

COMPARATIVE STUDY OF MANDIBULAR GLAND SECRETIONS OF WORKERS OF PONERINE ANTS

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(Received October 19, 1998; accepted February 12, 1999)

Abstract—The chemical contents of the mandibular glands of workers of eight species of ponerine ants have been analyzed and quantified. In three species (*Ectatomma* sp. from Brazil, *Odontomachus bauri*, and *Pachycondyla striata*) the contents were essentially a mixture of alkylpyrazines only. Three species (*Odontoponera transversa*, *Pachycondyla indica*, and *Pachycondyla obscuricornis*) contained a mixture of alkylpyrazines and oxygenated compounds and some simple terpenes; and the remaining two (*Diacamma vagans* and a *Diacamma* sp. from India) had only oxygenated compounds present. The two *Diacamma* species were notable in containing a dioxaspiroundecane (a spiroketal), not hitherto found in ants. All the 33 known mandibular gland analyses of workers of ponerine ant species have been brought together in order to seek some pattern in the type of glandular contents. Although the majority (24 species) produce alkylpyrazines, there is no observable pattern on a tribe or genus level.

Key Words—Hymenoptera, Formicidae, Ponerinae, mandibular gland, exocrine secretion, chemical analysis, alkylpyrazines.

INTRODUCTION

The large subfamily Ponerinae of the family Formicidae is regarded as a relatively primitive group of ants. This subfamily contains some of the most interesting and curious ants. Colony size varies considerably from as few as nine indi-

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viduals in some, e.g., *Pachycondyla (Bothroponera) sublaevis* (Peeters, 1990) to more than 52,000 in some *Leptogenys* sp. (Maschwitz et al., 1989). Some species have true queens while others have gamergates (mated, laying workers) (Peeters and Crewe, 1986). Workers of some species forage singly, some foragers recruit single individuals through tandem running and some practice mass recruitment, as in *Leptogenys nitida* (Duncan and Crewe, 1994). *Ectatomma ruidum* is said to practice cleptobiosis by locating the trails of other ant species to find workers carrying prey (Perfecto and Vandermeer, 1993). At least two species show a kind of primitive form of army ant behavior. *Pachycondyla marginata* in Brazil relocates its nest frequently and undertakes mass raids on termites (Leal and Oliveira, 1995), and a *Leptogenys* sp. nr. *mutabilis* in Malaysia forms large monogynous colonies, has frequent migrations, and makes mass raids in which all foraging activities are carried out collectively (Maschwitz et al., 1989).

Ponerine ants also appear to be chemically diverse, judged by the species that have been examined so far, in the products of their exocrine secretions. Blum and Hermann (1978) made the same point when only five species had been investigated. For example, some species have been found to produce a mixture of alkylpyrazines in their mandibular glands, but some species have only pyrazines while others contain mixtures with oxygenated compounds. Other ponerines produce simple alcohols and ketones in their mandibular glands, as do many ants from other subfamilies, but there is no discernible pattern. Other ponerines produce thioethers, some simple aromatic compounds, and some long-chain acids and derivatives.

Pyrazines are not confined to the ponerines, or to ants only, but in other ant subfamilies, pyrazines have generally been found in the poison glands (Attygalle and Morgan, 1984). However, there are exceptions. Alkylpyrazines have been found in the mandibular glands of *Myrmecia gulosa* (Myrmeciinae) (Brophy and Nelson, 1985), of *Wasmannia auropunctata* (Howard et al., 1982) and *Aphaenogaster rudis* (Wheeler et al., 1982) (both Myrmicinae), of *Calomyrmex splendidus* (Brown and More, 1979) and *Notoncus ectatommoides* (Brophy et al., 1982) (both Formicinae), and of *Iridomyrmex humilis* (now *Linepithema humile*) (Cavill and Houghton, 1974), *I. purpureus* (Cavill et al., 1985), *I. nitidus*, *I. rufoniger*, and *Dolichoderus clarkii* (Brophy, 1989) (all Dolichoderinae).

Brophy (1989) has reviewed the occurrence of pyrazines in insects, but the chemistry of the mandibular glands of ponerine workers has not yet been collated. We have collected all the available information on the exocrine chemistry of ponerine species, and because it still gives a fragmentary picture, we have taken advantage of opportunities to analyze further species to add to this information. We present here the accumulated data on mandibular gland chemistry and the analysis of eight further species. For the structure and naming of alkylpyrazines, see Figure 1.

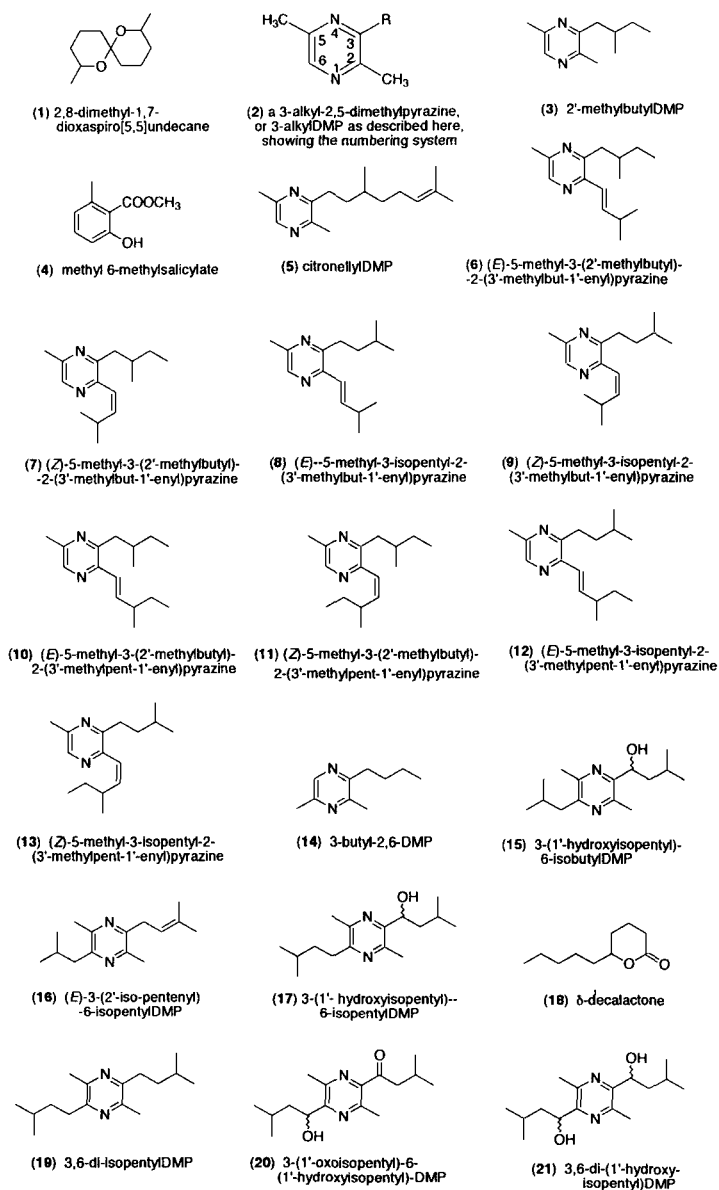


FIG. 1. Some of the substances found in the mandibular glands of ponerine ants, particularly the more complex pyrazines.

TABLE 1. LIST OF PONERINE SPECIES STUDIED WITH LOCATION OF THEIR COLLECTION

Tribe	Species, authority	Location, Country
Ectatommini	<i>Ectatomma</i> sp.	Maceió, AL, Brazil
Ponerini	<i>Diacamma vagans</i> (F. Smith, 1860)	Masinagudi, TN, India
	<i>Diacamma</i> sp.	Masinagudi, TN, India
	<i>Odontoponera transversa</i> F. Smith, 1857	Singapore
	<i>Pachycondyla indica</i> (Emery, 1899)	Bangalore, India
	<i>Pachycondyla obscuricornis</i> (Emery, 1890)	Viçosa, MG, Brazil
Odontomachini	<i>Pachycondyla striata</i> F. Smith, 1851	Viçosa, MG, Brazil
	<i>Odontomachus bauri</i> Emery, 1892	Maceió, AL, Brazil

AL = Alagoas, TN = Tamil Nadu, and MG = Minas Gerais

METHODS AND MATERIALS

For all species studied, foraging workers were collected (Table 1). The majority of the mandibular contents were determined from the analysis of whole heads, as the mandibular glands are the only source of low-molecular-mass volatile compounds. Where necessary, mandibular glands were isolated by carefully removing the exoskeleton of the cephalic capsule, starting from the posterior side. In this way the mandible with the attached gland remained intact. Either the head or dissected mandibles were sealed in thin-walled glass capillaries according to the solid-sampling technique (Morgan and Wadhams, 1972; Morgan, 1990).

Gas chromatography-mass spectrometry was carried out on a Hewlett Packard 5890 Gas Chromatograph and 5970 Mass Selective Detector quadrupole mass spectrometer with 70 eV ionization. Chromatography was carried out on a fused silica capillary column (12 m × 0.32 mm with a 0.3- μ m coating of polydimethylsiloxane; SGE, Milton Keynes, UK). Samples were heated in the injector to 150°C before crushing in a Keele solid-sample injector (Morgan, 1990). The oven was programmed from 30°C to 150°C at 8°C/min and then held isothermally. The carrier gas was helium at 1 ml/min.

Mass spectral identifications were confirmed wherever possible by comparison of retention times and mass spectra of synthetic standards. Where pure standards were not available, identification was based on comparison with spectra in our own collection and in computer libraries.

4-Methyl-4-hepten-3-one was prepared as described by Falk and Fry (1970), and 2,6-dimethyl-3-heptanol by the method of de Jong and Feringa (1991) and oxidized to the ketone with chromic acid.

TABLE 2. COMPOSITION OF MANDIBULAR GLANDS SECRETION OF *Diacamma vagans* AND *Diacamma* SPECIES WORKERS FROM INDIA ($N = 3$ EACH)

Component	Compound	Method of identification	Mean proportion (% \pm SD)	
			<i>D. vagans</i>	<i>D. sp.</i>
1	2-Heptanone	RT, MS	3.0 \pm 0.4	35.6 \pm 4.9
2	3,4-Dimethyl-2-heptanone	RT, MS	0.7 \pm 0.4	6.0 \pm 1.2
3	5-Methyl-2-heptanone	RT, MS	0.5 \pm 0.2	10.8 \pm 0.7
4	2-Octanone	MS	0.5 \pm 0.2	3.8 \pm 0.6
5	3-Methyl-2-octanone	RT, MS	0.5 \pm 0.1	1.3 \pm 0.2
6	2-Nonanone	MS	0.6 \pm 0.1	2.0 \pm 0.8
7	3-Methyl-2-nonanone	MS	16.0 \pm 4.4	6.6 \pm 0.5
8	(<i>E,E</i>)-2,8-Dimethyl-1,7-dioxaspiro[5,5]undecane	RT, MS	80.9 \pm 4.0	33.9 \pm 3.8
Mean total amount (ng)			89.0 \pm 21.2	63.6 \pm 10.8

RESULTS

Diacamma vagans and a *Diacamma sp.* Both species contained the same compounds, a mixture of ketones and a dioxaspiro-undecane (Table 2), in their mandibular glands, although in quite different proportions.

Ectatomma Species. The mandibular glands of the *Ectatomma* species, unidentified, possibly a new species, contained a mixture of seven pyrazines (Table 3). Two are of unknown structure but identical in mass spectra and of sim-

TABLE 3. COMPOSITION OF MANDIBULAR GLAND SECRETION OF *Ectatomma* SPECIES WORKERS FROM BRAZIL ($N = 10$)

Component	Compound	Method of identification	Mean proportion (% \pm SD)
1	2,5-Dimethyl-3-ethylpyrazine	RT, MS	1.0 \pm 1.7
2	2,5-Dimethyl-3-propylpyrazine	RT, MS	17.1 \pm 10.5
3	2,5-Dimethyl-3-isobutylpyrazine	RT, MS	2.6 \pm 2.3
4	2,5-Dimethyl-3-(2'-methylbutyl)pyrazine	RT, MS	56.5 \pm 14.4
5	2,5-Dimethyl-3-pentylpyrazine	RT, MS	19.8 \pm 9.8
6	Pyrazine of unknown structure with molecular formula $C_{16}H_{28}N_2O$	MS	1.6 \pm 5.6
7	Unknown structure with molecular formula $C_{16}H_{28}N_2O$	MS	1.4 \pm 4.3
Mean total amount (μ g)			1.03 \pm 0.90

TABLE 4. COMPOSITION OF MANDIBULAR GLAND SECRETION OF *Odontomachus bauri* WORKERS (*N* = 10)

Component	Compound	Method of identification	Mean proportion (% ± SD)
1	2,5-Dimethyl-3-ethylpyrazine	RT, MS	1.2 ± 2.9
2	2,5-Dimethyl-3-propylpyrazine	RT, MS	3.8 ± 3.1
3	2,5-Dimethyl-3-butylpyrazine	RT, MS	8.4 ± 15.9
4	2,5-Dimethyl-3-(2'-methylbutyl)pyrazine	MS	0.2 ± 0.4
5	2,5-Dimethyl-3-pentylpyrazine	RT, MS	73.9 ± 29.3
6	2,5-Dimethyl-3-hexylpyrazine	MS	7.9 ± 14.5
7	2,5-Dimethyl-3-(2'-methylhexyl)pyrazine	MS	0.2 ± 0.4
8	2,5-Dimethyl-3-heptylpyrazine	MS	4.7 ± 2.9
Mean total amount (μg)			1.62 ± 1.32

ilar relative retention to the two compounds with molecular formula $C_{16}H_{28}N_2O$ found by Tecle et al. (1987) in *Rhytidoponera metallica* from Australia.

Odontomachus bauri. Mandibular glands of workers of *Odontoponera bauri* contained a mixture of alkyl pyrazines, very similar to that of the *Ectatomma* species analyzed here, and as has been found in four other species of *Odontoponera* (see Table below). 2,5-Dimethyl-3-pentylpyrazine was by far the major component (Table 4).

Odontoponera transversa. Twenty individual glands of workers of *Odontoponera transversa* were analyzed. The secretion was found to consist of a mixture of oxygenated compounds and trisubstituted pyrazines (Table 5). The iso-

TABLE 5. COMPOSITION OF MANDIBULAR GLAND SECRETION OF *Odontoponera transversa* WORKERS (*N* = 20)

Component	Compound	Method of identification	Mean proportion (% ± SD)
1	4-Methyl-3-heptanone	RT, MS	29.4 ± 15.2
2	4-Methyl-3-heptanol	RT, MS	1.6 ± 1.6
3	2,6-Dimethyl-3-heptanone	RT, MS	1.0 ± 1.4
4	(<i>E</i>)-2-Isopropyl-5-methyl-2-hexenal	RT, MS	44.4 ± 19.1
5	(<i>Z</i>)-2-Isopropyl-5-methyl-2-hexenal	RT, MS	5.5 ± 3.7
6	2,5-Dimethyl-3-propylpyrazine	RT, MS	1.4 ± 1.0
7	2,5-Dimethyl-3-isobutylpyrazine	RT, MS	0.9 ± 0.9
8	2,5-Dimethyl-3-isopentylpyrazine	MS	0.4 ± 0.4
9	2,5-Dimethyl-3-pentylpyrazine	RT, MS	15.5 ± 4.1
Mean total amount (ng)			301.9 ± 262.1

TABLE 6. COMPOSITION OF MANDIBULAR GLAND SECRETION OF *Pachycondyla indica* WORKERS ($N = 2$)

Component	Compound	Method of identification	Mean proportion (%)
1	2,5-Dimethyl-3-ethylpyrazine	RT, MS	0.8 ^a
2	2,5-Dimethyl-3-isobutylpyrazine	RT, MS	0.3 ^a
3	2,5-Dimethyl-3-isopentyl-6(1'-hydroxyisopentyl)pyrazine	MS	1.3
4	Palmitoleic acid	RT, MS	1.2
5	Palmitic acid	RT, MS	10.6
6	Oleic acid	RT, MS	63.0
7	Stearic acid	RT, MS	22.5
8	Nonadecene	RT, MS	trace
9	Nonadecane	RT, MS	trace
Mean total amount (μg)			1.0

^aPresent in only one of the two specimens.

meric mixture of authentic isopropylhexenals used for confirmation of structure of components 4 and 5 were supplied by R. Lucas. These two components had earlier been found in trace quantities in the mandibular glands of *Dinoponera australis* (Oldham et al., 1994).

Pachycondyla species. Three species of *Pachycondyla* (*P. indica*, *P. obscuricornis*, and *P. striata*) have been added to the one species (*P. apicalis*) from Mexico already examined (Cruz López and Morgan, 1997). *P. indica* contained only traces of pyrazines and chiefly long-chain fatty acids (Table 6), while *P. obscuricornis* contained very volatile pyrazines (Table 7), and *P. striata* contained a complex mixture of 18 pyrazines (Table 8).

TABLE 7. COMPOSITION OF MANDIBULAR GLAND SECRETION OF *Pachycondyla obscuricornis* WORKERS ($N = 5$)

Component	Compound	Method of identification	Mean proportion (% \pm SD)
1	Benzaldehyde	RT, MS	2.2 \pm 1.6
2	2,5-Dimethylpyrazine	RT, MS	76.9 \pm 13.7
3	Limonene	RT, MS	3.0 \pm 3.6
4	Trimethylpyrazine	RT, MS	11.3 \pm 13.0
5	2,5-Dimethyl-3-ethylpyrazine	RT, MS	5.0 \pm 1.3
6	Indole	RT, MS	2.1 \pm 3.4
Mean total amount (ng)			48.4 \pm 34.8

TABLE 8. COMPOSITION OF MANDIBULAR GLAND SECRETION OF *Pachycondyla striata* WORKERS (N = 5)

Component	Compound	Method of identification	Mean proportion (% \pm SD)
1	2,5-Dimethyl-3-ethylpyrazine	RT, MS	1.8 \pm 0.9
2	2,5-Dimethyl-3-propylpyrazine	RT, MS	1.7 \pm 0.4
3	2,5-Dimethyl-3-isobutylpyrazine	RT, MS	2.6 \pm 1.9
4	2,5-Dimethyl-3-butylpyrazine	RT, MS	5.3 \pm 1.5
5	2,6-Dimethyl-3-butylpyrazine	RT, MS	3.5 \pm 0.7
6	2,5-Dimethyl-3-isopentylpyrazine	RT, MS	38.7 \pm 4.3
7	2,5-Dimethyl-3-pentylpyrazine	RT, MS	9.0 \pm 1.5
8	2,5-Dimethyl-3-isohexylpyrazine	MS	18.2 \pm 4.9
9	2,5-Dimethyl-3-hexylpyrazine	MS	3.6 \pm 0.8
10	2,5-Dimethyl-3-isoheptylpyrazine	MS	0.9 \pm 0.4
11	2,5-Dimethyl-3-heptylpyrazine	MS	2.5 \pm 0.4
12	2,5-Dimethyl-3-iso-octylpyrazine	MS	0.4 \pm 0.2
13	2,5-Dimethyl-3-octylpyrazine	MS	2.4 \pm 0.3
14	2,5-Dimethyl-3-isobutyl-6-(1'-hydroxypropyl)pyrazine	MS	0.4 \pm 0.2
15	2,5-Dimethyl-3-isopentyl-6-(1'-hydroxypropyl)pyrazine	MS	0.3 \pm 0.1
16	2,5-Dimethyl-3-isopentyl-6-(1'-hydroxybutyl)pyrazine	MS	0.6 \pm 0.2
17	2,5-Dimethyl-3-isopentyl-6-(1'-hydroxyisobutyl)pyrazine	MS	0.5 \pm 0.2
18	2,5-Dimethyl-3-isopentyl-6-(1'-hydroxyisopentyl)pyrazine	MS	2.4 \pm 1.1
19	Octadecane	RT, MS	0.2 \pm 0.1
20	Nonadecene	MS	1.8 \pm 0.3
21	Nonadecane	RT, MS	1.0 \pm 0.5
Mean total amount (ng)			1.8 \pm 0.6

DISCUSSION

Diacamma is one of the ponerine genera that produce no true queens but the dominant reproductive individual is called a gamergate (Peeters and Crewe, 1986). It was interesting to find the principal compound in one species and one of the principal compounds in the other was a dioxaspiroundecane (structure 1, Figure 1). This type of spiroketal has not been found before in ants, although it is common in the mandibular secretion of andrenid bees and polistine wasps. Both species contained the same mixture of simple ketones (Table 1).

Ectatomma is one of nine genera of the tribe Ectatommini, containing four

known species (*planidens*, *quadridens*, *ruidum*, and *tuberculatum*), all found in the Neotropics. The one collected here did not belong to these species. Besides the known alkylpyrazines, it contained two compounds identical in mass spectra and, as far as could be estimated, the same relative GC retention as two compounds found in an Australian species of *Rhytidoponera* (Teclé et al., 1987). Pratt (1990) reported that *E. ruidum* practices mass recruitment, and the mandibular gland contained an alarm pheromone.

Odontoponera transversa, the only species in this genus, is found throughout the Indo-Malayan region. Nothing has been reported of its behavior. Its mandibular glands contain three dominant alkylpyrazines, found in many other species.

Odontomachus, with over 100 species scattered throughout the tropics, are easily recognized by their specialized snapping mandibles. They are thought to navigate largely by visual clues (Oliveira and Hölldobler, 1989). Four species of *Odontomachus* have already been examined; they all, like *O. bauri*, contain a mixture of alkylpyrazines. The Odontomachini, with only six species examined, is the only tribe showing some uniformity, with only alkylpyrazines found in their mandibular glands.

Three species of *Pachycondyla*, all collected in India, were examined. They showed no great similarity in their mandibular gland chemistry. *P. indica* is the only ponerine species as yet known to have long-chain fatty acids in the gland. *P. obscuricornis* is unusual in having the very volatile dimethyl and trimethyl pyrazines, which do not seem to occur in any of the other pyrazine-dominated species. It has been recorded as one of the species that practices recruitment by tandem running (Hölldobler and Traniello, 1980). *P. striata* mandibular glands display the most complex mixture of pyrazines yet discovered and include a small quantity of alkanes.

There are 11 tribes of Ponerinae divided into 54 living genera. The contents of the mandibular glands of 33 species have now been examined (Table 9), but only three of these tribes and 17 genera are represented in the table. Yet a pattern might have been expected from that number. Of these 33 species, 20 contain only alkylpyrazines in their glands. A further four species contain some oxygenated compounds in addition to the pyrazines, while seven species contain volatile oxygenated compounds and two species (a *Megaponera* and a *Paltothyreus*, both from the Ponerini) contain sulfides and polysulfides. Of the six species from the Odontomachini, all produce alkylpyrazines. The structures of some of the more complex pyrazines are included in Figure 1.

The biosynthesis of pyrazines in insects has not been studied, but it is very likely that 2,5-dimethyl-3-alkylpyrazines are produced from the amino acid threonine, via a dimethyldihydropyrazine, which is condensed with an aldehyde to give a dimethylalkylpyrazine (Morgan, 1984). It is interesting to find that both citronellal and citronellyl DMP (5) are found together in *Rhytidoponera acicu-*

TABLE 9. CHEMICALS FROM MANDIBULAR GLANDS OF PONERINE ANTS

Tribe, genus, species	Chemicals ^a	Reference
Ectatommini <i>Ectatomma</i> sp.	Ethyl DMP, propyl DMP, isobutyl DMP, 2'-methylbutyl DMP (3), pentyl DMP, two pyrazines of unknown structure with molecular formula C ₁₆ H ₂₈ N ₂ O	This work
<i>Gnamptogenus pleurodon</i>	Methyl 6-methylsalicylate (4)	Duffield and Blum (1975)
<i>Rhytidoponera aciculata</i>	Citronellal, citronellic acid, citronellol, isopentyl DMP, citronellyl DMP (5)	Brophy et al. (1983)
<i>Rhytidoponera chalybaea</i> ^b	Isopentyl DMP	Brophy et al. (1981)
<i>Rhytidoponera metallica</i>	2-Methylbutyl DMP, isopentyl DMP, (<i>E</i>)- and (<i>Z</i>)-5-methyl-3-(2'-methylbutyl)-2-(3'-methylbut-1'-enyl)pyrazine, (6), (7) (<i>E</i>)- and (<i>Z</i>)-5-methyl-3-isopentyl-2-(3'-methylbut-1'-enyl)pyrazine, (8), (9) (<i>E</i>)- and (<i>Z</i>)-5-methyl-3-(2'-methylbutyl)-2-(3'-methylbut-1'-enyl)pyrazine, (10), (11) (<i>E</i>)- and (<i>Z</i>)-5-methyl-3-isopentyl-2-(3'-methylbut-1'-enyl)pyrazine, (12), (13) two pyrazines of unknown structure with molecular formula C ₁₆ H ₂₈ N ₂ O	Teclé et al. (1987)
<i>Rhytidoponera victorica</i>	Isobutyl DMP, 2-methylbutyl DMP (3), isopentyl DMP, two pyrazines of unknown structure with molecular formula C ₁₆ H ₂₈ N ₂ O	Brophy (1989)
Ponerini	3-Butyl-2,6-DMP (14), 3-pentyl-2,6-DMP	Longhurst et al. (1978)
<i>Brachyponera sennaarensis</i>	3-Methyl-2-nonanone, (<i>E,E</i>)-2,8-dimethyl-1,7-dioxaspiro[5,5]undecane (1)	This work
<i>Diacamma vagans</i>	2-Heptanone, 3,4-dimethyl-2-heptanone, 5-methyl-2-heptanone, 2-octanone, 3-methyl-2-octanone, 2-nonanone, 3-methyl-2-nonanone, (<i>E</i> , <i>E</i>)-2,8-dimethyl-1,7-dioxaspiro[5,5]undecane (1)	This work
<i>Dinoponera australis</i>	Isobutyl DMP, 2-methylbutyl DMP (3), isopentyl DMP, 3-(1'-hydroxyisopentyl)-2,5-dimethyl-6-isobutylpyrazine (15), (<i>E</i>)-2,5-dimethyl-3-(2'-isopentyl)-6-isopentylpyrazine (16), 3-(1'-hydroxyisopentyl)-2,5-dimethyl-6-isopentylpyrazine (17), and other minor products	Oldham et al. (1994)

<i>Dinoponera grandis</i>	Propyl DMP, isopentyl DMP	Hermann et al. (1984)
<i>Euponera</i> sp.	Isopentyl DMP	Brophy (1989)
<i>Harpegnathos saltator</i>	Isopentanol, 4-methyl-3-heptanone, 4-methyl-3-heptanol, 4-methyl-4-hepten-3-one, isobutyl 3-methylpentanoate	do Nascimento et al. (1993)
<i>Hypoponera opacior</i>	Isopentyl DMP	Duffield et al. (1976)
<i>Megaponera foetens</i>	Dimethyldisulfide, dimethyltrisulfide, benzyl methyl sulfide, ethyl methyl disulfide	Longhurst et al. (1979)
<i>Odontoponera trans-versa</i>	4-Methyl-3-heptanone, 4-methyl-3-heptanol, 2,6-dimethyl-3-heptanone, (<i>E</i>)-2-isopropyl-5-methyl-2-hexenal, (<i>Z</i>)-2-isopropyl-5-methyl-2-hexenal, propyl DMP, pentyl DMP	This work
<i>Pachycondyla apicalis</i>	Benzaldehyde, δ -decalactone (18)	Cruz López and Morgan (1997)
<i>Pachycondylae castanea</i>	Isopentyl DMP, 6-isopentenyl-3-isopentyl DMP (three isomers), 3,6-di-isopentyl DMP 3-(1'-hydroxyisopentyl)-6-isopentyl DMP, 3-(1'-oxoisopentyl)-6-(1'-hydroxyisopentyl)-DMP, 3,6-di-(1'-hydroxyisopentyl)DMP (two isomers, <i>meso</i> and <i>erythro</i> forms)	Fales et al. (1984, 1988)
<i>Pachycondylae castaneicolor</i>	Isopentyl DMP, (like <i>P. castanea</i> , but no details given)	This work
<i>Pachycondyla indica</i>	Palmitic acid, stearic acid, oleic acid	This work
<i>Pachycondyla obscuricornis</i>	Benzaldehyde, DMP, limonene, trimethylpyrazine, ethyl DMP, indole	This work
<i>Pachycondyla soror^d</i>	(Unidentified), 2-undecanone, (a methyl ester), 2-undecanol, 2-undecenol (two isomers), 2-dodecanol, methyl 5-methylsalicylate, 2-tridecanol, methyl 6-methylsalicylate	Longhurst et al. (1980)

TABLE 9. CONTINUED

Tribe, genus, species	Chemicals ^a	Reference
<i>Pachycondyla striata</i>	Ethyl DMP, propyl DMP, butyl DMP, butyl-2,6-DMP, isobutyl DMP, pentyl DMP, isopentyl DMP, hexyl DMP, isohexyl DMP, heptyl DMP, octyl DMP, 3-(1'-hydroxyisopentyl)-2,5-dimethyl-6-isopentylpyrazine, nonadecene, nonadecane	This work
<i>Pachycondyla villosa</i> ^c	4-Methyl-3-heptanone, 4-methyl-3-heptanol	Duffield and Blum (1973)
<i>Paltothyreus tarsatus</i>	Dimethyldisulphide, dimethyltrisulphide	Casnati et al. (1967), Crewe and Fletcher (1974)
<i>Ponera pennsylvanica</i>	Isopentyl DMP	Duffield et al. (1976)
<i>Sirebognathus aethiopicus</i>	Butyl DMP, pentyl DMP, hexyl DMP	Jones et al. (1998)
<i>Odontomachini</i>		
<i>Anochetus sedilloti</i>	3-s-Butyl-2,6-DMP	Longhurst et al. (1978)
<i>Odontomachus bauri</i>	Ethyl DMP, propyl DMP, butyl DMP, pentyl DMP, hexyl DMP, heptyl DMP	This work
<i>Odontomachus brunneus</i>	Ethyl DMP, propyl DMP, butyl DMP, pentyl DMP	Wheeler and Blum (1973)
<i>Odontomachus clarus</i>	Isopentyl DMP	Wheeler and Blum (1973)
<i>Odontomachus hastatus</i>	Isopentyl DMP	Wheeler and Blum (1973)
<i>Odontomachus troglodytes</i>	3-Butyl-2,6-DMP, 3-pentyl-2,6-DMP	Longhurst et al. (1978)

^aDMP: dimethyl pyrazine. Unless otherwise stated, the substitution is 3-(substituent)-2,5-dimethylpyrazine.

^bOriginally called *R. metallica* but corrected to *R. chalybaea* by Brophy et al. (1983).

^c*Pachycondyla* (= *Mesoponera*).

^d*Pachycondyla* (= *Bothroponera*).

^e*Pachycondyla* (= *Neoponera*).

lata (Brophy et al., 1983). Tetrasubstituted alkylpyrazines, found so far only in *Dinoponera australis* and three species of *Pachycondyla*—*P. castanea*, *P. castaneicolor*, and *P. striata* (Table 9)—are probably derived from the trisubstituted pyrazines by further alkylation (Oldham and Morgan, 1993). 2,6-Dimethyl-3-alkylpyrazines have been identified too many times for them to be misidentifications; they appear in four species of two tribes in Table 9. There seems to be no clear relation between the biosynthetic origin of the oxygenated compounds and the alkyl groups of the pyrazines except in the special cases of *Rhytidoponera aciculata* (above) and some minor products of *Dinoponera australis* (Oldham and Morgan, 1993). The oxygenated compounds found here are derived from acetate and propionate via acetogenin methods. 4-Methyl-3-heptanone and 4-methyl-3-heptanol, compounds common in other ant mandibular glands, appear in three species in the Ponerini but a variety of 2-alkanones are found in other ponerines.

For the great majority of these volatile secretions, we have no information about their communicative function. In early reports and more recently that by Pratt (1990), the mandibular glands of ponerines are said to be the source of alarm pheromones. In the one example we examined carefully, *Dinoponera australis*, we found no evidence of alarm generated by the alkylpyrazines of the mandibular glands (Oldham et al., 1994). From observations of behavior, we suspect this species uses the secretion to mark the area near the nest entrance, but we have no firm evidence.

Acknowledgments—We thank R. Lucas of Quest International for supplying isopropylhexenals and a number of alkylpyrazines.

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