# COMPARATIVE EXOCRINOLOGY OF THE FORMICIDAE

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Although formic acid was isolated from ants more than 300 years ago (Wray, 1670), it is only in the last two decades that the great natural products potential of these insects has been explored. A large number of recent investigations have established that formicid species in several subfamilies are eminently capable of biosynthesizing a wide range of substances in different exocrine glands. Most of these ant-derived compounds are pheromones that are utilized as key elements for regulating the social interactions which occur in the colonial milieu. At this juncture it seems particularly appropriate to survey the comparative exocrinology of the Formicidae in order to examine the emphases that particular genera have placed on selected classes of compounds. Such a treatment affords us with an excellent opportunity to explore the biosynthetic peculiarities and similarities characterizing species in most of the formicid subfamilies, hopefully as a prelude to comprehending the evolution of the natural product systems of ants.

MYRMICIINAE The proteinaceous venom of Myrmecia gulosa contains at least eight constituents with histamine accounting for about two percent of the dried secretion (Cavill et al., 1964). This venom also contains a hyaluronidase, shows kinin-like activity, and possesses a direct haemolytic factor. Similarly, the venom of M. pyriformis is fortified with compounds possessing the same range of pharmacological activities (Lewis and de la Lande, 1967) as are found in that of M. gulosa. In addition, the venom of M. pyriformis contains a powerful phospholipase A (Lewis et al., 1968).

The Dufour's gland secretion of M. gulosa contains a series of aliphatic hydrocarbons and is dominated by cis-8-heptadecene (62%) (Cavill and Williams, 1967). The alkanes, tetradecane (1%), pentadecane (17%), hexadecane (1%), and heptadecane (4%) are also present; the remaining compounds, which constitute 15% of the mixture, appear to be branched-chain hydrocarbons. The secretion of M. tricolor shows a similar pattern of hydrocarbons (Cavill and Williams, 1967).

PONERINAE Although the mandibular gland chemistry of ponerines in only three genera have been studied, it is clearly evident that species in this subfamily can produce widely different natural products. The results of these investigations are presented in Table 1.

Alkyl sulfides are only known as arthropod natural products because of their occurrence in the secretion of Paltothyreus tarsatus (Casnati et al., 1967). The presence of pyrazines in the glandular exudates of Odontomachus hastatus and O. haematodus (Wheeler and Blum, 1973) similarly identifies these products as distinctive since these nitrogenous compounds have not been identified as exocrine products in any other animals. On the other hand, 4-methyl-3-heptanone, the primary glandular constituent produced by N. villosa (Duffield and Blum, 1973), is a characteristic mandibular gland product of species in several myrmicine genera. At this time it seems reasonable to conclude that the Ponerinae will contri-

Table 1 - Compounds identified in the mandibular gland secretions of ponerine species*

| Species | Compound | Authority |
|---|---|---|
| Paltothyreus tarsatus | Dimethyldisulfide | Casnati et al., 1967 |
| Paltothyreus tarsatus | Dimethyltrisulfide | Casnati et al., 1967 |
| Odontomachus hastatus | 2,5-Dimethyl-3-isopentylpyrazine | Wheeler and Blum, 1973 |
| Odontomachus haematodus | 2,6-Dimethyl-3-pentyl-, butyl-, propyl-, and ethylpyrazines | Wheeler and Blum, 1973 |
| Neoponera villosa | 4-Methyl-3-heptanone | Duffield and Blum, 1973 |
| Neoponera villosa | 4-Methyl-3-heptanol | Duffield and Blum, 1973 |

*In workers

bute additional chemical surprises when the exocrine compounds produced in the mandibular glands of species in other genera are examined.

Although the chemistry of the Dufour's glands of no ponerine species has been described in detail, aliphatic hydrocarbons have been reported to be present in the secretions of Amblyopone australis (Cavill and Williams, 1967) and O. hastatus (Wheeler and Blum, 1973).

DORYLINAE The natural products chemistry of army ants has largely been neglected, notwithstanding the fact that chemical communication is highly developed in these virtually blind insects. Blum and Brand (1973) have identified 4-methyl-3-heptanone in the mandibular glands of males of Neivamyrmex harrisii. Workers of N. nigrescens produce skatole (3-methylindole) in their hypertrophied mandibular glands (Blum and Watkins, 1969) but this compound does not function as a releaser of alarm behaviour.

PSEUDOMYRMICINAE The mandibular gland secretion of workers of Pseudomyrmex gracilis is fortified with 4-methyl-3-heptanone (Blum et al., 1973c). This compound functions as an alarm pheromone for this very active pseudomyrmicine.

MYRMICINAE The natural products chemistry of some myrmicine species has been investigated in considerable detail in the last ten years. Although relatively few of the genera in this large subfamily have been chemically characterized, it is nevertheless evident that myrmicines biosynthesize a wide range of exocrine compounds in several different glands. Alarm pheromones, trail pheromones, and defensive compounds have been isolated from among the mandibular glands, poison gland, Dufour's gland and metapleural glands of species in a variety of genera scattered throughout the Myrmicinae.

Table 2 - Exocrine products identified in the poison gland secretions of myrmicine species*

| Species | Compound | Authority |
|---|---|---|
| *Solenopsis sp.* | *cis*- and *trans*-2-Methyl-6-*n*-nonylpiperidine | MacConnell *et al.*, 1973 |
| *Solenopsis xyloni* | *cis*- and *trans*-2-Methyl-6-*n*-undecylpiperidine | Brand *et al.*, 1972 |
| *Solenopsis richeri* | *cis*- and/or *trans*-2-Methyl-6-*n*-tridecylpiperidine | Brand *et al.*, 1972 |
| *Solenopsis invicta* | *cis*- and *trans*-2-Methyl-6-*n*-pentadecylpiperidine | MacConnell *et al.*, 1971 |
| *Solenopsis invicta* | *cis*- and/or *trans*-2-Methyl-6-(*cis*-4'-*n*-tridecenyl) piperidine | MacConnell *et al.*, 1971 |
| *Solenopsis invicta* | *cis*- and *trans*-2-Methyl-6-(*cis*-6'-*n*-pentadecenyl) piperidine | MacConnell *et al.*, 1971 |
| *Solenopsis xyloni* | 2-Methyl-6-*n*-undecyl-$\Delta^{1,2}$-piperideine | Brand *et al.*, 1972 |
| *Atta texana* | Methyl-4-methylpyrrole-2-carboxylate | Tumlinson *et al.*, 1971 |
| *Monomorium pharaonis* | 3-Butyl-5-methyloctahydroindolizine | Ritter *et al.*, 1973 |
| *Myrmicaria natalensis* | Limonene | Quilico *et al.*, 1960 |

* In workers

Poison gland products

Compounds identified in the poison glands of myrmicine species are listed in Table 2. The apparent emphasis on nitrogenous compounds may be a by-product of the proteinaceous themes that are generally stressed in the biosynthetic tissues of myrmicine poison glands. Species of fire ants in the genus Solenopsis are exceptional in producing venoms thoroughly dominated by 2,6-dialkylpiperidines (MacConnell et al., 1971) and polypeptides constitute relatively minor constituents (Brand et al., 1972). The venom of queens of certain Solenopsis species also appears to be singular because it lacks the alkaloids containing longer carbon chains that are characteristic of the venom of their workers (Brand et al., 1973a). Whether caste-specific venoms are routinely produced by ants remains to be determined.

Methyl 4-methylpyrrole-2-carboxylate, a nitrogen-containing constituent in the venom of Atta texana (Tumlinson et al., 1971), is utilized as a trail pheromone by this attine. This compound is one of several trail pheromones that are present in the venom of this species. The ability of myrmicines to employ minor components of protein-rich venoms in order to lay trails may be widespread among the species in this highly successful subfamily (Blum and Ross, 1965).

The indolizine identified in the venom of Monomorium pharaonis represents the first compound with this skeleton isolated from animals (Ritter et al., 1973). The exact role of this pheromone in the biology of M. pharaonis has not been determined. Similarly, the function of limonene, a poison gland product of Myrmicaria natalensis (Quilico et al., 1960) is unknown, but it is very possible that this monoterpene hydrocarbon is utilized as a defensive compound.

Dufour's gland products

Limited investigations on the chemistry of the myrmicine Dufour's gland secretion indicates that this exocrine structure is an excellent source of hydrocarbons. Cavill et al., (1967) reported that the secretion of Aphaenogaster longiceps contained the sesquiterpene α-farnesene and that this compound comprised 4% of the ant's weight. α-farnesene was also identified as a minor constituent in the Dufour's gland of Myrmica rubra (Morgan and Wadhams, 1972). In addition, this secretion contained 19 other hydrocarbons and was dominated by 8-heptadecene (53%) and pentadecane (14%). Normal alkanes in the range $C_{13}-C_{19}$ were present in addition to several of the corresponding alkenes. The presence of homofarnesene and bishomofarnesene further demonstrated the well-developed ability of this gland to synthesize sesquiterpenoid substances.

The Dufour's gland secretions of S. richteri, S. invicta, and S. geminata contain n-heptadecane as well as certain other hydrocarbons (Brand et al., 1972) and Pogonomyrmex species produce a series of mono- and dimethyl-branched hydrocarbons in their glandular tissues (Regnier et al., 1973).

Metapleural gland products

Phenylacetic acid has been identified in the metapleural glands of Atta sexdens (Schildknecht and Koob, 1970), Messor barbarus, and Myrmica rubra (Schildknecht and Koob, 1971). It is the major glandular constituent present and may reach 30 μg/gland in A. sexdens. This glandular secretion of A. sexdens, M. barbarus and Acromyrmex sp. also contains trace amounts of indole-3-acetic acid (Schildknecht and Koob, 1970; 1971), and, in addition to this acid, the metapleural exudates of these three species, as well as that of M. rubra, contain β-hydroxydecanoic acid (Schildknecht and Koob, 1971). This latter compound, assigned the trivial epithet myrmicacin, is accompanied by lesser amounts of β-hydroxyoctanoic acid and β-hydroxyhexanoic acid in the secretion of A. sexdens.

Schildknecht and Koob (1971) believe that the fungus garden of A. sexdens is chemically regulated by these acids. Thus, phenylacetic acid is reported to function as a bactericide, indole-3-acetic acid as a mycelial growth stimulant, and β-hydroxydecanoic acid as a fungicide to exclude the spores of foreign fungi. However, no experimental proof is offered to demonstrate that the fungus garden of this species is indeed protected by these compounds in the colonial milieu. Furthermore, the presence of these compounds in the secretion of M. rubra, a non-fungus grower, cannot readily be reconciled with the presumed functions of these acids.

Mandibular gland products

Myrmicines biosynthesize an extraordinary variety of ethyl ketones in their mandibular glands (Table 3). Seven of the identified compounds are 3-ketones and these compounds, which are utilized as both alarm pheromones and defensive products, must be regarded as rather characteristic natural products of this subfamily. Although specific ethyl ketones are generally synthesized by most species in a genus (McGurk et al., 1966; Crewe and Blum, 1970; 1972; Crewe et al., 1972), these ketones have such a widespread distribution in the Myrmicinae that they appear to possess limited chemosystematic significance. On the other hand, the presence of genus-specific compounds may be regarded as a virtual character state possessing definite taxonomic value.

Thus, the presence of 4,6-dimethyl-4-octen-3-one in Manica species (Fales et al., 1972) provides strong biochemical support for the separation of this genus from Myrmica (Weber, 1947), the species of which lack this ketone (Crewe and Blum, 1970). The presence of o-aminoacetophenone in the mandibular gland secretion of Mycocepurus goeldii (Blum et al., 1973a) a compound which has not been detected in other attine genera (Crewe and Blum, 1972), is consistent with the conclusion that Mycocepurus has diverged from the mainstream of attine evolution (Weber, 1958). The other aromatic compound identified in these myrmicine secretions, p-xylene (Blum et al., 1973b),

Table 3 - Exocrine products identified in the mandibular gland secretions of myrmicine species*

| Species | Compound | Authority |
|---|---|---|
| *Crematogaster africana* | 2-Hexenal | Bevan *et al.*, 1961 |
| *Atta texana*; *Crematogaster jehovae* | 2-Heptanone | Moser *et al.*, 1968 |
| *Manica mutica* | 4-Methyl-3-hexanone | Fales *et al.*, 1972 |
| *Myrmica brevinodis* | 3-Octanone | Crewe and Blum, 1970 |
| *Crematogaster clariventris* | 3-Octanol | Crewe *et al.*, 1972 |
| *Pogonomyrmex barbarus* | 4-Methyl-3-heptanone | McGurk *et al.*, 1966 |
| *Trachymyrmex seminole* | 4-Methyl-3-heptanol | Crewe and Blum, 1972 |
| *Myrmica americana* | 3-Nonanone | Crewe and Blum, 1970 |
| *Crematogaster clara* | 6-Methyl-3-octanone | Crewe *et al.*, 1972 |
| *Myrmica scabrinodis* | 6-Methyl-3-octanol | Crewe and Blum, 1970 |
| *Manica bradleyi* | 3-Decanone | Fales *et al.*,1972 |
| *Manica hunteri* | 4, 6-Dimethyl-4-octen-3-one | Fales *et al.*, 1972 |
| *Messor semirufus* | *p*-Xylene | Blum *et al.*, 1973b |
| *Mycocepurus goeldii* | *o*-Aminoacetophenone | Blum *et al.*, 1973a |
| *Atta sexdens* | Citral (both isomers) | Butenandt *et al.*, 1959 |
| *Atta laevigata* | Citronellol | Blum *et al.*, 1968b |

*in workers

Table 4 - Exocrine products identified in the anal gland secretions of dolichoderine species*

| Species | Compound | Authority |
|---|---|---|
| Ketones | | |
| *Iridomyrmex pruinosus* | 2-Heptanone | Blum *et al.*, 1963 |
| *Dolichoderus clarki* | 4-Methyl-2-hexanone | Cavill and Hinterberger, 1960 |
| *Tapinoma nigerrimum* | 6-Methyl-5-hepten-2-one | Trave and Pavan, 1956 |
| *Tapinoma nigerrimum* | 2-Methyl-4-heptanone | Trave and Pavan, 1956 |
| Cyclopentanoid monoterpenes | | |
| *Iridomyrmex humilis* | Iridomyrmecin | Fusco *et al.*, 1955 |
| *Iridomyrmex conifer* | Isoiridomyrmecin | Cavill *et al.*, 1956 |
| *Iridomyrmex detectus* | Iridodial | Cavill and Ford, 1960 |
| *Dolichoderus anthoclinea* | Dolichodial | Cavill and Hinterberger, 1960 |
| *Iridomyrmex nitidus* | Isodihydronepetalactone | Cavill and Clark, 1967 |

* In workers

also appears to be a diagnostic natural product of species in the genus Messor.

Although myrmicines do not emphasize the biosynthesis of terpenoid constituents in their mandibular glands, the presence of monoterpenes in the secretions of Atta spp. (Butenandt et al., 1959; Blum et al., 1968) demonstrates that members of at least some genera possess the capacity to produce this class of compounds.

DOLICHODERINAE The anal glands, tissues essentially restricted in their distribution to species in the Dolichoderinae, have been the source of all the natural products identified in members of this subfamily (Table 4). With the apparent exception of 2-heptanone, all of these exocrine products are of terpenoid origin, and the cyclopentanoid monoterpenes (i.e. iridomyrmecin) are particularly characteristic dolichoderine compounds. Only four ketones have been detected among the anal gland products, and one of these compounds, 2-methyl-4-heptanone (Trave and Pavan, 1956), is known only as an insect natural product due to its occurrence in the secretions of Tapinoma species. Similarly, 4-methyl-2-hexanone has a very restricted distribution in the Dolichoderinae (Cavill and Hinterberger, 1960) and has not been isolated from the secretions of species in any other insect taxa.

One of the biochemical peculiarities of the anal glands is their well-developed ability to synthesize a variety of cyclopentanoid monoterpenes (Table 4). These compounds, which appear to be defensive products, are widely distributed among the dolichoderine genera, and indeed, may be common features of all genera in this subfamily. The presence of four different isomers of iridodial in species in three genera (McGurk et al., 1968) indicates that these compounds are not synthesized with complete enzymatic stereospecificity. However, the ability of these dolichoderines to produce a different predominant isomer of iridodial is suggestive of the presence of highly selective pathways in each species for the synthesis of these compounds.

FORMICINAE Formicine ants have proven to be the richest source of natural products in the Insecta. The secretions of both the Dufour's gland and mandibular glands are outstanding sources of unique exocrine products and it is almost certain that new compounds will be identified as additional formicine species are chemically characterized.

Poison gland products

Formic acid appears to be a ubiquitous product of the formicine poison gland. No additional volatile organic compounds have been identified in the formicine venoms since Wray (1670) distilled this compound from workers of Formica rufa. It is not uncommon for the venomous exudates of Formica species to consist of 60% aqueous formic

Table 5 - Exocrine products identified in the Dufour's gland secretions of formicine species*

| Species | Compound | Authority |
|---|---|---|
| *Formica fusca* | *n*-Decane | Bergström and Löfqvist, 1968 |
| *Lasius unbratus* | *n*-Undecane | Quilico *et al.*, 1957 |
| *Anoplolepis custodiens* | *n*-Dodecane | Schreuder and Brand, 1972 |
| *Acanthomyops claviger* | *n*-Tridecane | Regnier and Wilson, 1968 |
| *Lasius alienus* | *n*-Pentadecane | Bergström and Löfqvist, 1970 |
| *Lasius carniolicus* | 3-Methylundecane | Bergström and Löfqvist, 1970 |
| *Camponotus ligniperda* | 5-Methylundecane | Bergström and Löfqvist, 1972 |
| *Formica fusca* | Tridecene | Bergström and Löfqvist, 1970 |
| *Camponotus herculeanus* | 9-Tridecene | Bergström and Löfqvist, 1972 |
| *Formica sanguinea* | 1-Dodecanol | Bergström and Löfqvist, 1968 |
| *Lasius niger* | *n*-Decyl acetate | Bergström and Löfqvist, 1970 |
| *Formica subintegra* | *n*-Dodecyl acetate | Regnier and Wilson, 1971 |
| *Formica pergandei* | *n*-Tetradecyl acetate | Regnier and Wilson, 1971 |
| *Acanthomyops claviger* | 2-Tridecanone | Regnier and Wilson, 1968 |
| *Lasius alienus* | 2-Pentadecanone | Bergström and Löfqvist, 1970 |
| *Lasius flavus* | 4-Hydroxy-9-hexadecenolide | Bergström and Löfqvist, 1970 |
| *Polyergus rufescens* | Farnesene | Bergström and Löfqvist, 1968 |
| *Camponotus ligniperda* | Farnesyl acetate | Bergström and Löfqvist, 1972 |
| *Formica nigricans* | Geranylgeranyl acetate | Bergström and Löfqvist, 1973 |

*In workers

acid (Osman and Brander, 1961). Free amino acids and peptides have been identified in the venoms of F. polyctena (Osman & Brander, 1961) and Camponotus pennsylvanicus (Hermann and Blum, 1968).

Dufour's gland products

A great diversity of both hydrocarbons and oxygenated compounds are biosynthesized in the formicine Dufour's gland. Although it has not proven practical to list the large number of compounds that have been identified in these secretions, the substances designated in Table 5 are representative of those that have been reported to be present.

The Dufour's gland secretions of formicines are rich in straight-chain hydrocarbons, but in addition, they are enriched with alkenes and branched-chain alkanes (Table 5). Significantly, alcohols, ketones, and esters of the same chain length as the hydrocarbons are usually present. Thus these oxygenated compounds may be metabolically related to the hydrocarbons so that the diversity of compounds biosynthesized by the Dufour's gland may reflect the ability of this tissue to oxidize the host of alkanes present. Although many of these compounds clearly function as either alarm pheromones or defensive compounds, Bergström and Löfqvist (1971) have suggested that the Dufour's gland secretion may function as an alarm-defense-recognition system. The high-boiling oxygenated compounds, which are present as trace components, would serve as ideal "markers" that could identify a foreign individual when superimposed on its own species-specific odour.

Mandibular gland products

The mandibular glands of formicine ants in several genera constitute one of the richest sources of terpenes in the Insecta (Table 6). Species in the genus Lasius are particularly versatile terpenoid chemists, and mono-, sesqui-, and diterpenes have been identified among the products in their mandibular gland secretions. Several of these terpenes (i.e. perillen, dendrolasin) are only known as animal natural products because of their occurrence in these formicine species.

Species in certain formicine genera may constitute ideal candidates for studying both the syntheses and functions of caste-specific compounds. Thus, males in the genera Acanthomyops and Lasius generally produce monoterpene alcohols in their mandibular glands whereas workers of the same species often synthesize the corresponding aldehydes (Law et al., 1965), with certain compounds being common to both castes (Regnier and Wilson, 1968; 1969). In contrast, males of certain Camponotus species, biosynthesize novel aromatic compounds in their mandibular glands (Brand et al., 1973b; 1973c) whereas the workers of these species do not produce detectable volatile compounds in these exocrine structures. Since these compounds play an important role in priming females for flight (Hölldobler and Maschwitz, 1965), the identification of these compounds provides an excellent tool for studying the mating biology of these species.

Table 6 - Exocrine products identified in the mandibular gland secretions of formicine species*

| Species | Compound | Authority |
|---|---|---|
| *Lasius niger* | 1-Octanol | Bergström and Löfqvist, 1970 |
| *Camponotus nearcticus* (males) | 2, 4-Dimethyl-2-hexenoic acid | Brand *et al.*, 1973b |
| *Lasius umbratus* | Citronellol | Blum *et al.*, 1968a |
| *Acanthomyops claviger* | Citral (both isomers) | Chadha *et al.*, 1962 |
| *Acanthomyops claviger* | Citronellal | Chadha *et al.*, 1962 |
| *Lasius neoniger* | 2, 6-Dimethyl-5-hepten-1-al | Law *et al.*, 1965 |
| *Acanthomyops claviger* | 2, 6-Dimethyl-5-hepten-1-ol | Regnier and Wilson, 1968 |
| *Lasius fuliginosus* | Perillen | Bernardi *et al.*, 1967 |
| *Camponotus rasilis* (males) | Methyl anthranilate | Brand *et al.*, 1973b |
| *Camponotus nearcticus* (males) | Methyl 6-methylsalicylate | Brand *et al.*, 1973b |
| *Camponotus ligniperda* (males) | Mellein (3, 4-dihydro-8-hydroxy-3-methylisocoumarin) | Brand *et al.*, 1973c |
| *Camponotus herculeanus* (males) | 10-Methyldodecanoic acid | Brand *et al.*, 1973c |
| *Lasius fuliginosus* | Farnesal | Bernardi *et al.*, 1967 |
| *Lasius alienus* | 2, 3-Dihydrofarnesal | Bergström and Löfqvist, 1970 |
| *Lasius fuliginosus* | Dendrolasin | Quilico *et al.*, 1957 |
| *Lasius carniolicus* | Geranylgeranial | Bergström and Löfqvist, 1970 |
| *Lasius carniolicus* | Geranylcitronellal | Bergström and Löfqvist, 1970 |

*In workers unless indicated

Examination of other species in other formicine genera for caste-specific exocrine compounds promises to yield valuable information on the roles of pheromones as species isolation agents.

Conclusions

Among the social insects, ants would appear to constitute the pheromonal chemists par excellence. Many of the exocrine compounds derived from ants are unique natural products and are only known as animal natural products because of their synthesis by these insects. As a consequence, it is difficult to generalize about the natural product emphases of ants, especially since relatively few taxa have been chemically explored. Furthermore, when trace components of glandular secretions are identified, it becomes obvious that the exocrine compounds in a single gland can exhibit a remarkable diversity. The identification of 37 compounds in the Dufour's glands of two Camponotus species (Bergström and Löfqvist, 1972) clearly illustrates the chemical complexity that may characterize the blend of products biosynthesized in a single gland.

When it comes to the synthesis of hydrocarbons, ants may have no peers in the animal kingdom. At least 47 hydrocarbons have been identified in the Dufour's gland secretions of ants and it is likely that additional hydrocarbons will be characterized, especially in the case of those secretions that are utilized as species-isolation agents (Regnier et al., 1973). The great emphasis that ants place on hydrocarbons is illustrated by the fact that 37 of the 46 compounds identified in the Dufour's gland secretions of three Formica species (Bergström and Löfqvist, 1973) belong to this class of compound. Furthermore, it will not come as a surprise if many of the ketones and alcohols identified in these secretions are derived from the corresponding hydrocarbons.

The mandibular gland secretions of species in different subfamilies are sufficiently diverse to indicate some biosynthetic trends. The pyrazines and sulfides identified in ponerine species may indicate that the members of this primitive subfamily possess an extraordinary natural products potential which is not shared by more highly-developed species. On the other hand, the presence of 4-methyl-3-heptanone in Neoponera villosa (Duffield and Blum, 1973) demonstrates that ponerines share some compounds with species in other subfamilies. This ketone has also been identified in doryline, myrmicine, and pseudomyrmicine species and appears to be the most widespread alarm pheromone encountered in the Formicidae. This 3-alkanone is typical of myrmicine natural products and is one of seven ethyl ketones identified in species in this subfamily (Table 3). The occurrence of 2-heptanone in a few species (Moser et al., 1968; Crewe et al., 1972) demonstrates that myrmicines also have the capacity to synthesize methyl ketones in their mandibular glands.

The mandibular gland secretions of formicine ants are generally dominated by mono-, sesqui-, and diterpenes. However, species in the genus Formica appear to be singular in not producing any detectable volatiles in these glands. In the genera Acanthomyops and Lasius, males of several species possess some caste-specific monoterpenes which are not found in their workers (Law et al., 1965) and these compounds may play a role in the mating biologies of these species. On the other hand, males of certain Camponotus species produce several caste-specific aromatic compounds in their mandibular glands (Brand et al., 1973b; 1973c) and workers of the species lack detectable volatiles in these glands.

The anal glands of dolichoderines are also an excellent source of monoterpenes with the cyclopentanoid monoterpenes (i.e. iridomyrmecine, dolichodial) being particularly characteristic and appearing to function as effective defensive compounds. The alarm pheromones produced in these glands are typically methyl ketones although a 4-ketone has been identified in the secretion of a Tapinoma species (Trave and Pavan, 1956). However, one of the methyl ketones, 2-heptanone is not an isoprenoid, and it thus appears that the anal glands are not restricted to the biosynthesis of terpenoid natural products. Indeed, workers in one population of Conomyrma pyramicus, which produce 2-heptanone in their anal glands (Blum and Warter, 1966), also produce the monoterpene iridodial (McGurk et al., 1968).

It appears that the Dufour's gland secretions of species in the more primitive subfamilies consist entirely of hydrocarbons, some of which are sesquiterpenes. Hydrocarbons have been identified in the secretions of myrmiciines, ponerines, dorylines, myrmicines and formicines. However, it is only in the Formicinae that a variety of alcohols, ketones, lactones, and esters have been detected as concomitants of hydrocarbons in the Dufour's gland secretions. The only exception among the formicines is Anoplolepis custodiens, which synthesizes nothing but hydrocarbons in the Dufour's gland (Schreuder and Brand, 1972). The oxygenated compounds produced in the Dufour's gland of formicines are generally high-boiling substances which may play an important role as constituents of an alarm-defense-recognition system (Bergström and Löfqvist, 1971).

The venoms of species in most subfamilies appear to be proteinaceous and that of the myrmiciine Myrmecia gulosa is qualitatively similar to wasp venoms (Cavill et al., 1964). Fire ant venoms appear to be distinctive because they are dominated by 2, 6-dialkylpiperidines and peptides constitute minor components (MacConnell et al., 1971; Brand et al., 1972). In some cases trace constituents of myrmicine venoms are utilized as trail pheromones, and that of Atta texana has been identified as methyl 4-methylpyrrole-2-carboxylate (Tumlinson et al., 1971). The identification of an indolizine in the venom of Monomorium pharaonis (Ritter et al., 1973), further demonstrates the extraordinary diversity of nitrogenous compounds which are found in myrmicine venoms. Formicine venoms essentially consist of highly concentrated formic acid solutions which are ejected in admixture with the remarkable contents of the Dufour's gland. This double barrelled venomous exudate is a formidable defensive device which would appear to more than compensate for the loss of a functional sting in the members of this subfamily.

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