spektrum dieser Substanzen wird hier anhand von Beispielen dargestellt. Es handelt sich um flüchtige organische Komponenten, wobei die meisten der Kommunikation dienen, als Teil der sozialen Organisation. Anschauliche Beispiele für die chemischen Fähigkeiten der Ameisen finden sich unter ihren Spurpheromonen, Abwehrsekreten, Alkaloidgiften, Antibiotika, Alarmpheromonen, Territoriumsmarkierungen und anderen. In vielen, aber bei weitem nicht allen Fällen kennen wir die Funktion dieser Stoffe. Hingegen wissen wir nur sehr wenig darüber, wie die Stoffe möglicherweise zusammen wirken, um dadurch noch mehr Information zu übermitteln. Dieser Übersichtsartikel richtet sich an eine breite entomologische Leserschaft und zielt darauf ab, die große chemische Diversität bei Ameisen zu veranschaulichen. Die Stoffe sind entsprechend den Drüsen, in denen sie gefunden wurden, angeordnet.

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