Journal of Chemical Ecology, Vol. 13, No. 8, 1987

NOVEL PYRAZINES FROM THE HEAD OF AUSTRALIAN PONERINE ANT *Rhytidoponera metallica*

BERHANE TECLE,[1] CHANG-MING SUN, JOSEPH J. BROPHY, and ROBERT F. TOIA

Department of Organic Chemistry
University of New South Wales
P.O. Box 1, Kensington
New South Wales 2033, Australia

(Received August 11, 1986; accepted October 27, 1986)

Abstract—The novel pyrazines, (*E*)- and (*Z*)-5-methyl-3-(2-methylbutyl)-2-(3-methylbut-1-enyl)pyrazine, (*E*)- and (*Z*)-5-methyl-3-isopentyl-2-(3-methylbut-1-enyl)pyrazine, (*E*)- and (*Z*)-5-methyl-3-(2-methylbutyl)-2-(3-methylpent-1-enyl)pyrazine, (*E*)- and (*Z*)-5-methyl-3-isopentyl-2-(3-methylpent-1-enyl)pyrazine, together with the known pyrazines, 2,5-dimethyl-3-(2-methylbutyl)pyrazine and 2,5-dimethyl-3-isopentylpyrazine, have been identified from the head of the Australian ponerine ant *Rhytidoponera metallica*. Alkanes and alkenes, in small amounts, were also detected.

Key Words—Ant, *Rhytidoponera metallica*, pyrazine, GC-MS, Hymenoptera, Formicidae, ponerine.

INTRODUCTION

Chemical investigations on ants of the subfamily Ponerinae (Formicidae) have been notable for the fact that pyrazines have been detected in the heads of the majority of species from various genera to date examined, e.g., *Anochetus*, *Odontomachus*, *Ponera*, *Hypoponera*, *Rhytidoponera*, *Brachyponera*, *Mesoponera*, and *Dinoponera* (Attygale and Morgan, 1984; Fales et al., 1984; Herman et al., 1984). In most of the species that did not contain pyrazines, sulfides have been detected (Casnati et al., 1967; Crew and Fletcher, 1974; Longhurst et al., 1979, 1980). Although pyrazines have been detected in other subfamilies of the Formicidae (Dolichoderinae, Myrmicinae, Myrmeciinae, and Formi-

---

[1] Present address: Pesticide Chemistry and Toxicology Laboratory, 210 Wellman Hall, University of California, Berkeley, California 94720.

cinae) (Attygale and Morgan, 1984; Brophy and Nelson, 1985), their occurrence is less common than in the Ponerinae.

Where activity tests have been carried out on the cephalic secretions (not only on the Ponerinae), alarm responses have been noted (Wheeler and Blum, 1973; Longhurst et al., 1978; Duffield et al., 1976; Howard et al., 1982; Brown and Moore, 1979). It is also of interest to note that an alarm pheromone is produced in the heads of doryline ants of the genera *Eciton*, *Nomamyrmex*, and *Labidus* and that in the case of *Eciton* and *Nomamyrmex*, the crushed worker heads emit a ''meaty odor'' assumed to be associated with the alarm substance (Brown, 1960). This observation is suggestive of the presence of pyrazines.

Ponerine ants of the genus *Rhytidoponera* have, to date, received relatively little attention. Two Australian species, *R. chalybaea* (at the time identified as *R. metallica*) (Brophy et al., 1981, 1984) and *R. aciculata* (Brophy et al., 1983), have been examined and both yielded 2,5-dimethyl-3-isopentylpyrazine (2) (the pyrazine most commonly detected in insects) and *R. chalybaea* also yielded 2,5-dimethyl-3-citronellylpyrazine. In each case the pyrazine(s) were isolated from the heads of the ants.

Study of *R. metallica* has been limited to an examination of the contents of its pygidial gland, which was shown to contain isogeraniol, *m*-hydroxybenzaldehyde, heptadecene, and heptadecadiene (Meinwald and Wiemer, 1983). We report here results of our investigations on secretions obtained from the heads of *R. metallica*.

METHODS AND MATERIALS

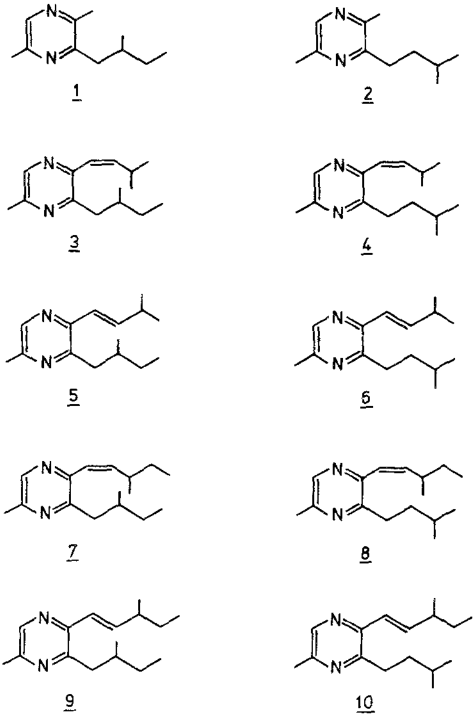
Identification of Ants. The ants used in this investigation were identified as *Rhytidoponera metallica* by Dr. R.F. Crozier, School of Zoology, University of New South Wales. Samples of the ants have been lodged with the Australian National Insect Collection, Canberra.

Extraction of R. metallica. The ants, which are approx. 8 mm in length and weighed approx. 5 mg, were collected in Centennial Park, Randwick, New South Wales. The heads of approx. 700 ants were removed and, after grinding with sodium sulfate, were extracted with dichloromethane (150 ml) in a Soxhlet apparatus for 10 hr. The extract was washed with sodium bicarbonate solution (2 × 20 ml) and water (2 × 20 ml) and dried over magnesium sulfate. Removal of the solvent yielded a pale yellow oil (51 mg) which was examined by combined gas chromatography–mass spectrometry (GC-MS).

Hydrogenation of Extract of R. metallica. A portion of the above extract of (20 mg) in ethanol (5 ml) was hydrogenated over Adams catalyst at room temperature and atmospheric pressure for 2 hr. Filtration through magnesium sulfate and removal of the ethanol gave a light yellow oil which was examined as above.

General Method for Synthesizing Alkenyl Pyrazines. The method generally follows that outlined by Wheeler et al. (1981). 2,5-Dimethyl-3-isopentylpyrazine and 2,5-dimethyl-3-(2-methylbutyl)pyrazine were prepared as previously described (Klein and Spoerri, 1951) in 19% and 10% yields, respectively by treatment of 2,5-dimethylpyrazine (Aldrich) with the appropriate alkyl lithium in petroleum ether (bp 40–60°C). The dimethylalkyl pyrazines (0.5 g, 0.03 mmol) so obtained were subsequently acylated with the desired ethyl ester at −78°C using lithium diisopropylamide as base, in 40–50% yields. Reduction of the pyrazyl ketones (0.1 g, 0.004 mmol) so formed with sodium borohydride in methanol at 40–50°C yielded the corresponding alcohols in 80–90% yields. The alcohols (0.08 g, 0.003 mmol) were treated with *p*-toluenesulfonyl chloride in the conventional manner to yield the tosyl esters which, without isolation, were refluxed in pyridine (15 hr) to yield the alkenyl pyrazines (70–80%) as pale yellow oils. In each case GC-MS examination of the synthetic pyrazines indicated that the ratio of *E* isomer to *Z* isomer was approx. 9 : 1.

E-5-Methyl-3-(2-methylbutyl)-2-(3-methylbut-1-enyl)pyrazine (5, Scheme 1): found 233.2031 (MH$^+$); calc. for $C_{15}H_{25}N_2$, 233.2067. [^{1}H]NMR (60 MHz) δ 0.78(d, J = 6 Hz, 3H); 1.02(d, J = 6 Hz, 6H); 1.10(t, J = 7 Hz, 3H); 1.2-



SCHEME 1.

1.8(m, 3H); 2.2(m, 1H); 2.41(s, 3H); 2.62(d, $J = 8$ Hz, 2H); 6.49(d, $J = 15$ Hz, 1H); 6.86(m, 1H); 8.18(s, 1H).

E-5-Methyl-3-isopentyl-2-(3-methylbut-1-enyl)pyrazine (6): found 233.2031 (MH^+); calc. for $C_{15}H_{25}N_2$, 233.2067. [^{1}H]NMR (60 MHz) δ 0.90(d, $J = 6$ Hz, 6H); 1.05(d, $J = 7$ Hz, 6H); 1.30–1.80(m, 3H); 2.35(m, 1H); 2.45(s, 3H); 2.78(m, 2H); 6.46(d, $J = 16$ Hz, 1H); 6.86(m, 1H); 8.16(s, 1H).

E-5-Methyl-3-(2-methylbutyl)-2-(3-methylpent-1-enyl)pyrazine (9): found 247.2179 (MH^+); calc. for $C_{16}H_{27}N_2$, 247.2174. [^{1}H]NMR (300 MHz) δ 0.86(d, $J = 6$ Hz, 3H); 0.91 (t, $J = 7$ Hz, 6H); 1.11 (d, $J = 7$ Hz, 3H); 1.19–1.48(m, 5H); 2.17–2.35(m, 1H); 2.49(s, 3H); 2.56–2.65(m, 1H); 2.82–2.90(m, 1H); 6.57(d, $J = 16$ Hz, 1H); 6.74(dd, $J = 16, 8$ Hz, 1H); 8.20(S, 1H).

E-5-Methyl-3-isopentyl-2-(3-methylpent-1-enyl)pyrazine (10): found 247.2155 (MH^+); calc. for $C_{16}H_{27}N_2$, 247.2174. [^{1}H]NMR (300 MHz) δ 0.91(t, $J = 7$ Hz, 3H); 0.96(d, $J = 6$ Hz, 6H); 1.11(d, $J = 6$ Hz, 3H); 1.40–1.59 (m, 4H); 1.62–1.70(m, 1H); 2.16–2.33(m, 1H); 2.48(s, 3H); 2.73–2.84(m, 2H); 6.54(d, $J = 15$ Hz, 1H); 6.73(dd, $J = 15, 8$ Hz, 1H); 8.19(s, 1H).

Hydrogenation of the synthetic pyrazines was carried out in the same manner as for the ant extract.

Interconversion of the synthetic *E* and *Z* isomers was achieved by irradiation of a deoxygenated dilute solution of the *E* pyrazine in pentane for 5 min at 300 nm.

Spectroscopy and Gas Chromatography. Mass spectra were obtained on an AEI MS12 mass spectrometer coupled to a Shimadzu GC6 AMP gas chromatograph. Separations were effected on SCOT columns, either (a) OV-1 (30 m × 0.5 mm) programmed from 90°C to 250°C at 5°C/min or (b) FFAP (85 m × 0.5 mm) programmed from 80°C to 225°C at 5°C/min, with helium as carrier gas. The mass spectrometer was operated at 8000 V and 70 eV ionizing voltage. Spectra were acquired and processed by a VG Digispec Display data system. Accurate mass measurements were obtained on an AEI MS902 mass spectrometer under chemical ionization conditions (isobutane reagent gas) using a chart timing method (Brophy et al., 1979). [^{1}H]NMR spectra were recorded in $CDCl_3$ solution on either a Varian EM 360 (60 MHz) or a Bruker CXP 300 (300 MHz) spectrometer.

RESULTS AND DISCUSSION

A GLC trace of the total extract of the heads of *R. metallica* is shown in Figure 1 and the assignments are given in Table 1. A chemical ionization mass spectrum of this crude extract was run using isobutane as reagent gas under conditions where all hydrocarbons fail to be protonated. This spectrum demonstrated the presence of components with molecular weights of 178, 232, 246, 264, and 278 and subsequent high-resolution mass spectrometry indicated that

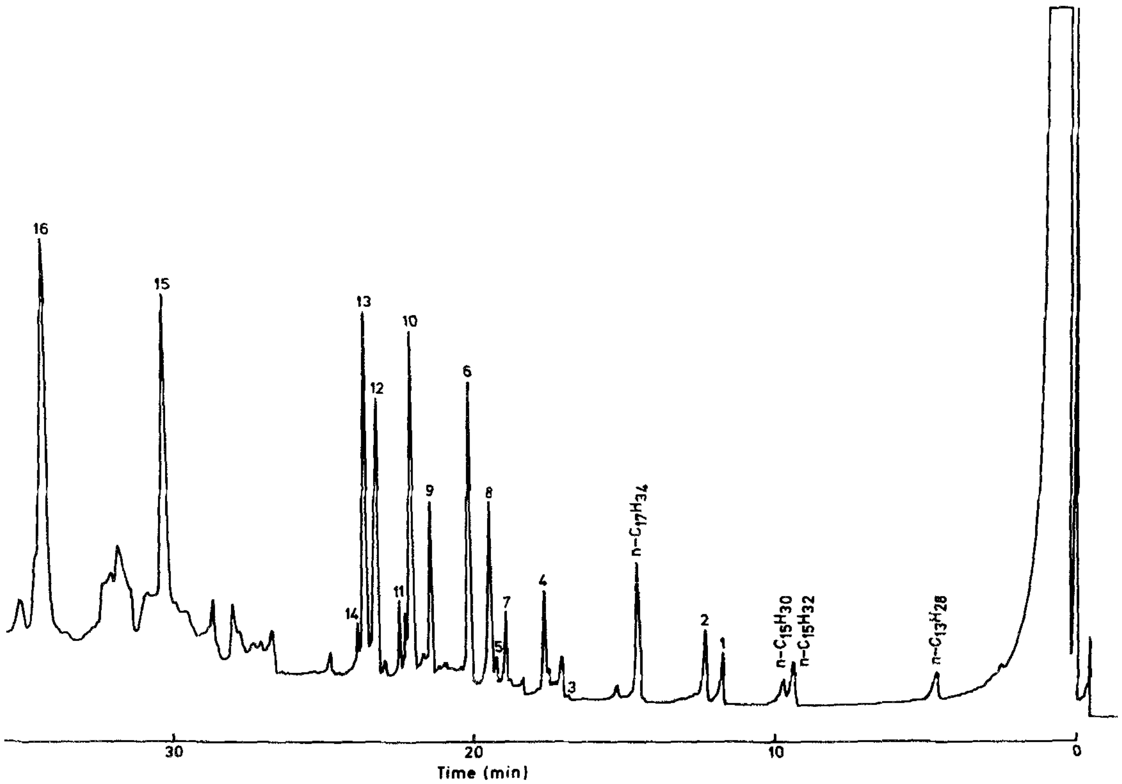


FIG. 1. GLC trace of the volatile extractives from the head of *Rhytidoponera metallica* run on FFAP, programmed from 80°C to 225°C at 5°C/min.

TABLE 1. COMPOUNDS IDENTIFIED IN HEAD OF *Rhytidoponera metallica*

Number	Compound
1	2,5-Dimethyl-3-(2-methylbutyl)pyrazine
2	2,5-Dimethyl-3-isopentylpyrazine
3	Z-5-Methyl-3-(2-methylbutyl)-2-(3-methylbut-1-enyl)pyrazine
4	Z-5-Methyl-3-isopentyl-2-(3-methylbut-1-enyl)pyrazine
5	E-5-Methyl-3-(2-methylbutyl)-2-(3-methylbut-1-enyl)pyrazine
6	E-5-Methyl-3-isopentyl-2-(3-methylbut-1-enyl)pyrazine
7	Z-5-Methyl-3-(2-methylbutyl)-2-(3-methylpent-1-enyl)pyrazine
8	Z-5-Methyl-3-isopentyl-2-(3-methylpent-1-enyl)pyrazine
9	E-5-Methyl-3-(2-methylbutyl)-2-(3-methylpent-1-enyl)pyrazine
10	E-5-Methyl-3-isopentyl-2-(3-methylpent-1-enyl)pyrazine
11	Unknown, suspected mol wt 264
12	$C_{16}H_{28}N_2O$
13	$C_{16}H_{28}N_2O$
14	Unknown, suspected mol wt 264
15	Diisobutyl phthalate
16	Dibutyl phthalate

the formulas for these ions were m/z 178, $C_{11}H_{18}N_2$; m/z 232, $C_{15}H_{24}N_2$; m/z 246, $C_{16}H_{26}N_2$; m/z 264, $C_{16}H_{28}N_2O$; and m/z 278, $C_{16}H_{22}O_4$, respectively. Subsequent GC-MS analysis of the extract under electron inpact (EI) conditions indicated that there were two compounds of mol wt 178, four compounds of mol wt 232, and four compounds of mol wt 246. In addition, at least two compounds which did not show molecular ions but whose molecular weight was assumed to be 264 were present, as well as two phthalate esters which were assumed to be butyl phthalates.

Hydrogenation of the crude extract led to a more simple GLC pattern (Figure 2, Table 2). Whereas the compounds of mol wt 178 remained unaltered, two peaks whose mass spectra showed mol wt 234 appeared at the expense of the four isomers of mol wt 232. Similarily, two new peaks whose mass spectra showed mol wt 248 appeared at the expense of the four of mol wt 246. The peaks suspected to be of mol wt 264 remained unchanged, as did those for the phthalate esters.

The mass spectra of peaks (a) and (b) of mol wt 234 in the hydrogenation mixture (see Table 3) indicated that the compounds were probably trisubstituted pyrazines with side chains of one, five, and five carbon atoms, while the peaks (c) and (d) of mol wt 248 appeared to be trisubstituted pyrazines with side chains of one, five, and six carbon atoms. The orientation of these groups in the two sets of hydrogenated pyrazines was not known.

The two pyrazines (1) and (2) of mol wt 178 were identified as 2,5-di-

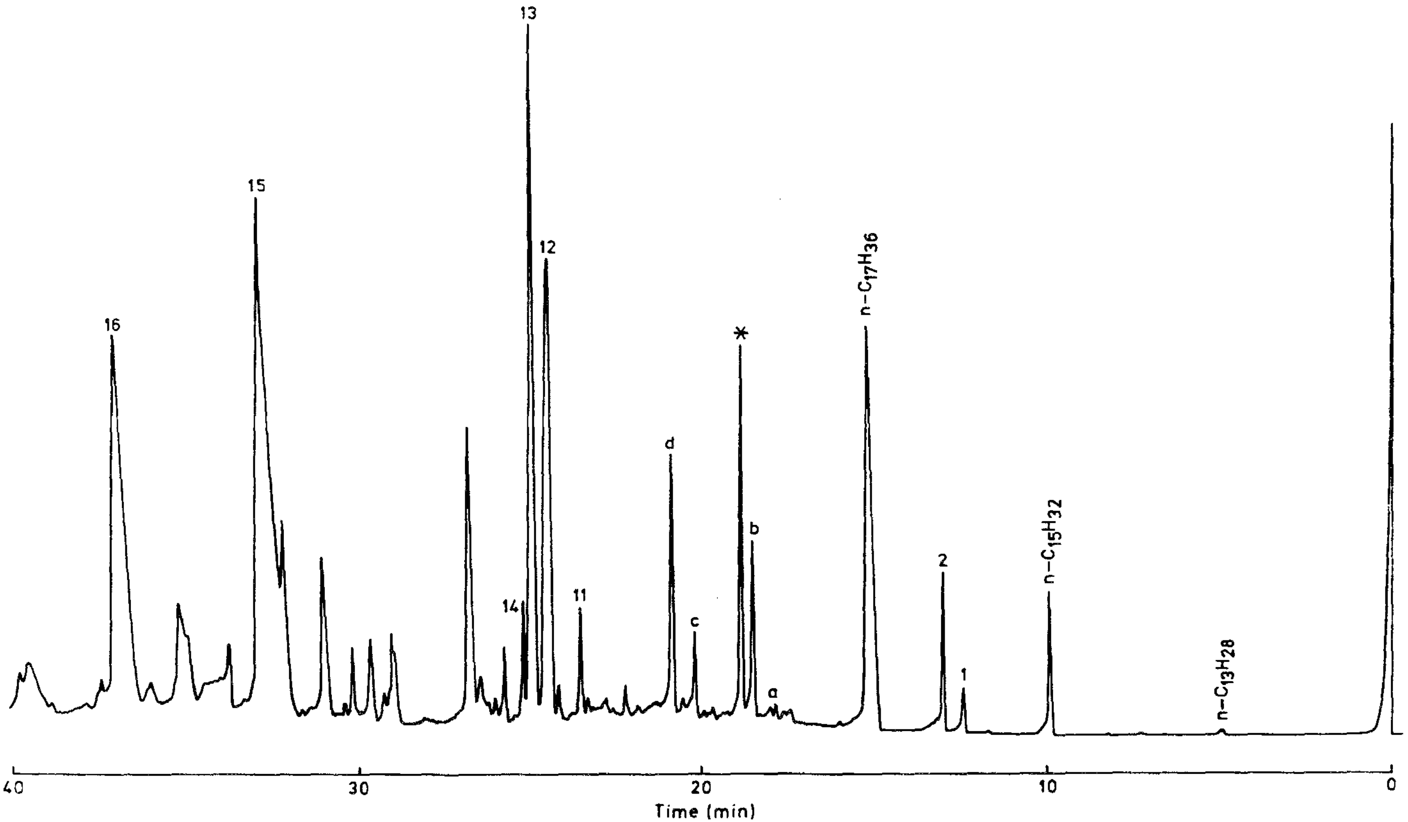


FIG. 2. GLC trace of the hydrogenated extract from the heads of *Rhytidoponera metallica* run on an FFAP column programmed from 80°C to 225°C at 5°C/min. The peak marked with an asterisk is a solvent impurity of mol wt 220.

TABLE 2. COMPOUNDS IDENTIFIED IN HYDROGENATED EXTRACT FROM HEAD OF *Rhytidoponera metallica*

Number	Compound
1	2,5-Dimethyl-3-(2-methylbutyl)pyrazine
2	2,5-Dimethyl-3-isopentylpyrazine
a	5-Methyl-2-isobutyl-3-(2-methylbutyl)pyrazine
b	5-Methyl-2,3-diisobutylpyrazine
c	5-Methyl-2-(3-methylpentyl)-3-(2-methylbutyl)pyrazine
d	5-Methyl-2-(3-methylpentyl)-3-isopentylpyrazine
11	Unknown, suspected mol wt 264
12	$C_{16}H_{28}N_2O$
13	$C_{16}H_{28}N_2O$
14	Unknown, suspected mol wt 264
15	Diisobutylphthalate
16	Dibutylphthalate

methyl-3-(2-methylbutyl)pyrazine and 2,5-dimethyl-3-isopentylpyrazine, respectively, on the basis of their mass spectra. This was confirmed by coinjection with authentic compounds on a FFAP column, known to be able to separate the 2,3,5 isomer from the slower eluting 2,3,6-trisubstituted pyrazines (Wheeler and Blum, 1973).

Since the two pyrazines of mol wt 178 had the 2,3,5 substitution, it was thought likely that the four suspected pyrazines of mol wt 232 and the four of mol wt 246 also had the same substitution pattern and also that one of the substituents may have been either the 2-methylbutyl or isopentyl group, i.e., that these eight unknown pyrazines involved further elaboration on the already identified pyrazines of mol wt 178. Moreover, the results from the hydrogenation experiment suggested these compounds to be dialkyl alkenyl pyrazines.

As noted above, hydrogenation of each of the pyrazines of mol wt 232 and 246 cause the uptake of one molar equivalent of hydrogen, indicating one of the side chains contained an olefinic bond. That this double bond was in a five-carbon side chain in compounds (3)–(6) and in the six-carbon side chain in compounds (7)–(10) was also deduced from their mass spectra (Table 3). Thus ions at m/z 176 and 190 for compounds (3)–(6) and (7)–(10), respectively, arose from loss of C_4H_8 by McLafferty-type rearrangement of a C-5 saturated side chain in each case. There was no significant peak corresponding to the loss of C_5H_{10} in compounds (7)–(10). Such a peak would be expected to occur if the olefinic bond were in the C-5 chain in compounds (7)–(10).

The relative placement of the two large side chains in (3)–(10) could be determined by consideration of the results obtained in the structural elucidation of 5-methyl-3-*n*-propyl-2-(1-butenyl)pyrazine from the ant *Aphaenogaster rudis*

TABLE 3. MASS SPECTRA OF PYRAZINES

Compound	Mass spectrum
1	(M^+)178(1%), 177(1), 163(8), 149(4), 135(0.5), 122(100)
2	(M^+)178(1%), 177(1), 163(8), 149(0.5), 135(10), 122(100)
3	(M^+)232(55%), 217(23), 203(13), 189(9), 177(20), 176(45), 161(100), 149(53), 147(30), 133(32), 122(8)
4	(M^+)232(53%), 217(19), 203(0.5), 189(33), 177(15), 176(58), 161(100), 147(28), 133(58), 122(3)
5	(M^+)232(15%), 217(9), 203(9), 189(10), 176(20), 161(23), 147(13), 133(100), 122(5)
6	(M^+)232(3%), 217(8), 189(11), 176(34), 161(30), 147(8), 133(100), 122(1)
7	(M^+)246(100%), 231(50), 217(50), 203(1), 190(25), 176(40), 175(57), 161(95), 147(40), 135(40), 133(35), 122(20)
8	(M^+)246(75%), 231(45), 217(20), 203(33), 190(45), 176(25), 175(80), 161(100), 147(27), 133(90), 122(25)
9	(M^+)246(7%), 231(5), 217(10), 190(24), 176(5), 175(8), 161(18), 147(23), 133(100), 122(3)
10	(M^+)246(5%), 231(10), 217(8), 203(7), 190(35), 176(3), 175(17), 161(23), 147(10), 133(100), 122(7)
11	231(3%), 208(19), 207(36), 190(15), 178(22), 163(17), 161(12), 149(100), 136(25), 135(20), 133(20), 122(41)
12	(M^+)264(0.5%), 249(1), 231(1), 208(13), 207(38), 190(7), 178(22), 177(6), 163(7), 161(7), 151(10), 149(16), 135(100), 122(23)
13	(M^+)264(0.2), 249(1), 235(0.5), 231(1), 208(13), 207(53), 190(5), 178(16), 163(6), 161(7), 151(8), 147(7), 135(100), 122(25)
14	208(8%), 207(38), 190(15), 163(5), 161(8), 151(11), 135(100), 122(27)
15	223(18%), 205(6), 189(1), 167(10), 150(20), 149(100), 104(12), 57(80)
16	239(1%), 238(1), 223(6), 205(6), 150(10), 149(100), 104(6), 57(25)
a	(M^+)234(2%), 219(7), 205(5), 191(15), 178(100), 163(45), 149(11), 135(15), 122(87)
b	(M^+)234(1%), 219(7), 191(12), 178(72), 163(40), 149(5), 135(25), 122(100)
c	(M^+)248(5%), 233(8), 219(13), 192(65), 191(28), 178(100), 177(30), 163(75), 149(17), 135(22), 122(93)
d	(M^+)248(3%), 233(6), 219(7), 205(9), 192(50), 191(17), 178(60), 177(20), 163(40), 149(10), 135(25), 122(100)

(Wheeler et al., 1982). It was observed that the occurrence of an alkenyl group adjacent to a large alkyl group (in this case *n*-propyl) diminished the intensity of the peak due to the McLafferty rearrangement. When the alkenyl group was adjacent to a methyl group or hydrogen, this rearrangement led to the base peak of the mass spectrum. It was also found that no matter what the substitution, the mass spectra of the *E* and *Z* alkenes differed quite considerably.

On the basis of these considerations candidate 2-alkenyl-3-alkyl-6-methyl- and 2-alkenyl-3-alkyl-5-methylpyrazines were synthesized for comparison with the natural compounds. Full details of the compounds synthesized will be published elsewhere.

It was determined that compound (3) was (Z)-5-methyl-3-(2-methylbutyl)-2-(3-methylbut-1-enyl)pyrazine while peak (5) was (*E*)-5-methyl-3-(2-methylbutyl)-2-(3-methylbut-1-enyl)pyrazine. Compound (4) was (Z)-5-methyl-3-isopentyl-2-(3-methylbut-1-enyl)pyrazine and (6) was (*E*)-5-methyl-3-isopentyl-2-(3-methylbut-1-enyl)pyrazine. The *Z*,*E* relationship of these two pairs of compounds was shown by conversions of synthetic (5) into (3) and (6) into (4) by short irradiation of the *E* isomers. Similarly, the structure of compound (7) was shown to be (Z)-5-methyl-3-(2-methylbutyl)-2-(3-methylpent-1-enyl)pyrazine and (9) was (*E*)-5-methyl-3-(2-methylbutyl)-2-(3-methylpent-1-enyl)pyrazine, while (8) was (Z)-5-methyl-3-isopentyl-2-(3-methylpent-1-enyl)pyrazine and (10) was (*E*)-5-methyl-3-isopentyl-2-(3-methylpent-1-enyl)pyrazine. Once again the *E*, *Z* relationship of the pairs of isomers was shown by the photochemical conversion of the *E* into *Z* isomers. In every case mass spectra of the synthetic and natural compounds were identical, while the synthetic material enhanced the GLC peak of the natural material on a FFAP column.

The remaining compounds (11)–(14), of formula $C_{16}H_{28}N_2O$, whose mass spectra appear in Table 3 have so far eluded structural elucidation.

Also detected by GC-MS in the extract from the head were a series of *n*-alkanes and alkenes. These are indicated on Figure 1.

The mixture of 10 (possibly 14) pyrazines detected in the head of *R. metallica* represents the most complicated group of these compounds yet found; previously a series of five 2,6-dimethyl-3-*n*-alkylpyrazines had been found in the heads of an *Odontomarchus* species (Wheeler and Blum, 1973). Of the 10 compounds, 2,5-dimethyl-3-isopentylpyrazine (2) represents the pyrazine most commonly encountered in the Hymenoptera, having been identified from ants, bees, and wasps (Attygale and Morgan, 1984; Wheeler et al., 1982). 2,5-Dimethyl-3-(2-methylbutyl)pyrazine (1) has been detected once previously, from an Australian formicine ant of the genus *Calomyrmex* (Brown and Moore, 1979). In this ant it also cooccurs with 2,5-dimethyl-3-isopentylpyrazine.

Of the remaining eight pyrazines identified (3)–(10), no analogs as yet exist in nature. The presence of the more complex side chain in the 2 position so far has analogy only in 5-methyl-3-*n*-propyl-2-(1-butenyl)pyrazine, isolated from the heads of the myrmicine ant *Apaenogaster rudis* (Wheeler et al., 1982). The vagaries of the mass spectra of the various alkenyl pyrazines noted by Wheeler have been fully reflected in the mass spectra of the alkenyl pyrazines from *R. metallica*. It was not until the olefinic bond was hydrogenated that mass spectra more characteristic of alkyl pyrazines (Brophy and Cavill, 1980) were observed.

The only other olefinic pyrazines reported from the Hymenoptera have been (*Z*)- and (*E*)-2,5-dimethyl-3-styrylpyrazines, isolated from the Argentine ant *Iridomyrmex humilis* (Cavill and Houghton, 1974). In this case it was shown, by extraction of the ants in the dark, that the *Z*:*E* ratio was 1:3; extraction under ordinary laboratory conditions resulted in the detection of only the *Z* isomer. It was suggested that the natural compound in that ant was, in fact, the *E* isomer, with isomerization occurring during extraction and isolation.

With the olefinic pyrazines detected in *R. metallica*, the *Z*:*E* isomer ratio was approx. 2:3, and this was reproducible over a number of extractions carried out under ordinary laboratory conditions. The synthetic *E* isomers could be converted to an approx. 1:1 mixture of *E* and *Z* isomers by irradiation at 300 nm for 5 min as noted above.

Of the two major remaining unidentified compounds, (12) and (13), the formulas of $C_{16}H_{28}N_2O$ and retention time on FFAP suggest an addition of the elements of methanol to the compounds (3)–(6). It is unlikely that these are artifacts since care had been taken to ensure that methanol did not come into contact with the extract. To date these compounds have eluded structural assignment.

The glandular origin of the pyrazines in the head of *R. metallica* has not been determined but, in light of previous reports, is assumed to be the mandibular gland. Behavioral tests have not been carried out.

The ubiquitous phthalate esters, (15) and (16), are considered to be artifacts, possibly having been acquired by the ant in the course of its food gathering, although contamination from solvents and glassware in the laboratory cannot be ruled out.

Acknowledgments—We thank Dr. R. F. Crozier of the University of New South Wales for identifying the ants, Mr. D. Nelson of the School of Chemistry for the chemical ionization and high-resolution mass spectra, and the Australian Government, through ADAB, for a scholarship to B.T. and through ARGS for support to C.M.S.

REFERENCES

Attygale, A.B., and Morgan, E.D. 1984. Chemicals from the glands of ants. *Chem. Soc. Rev.* 13:245–278.

Brophy, J.J., and Cavill, G.W.K. 1980. Naturally occurring pyrazines and their mass spectral characterization. *Heterocycles* 14:477–504.

Brophy, J.J., and Nelson, D. 1985. 2,5-Dimethyl-3-*n*-propylpyrazine from the head of the bull ant *Myrmecia gulosa* (Fabr.) *Insect Biochem.* 15:363–365.

Brophy, J.J., Nelson, D., Goldsack, R.J., Lidgard, R.O., and Melley, D.P. 1979. Elemental compositions from low resolution magnetic mass spectrometers. *Lab. Pract.* 28:615–619.

Brophy, J.J., Cavill, G.W.K., and Plant, W.D. 1981. Volatile constituents of an Australian ponerine ant *Rhytidoponera chalybaea. Insect Biochem.* 11:307–310. (species correction, *Insect Biochem.* 1984. 14:738).

Brophy, J.J., Cavill, G.W.K., and Duke, R.K. 1983. Volatile constituents in a methylene chloride extract of a ponerine ant *Rhytidoponera aciculata* (Smith). *Insect Biochem.* 13:503–505.

Brown, W.L., Jr. 1960. The release of alarm and attack behavior in some New World army ants. *Psyche* 66:25–27.

Brown, W.V., and Moore, B.P. 1979. Volatile secretory products from an Australian formicine ant of the genus *Calomyrmex. Insect Biochem.* 9:451–460.

Casnati, G., Ricca, A., and Pavan, M. 1967. Sulla secrezione difensiva glandole mandibolari di *Paltothyreus tarsatus* (Fabr). (*Hymenoptera Formicidae*). *Chim. Ind.* 49:57–58.

Cavill, G.W.K., and Houghton, E. 1974. Some pyrazine derivatives from the Argentine ant *Iridomyrmex humilis. Aust. J. Chem.* 27:879–889.

Crew, R.M., and Fletcher, D.J.C. 1974. Ponerine ant secretions: The mandibular gland secretion of *Paltothyreus tarsatus* Fabr. *J. Entomol. Soc. S. Afr.* 37:291–298.

Duffield, R.M., Blum, M.S., and Wheeler, J.W. 1976. Alkylpyrazine alarm pheromones in primitive ants with small colonial units. *Comp. Biochem. Physiol.* 54B:439–440.

Fales, H.M., Blum, M.S., Bain, Z., Jones, T.S., and Don, W. 1984. Volatile compounds from ponerine ants of the genus *Mesoponera. J. Chem. Ecol.* 10:651–665.

Herman, H.R., Blum, M.S., Wheeler, J.W., Overal, W.L., Schmidt, J.O., and Chao, J.T. 1984. Comparative anatomy and chemistry of the venom apparatus and mandibular glands in *Dinoponera grandis* (Guerin) and *Paraponera clavata. Ann. Entomol. Soc. Am.* 77:272–279.

Howard, D.F., Blum, M.S., Jones, T.H., and Tomalski, M.D. 1982. Behavioral responses to an alkylpyrazine from the mandibular gland of *Wasmannia auropunctata. Insectes Soc.* 29:369–374.

Klein, B., and Spoerri, P. 1951. The action of organolithium compounds on 2,5-dimethylpyrazine II. *J. Am. Chem. Soc.* 73:2949–2951.

Longhurst, C., Baker, R., House, P.E., and Speed, W. 1978. Alkylpyrazines in ponerine ants: Their presence in three genera, and cast specific behavioral responses to them in *Odontomachus troglodytes. J. Insect Physiol.* 24:833–837.

Longhurst, C., Baker, R., and House, P.E. 1980. A multicomponent mandibular gland secretion in the ponerine ant *Bothroponera soror* (Emery). *J. Insect Physiol.* 26:551–555.

Meinwald, J., and Wiemer, D.F. 1983. Pygidial gland secretions of the ponerine ant *Rhytidoponera metallica. Naturwissenschaften* 70:46–47.

Wheeler, J.W., and Blum, M.S. 1973. Alkylpyrazine alarm pheromones in ponerine ants. *Science* 182:501–503.

Wheeler, J.W., and Blum, M.S. 1973. Alkylpyrazine alarm pheremones in ponerine ants. *Science* 182:501–503.

Wheeler, J.W., Avery, J., Olubajo, O., Shamim, M.T., Storm, C.B., and Duffield, R.M. 1982. Alkyl pyrazines from Hymenoptera: Isolation, identification and synthesis of 5-methyl-3-*n*-propyl-2-(1-butenyl)pyrazine from *Aphaenogaster* ants (Formicidae). *Tetrahedron* 38:1939–1948.