

STRUCTURE AND SYNTHESIS OF TETRASUBSTITUTED PYRAZINES IN ANTS  
IN THE GENUS MESOPONERA

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ABSTRACT

The structures of twelve new pyrazines present in Mesoponera species have been elucidated using mass spectrometry and confirmed by synthesis.

Ants in the genus Mesoponera are found in the Old World tropics with the exception of two sibling species that occur in New Zealand. M. castanea is found mainly in the North Island whereas M. castaneicolor, characterized by the presence of alate queens, is widely distributed on both islands. In a recent communication we described the poison gland constituents of these ants as a series of simple aliphatic primary and secondary amines ranging from isoamylnonylamine to heptylnonylamine, along with their corresponding formamides, acetamides and isovaleramides.<sup>1</sup> Exclusively in the cephalic extracts, we also noted a series of compounds whose mass spectra in no way resembled the aforementioned substances, and whose nature awaited the accumulation of sufficient extract to allow accurate mass measurement of several ions in one of the peaks. With this data in hand, we have now been able to deduce their structures solely from their mass spectra as an interesting new series of tetrasubstituted pyrazines. Synthesis of several of the compounds confirms our assignments.

EXPERIMENTAL

Workers of M. castanea were collected at Ohinetonga Scenic Reserve, Owhaanga, New Zealand. M. castaneicolor workers were collected at Aorere Valley, Northwestern Nelson Province, 18 miles from Collingwood. Workers were decapitated and heads were placed in methylene chloride and mailed to the United States (N.I.H.) for analysis. Mass spectra were obtained using either LKB-9000 or LKB-2091 spectrometers operating in the electron impact mode at 70 electron volts with source temperatures of 270°C and 50 uamp ionizing current. A packed column (2.5mm x 2m) with 3% OV-17 on 100-mesh Supelcoport (Supelco, Bellefonte, PA.) was used in the former with a separator at 270°C, while a capillary column (.32mm x 30m) coated with OV-17 directly coupled to the spectrometer was used in the latter. The packed column invariably gave better results in eluting the more polar alcohols while the capillary column was required to completely separate many of the components. High resolution measurements were made using a JEOLCO OISG-2 using a photoplate at 20,000 resolution in the EI mode.

SYNTHESIS

All melting points are uncorrected and were determined on a Thomas-Hoover melting point apparatus. The IR spectra were recorded on a Nicolet-1605X FT-IR. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian XL-300 NMR spectrometer using tetramethylsilane as internal standard. During synthesis, mass spectra were recorded on a Finnigan MAT ion trap detector with automatic gain control accessory. Thin layer chromatography (TLC) was performed on Whatman glass plates coated with 0.25 mm of silica gel (60A MK6F, fluorescent at 254 nm). Flash chromatography was performed on 70-230 mesh silica gel 60. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

1,1'-(3,6-Dimethyl-2,5-pyrazinediyl)bis-3-methyl-1-butanone (8). To a stirring solution of 1-(3,6-dimethyl-2-pyrazinyl)-3-methyl-1-butanone (6.7g, 34.9  $\mu\text{mole}$ ) prepared earlier<sup>2</sup> (contaminated with about 10% of 1-(3,5-dimethyl-2-pyrazinyl)-3-methyl-1-butanone), isovaleraldehyde (10.6g, 139.4  $\mu\text{mole}$ ), water (35 ml), glacial acetic acid (50ml) and concentrated sulfuric acid (10ml) at 3-5°C, was added concurrently 70% t-butylhydroperoxide (9g, 70  $\mu\text{mole}$ ) and a solution of ferrous sulfate heptahydrate (19.4g, 70  $\mu\text{mole}$ ) in water (50 ml) over a 15 minute period. The resulting heterogeneous mixture was stirred for 16 hours, during which time the temperature was raised to 21°C. Solid sodium sulfite was then added until a test with starch-iodide paper was negative. The mixture was next poured over water (300 ml) and extracted with methylene chloride (3x125ml). The combined organic layers were washed with water (200ml), saturated aqueous sodium bicarbonate solution (200ml) and dried ( $\text{MgSO}_4$ ). Removal of the solvent under reduced pressure gave 8.1g of crude brown oil. Column chromatography (200g silica gel 60, eluted with 5% ethyl acetate/hexane) followed by circular chromatography (4 mm plate, 1g x 5 runs, 5% ethyl acetate/hexane) gave a 45% yield (4.33g, 15.7  $\mu\text{mole}$ ) of 8 as a low melting yellow solid, m.p. 39.5-41°C. Apparently no diacyl product was formed from the 1-(3,5-dimethyl-2-pyrazinyl)-3-methyl-1-butanone present as a contaminant. Rf 0.68 in ethyl acetate/hexane (1/4); IR(KCl) 2959, 2931, 2873, 1700, 1411, 1368, 1010, 924  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ ) 0.99(12H,d, $J=6.7\text{Hz}$ ), 2.25(2H,m), 2.77(6H,s), 3.04(4H,d, $J=7.0\text{Hz}$ );  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ )  $\delta$  22.67, 22.71, 24.80, 48.40, 147.09, 149.60, 203.15; Anal. Calcd for  $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_2$ : C, 69.53; H, 8.75; N, 10.14. Found: C, 69.42; H, 8.86; N, 10.01.

Reduction of 8: To a stirring solution of the diketone (1.0g, 3.6  $\mu\text{mole}$ ) in 2-propanol at 15°C was added a solution of sodium borohydride (17mg, 0.45  $\mu\text{mole}$ ) in 0.6ml 2-propanol. The progress of the reaction was monitored by TLC. Additional sodium borohydride (25.5mg, 0.67  $\mu\text{mole}$ ) was added until TLC analysis showed the disappearance of starting material.

The reaction mixture was diluted with water (50ml) and extracted with methylene chloride (3 x 25ml). The combined organic extracts were washed with saturated aqueous ammonium chloride (40ml), then with water (40ml) and the solvent was removed on a rotary evaporator to give 1.05g of a pale yellow oil. Silica gel chromatography (ethyl acetate/hexane) gave pure products. Compound 5 (370mg, 37%), compound 6a (10mg, 1%), compound 6b (60mg, 6%). In a second experiment using equimolar amounts of sodium borohydride and diketone and allowing the reaction to proceed at 21°C for 16 hrs, only the two diastereomeric diols were obtained in equal amounts in an overall yield of 70%.

Diastereomer 6a: mp 129.5-130°C; Rf 0.24 ethyl acetate/hexane (1/4); IR(KCl): 3600-3200, 3338, 2954, 2933, 2922, 2867, 1422, 1368, 1266, 1068, 706  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ ) 0.96(6H,d, $J=6.7\text{Hz}$ ), 1.07(6H,d, $J=6.7\text{Hz}$ ), 1.3-1.5(4H,m), 2.06(2H,heptet), 2.5(6H,s), 4.11(2H,br. s), 4.88(2H,br. s, $J=8.5\text{Hz}$ );  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ ) 19.99, 21.48, 23.78, 24.86, 47.22, 67.85, 145.62, 153.26; Anal. Calcd for  $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_2$ : C, 68.53; H, 10.07; N, 9.99. Found: C, 68.58 H, 10.35; N, 9.81.

Diastereomer 6b: mp 99.5-100.5°C; Rf 0.17 ethyl acetate/hexane (1/4); IR(KCl): 3600-3200, 3503, 2951, 2926, 2912, 2893, 2870, 1416, 1367, 1292, 1054, 968, 894  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ ) 0.96(6H,d, $J=6.7\text{Hz}$ ), 1.07(6H,d, $J=6.7\text{Hz}$ ), 1.3-1.5(4H,m), 2.06(2H,heptet), 2.5(6H,s), 4.11(2H,br.s), 4.88(2H,br.s, $J=8.5\text{Hz}$ );  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ ) 20.03, 21.45, 23.80, 24.89, 47.26, 67.83, 145.54, 153.23; Anal. Calcd. for  $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_2$ : C, 68.53; H, 10.07; N, 9.99. Found: C, 68.15; H, 10.26; N, 9.73.

1-[5-(3-Methyl-1-butanol)-3,6-dimethyl-2-pyrazinyl]-3-methyl-1-butanone 5: Rf 0.49 ethyl acetate/hexane(1/4);  $^1\text{H}$  NMR( $\text{CDCl}_3$ ) 0.96(3H,d, $J=6.5\text{Hz}$ ), 0.99(6H,d, $J=6.5\text{Hz}$ ), 1.08(3H,d, $J=6.5\text{Hz}$ ), 1.42(2H,m), 2.08(1H,m), 2.25(1H,m), 2.55(3H,s), 2.77(3H,s), 3.04(2H,d, $J=6.9\text{Hz}$ ), 4.13 (1H,br.s), 4.19(1Hdd, $J=8.9,4.1\text{Hz}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ), 20.22, 21.39, 22.73, 22.76, 23.78, 24.84, 24.91, 46.97, 48.29, 68.12, 144.97, 146.04, 149.78, 156.87, 203.23; Anal. Calcd for  $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_2$ : C, 69.03; H, 9.41; N, 10.06. Found: C, 69.20; H, 9.34; N, 10.33.

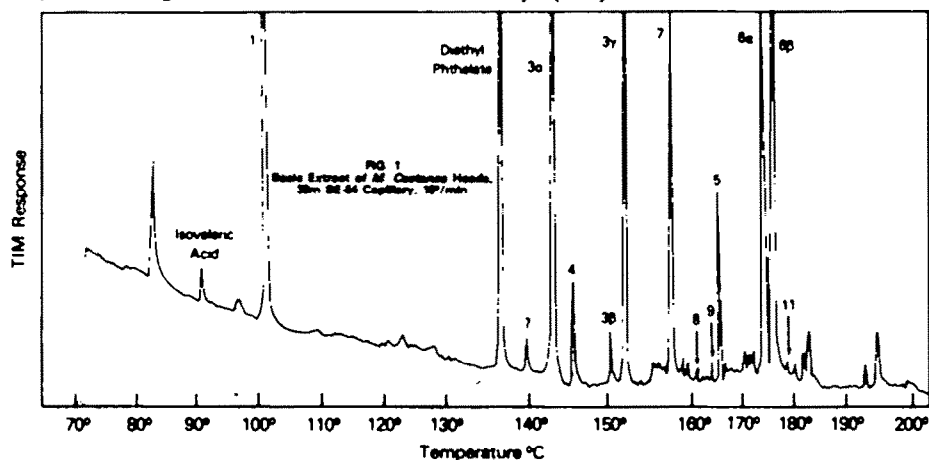
Conversion of 5 to 8. A fraction of a mg of 5 was stirred in 0.5ml of methylene chloride with 10 mg of activated  $\text{MnO}_2$  for one hour. Direct GC-MS analysis showed that about 7% conversion to the earlier eluting diketone (Table I, compound 8) had taken place.

Conversion of 6 $\beta$  to 7. A fraction of a mg of 6 $\beta$  in 0.5 ml of ethyl acetate was combined with 10mg of 10% Pd-on-C and hydrogen bubbled through the solution for 1 hr. GC-MS analysis showed that approximately 6% had been converted to the earlier eluting monoalcohol (Table I, compound 7).

Conversion of 6 $\beta$  to 4. A fraction of a mg of 6 $\beta$  in 0.5 ml of methylene chloride was treated with 1 drop of POCl<sub>3</sub> and heated for 1 hr. The solution was then treated with an excess of 50% KOH and back extracted with methylene chloride. GC-MS analysis of the mixture revealed conversion to the  $\alpha,\alpha'$ -dichloro analogue (80%) [281(M<sup>+</sup>-Cl, 40), 260 (M<sup>+</sup>-C<sub>4</sub>H<sub>8</sub>, 68) 225(M<sup>+</sup>-C<sub>4</sub>H<sub>8</sub>Cl, 100) 203(M<sup>+</sup>-C<sub>3</sub>H<sub>7</sub>Cl<sub>2</sub>, 49)], the monochloro monoolefin (10%) [245(M<sup>+</sup>-Cl, 52), 244(M<sup>+</sup>-HCl, 100), 229(244-CH<sub>3</sub>, 96), 224(M<sup>+</sup>-C<sub>4</sub>H<sub>8</sub>, 54)], and the diolefin, presumably conjugated, (10%) [244(M<sup>+</sup>, 100), 229 (M<sup>+</sup>-CH<sub>3</sub>, 98, 214(18), 203(26), 201(34), 199(32), 189(23), 91(30), 77(26)]. The total mixture was then hydrogenated in the same medium with 10 mg of 10% Pd-on-C for 1 hr and again analyzed by GC-MS. The diolefin and dichloro analogues were unchanged but the monochloro monoolefin was replaced by a peak corresponding to the fully saturated analogue (MS: Table I, compound 4).

### RESULTS

Figure 1 shows a typical gas chromatogram obtained on the basic fraction of one of the cephalic extracts of *M. castaneae*. These bases were much more abundant in *M. castaneae* than in *M. castaneicolor*, so extracts of the former were used for all structural analyses. Samples of total extracts in methylene chloride were found to contain many lipids similar to those reported earlier eluting above 200°C. One peak in the total extracts, important in view of the findings below, eluted shortly after the solvent at 91°C and was identified as isovaleric acid. A second peak eluting at 97°C was identified as methyl phenylacetate.



The first pyrazine peak seen in Figure 1, eluting at 103°C, was easily identified by virtue of an intense ion at  $m/z$  122 (Table I, compound 1, ion structure a). This is a feature characteristic of all monoalkylated 2,5-dimethylpyrazines without branching at the methylene carbon atom adjacent to the heterocyclic ring and results from a McLafferty rearrangement involving loss of part of the side chain<sup>3a</sup>. The molecular ion at  $m/z$  178 established the side chain as a pentyl group, and comparison with the above reference showed it to be 2,5-dimethyl-3-isopentylpyrazine (1).

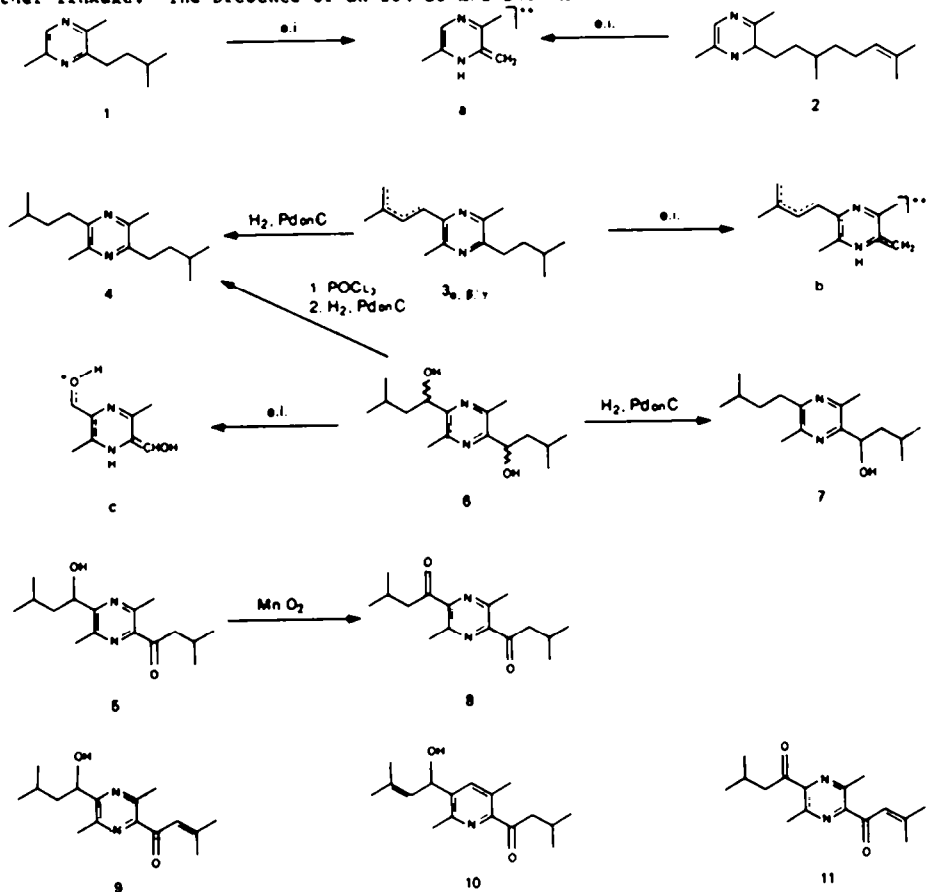
Three of the four peaks eluting at 143°C-153°C shortly after some diethyl phthalate contaminant, all appeared to have molecular ions at  $m/z$  246 (Table I, compounds 3 $\alpha$ , 3 $\beta$ , 3 $\gamma$ ). Assuming a formula C<sub>16</sub>H<sub>26</sub>N<sub>2</sub>, these substances are isomeric with 2,5-dimethyl-3-citronellylpyrazine (2)<sup>3d</sup> but differ in that the typical peak at  $m/z$  122 (ion a) resulting from loss of most of the side chain in the former has been replaced by ions at  $m/z$  189 and 190 (ion b) in all of the latter. Thus, four rather than nine carbons have been lost in the benzylic cleavages ( $m/z$  189) and McLafferty rearrangements ( $m/z$  190) and the presence of two 5 carbon side chains is indicated. Interestingly, only the saturated side chain is lost in these processes. As Biemann has shown<sup>3b</sup>, when two side chains are present in pyrazines, the second is usually lost by direct cleavage

rather than rearrangement, and this process is responsible here for the minor peak at  $m/z$  135.

On catalytic hydrogenation (Pd-on-C) all of these peaks disappeared only to augment the intensity of the small peak eluting second in the series at  $146^\circ\text{C}$  (Table I, compound 4) whose spectrum showed an abundant fragment ion at  $m/z$  192 and a molecular ion at  $m/z$  248. This is clearly an *a,b*-dipentyl-*c,d*-dimethylpyrazine and by analogy with 1, the substitution pattern shown in 4 was suggested. Comparison of its spectrum with that of a synthetic sample obtained by  $\text{POCl}_3$  dehydration and hydrogenation of synthetic diol 6 (see experimental) confirmed the location and branched nature of the side chains as shown in 3  $\alpha$ ,  $\beta$ ,  $\gamma$  and 4. The higher intensities of the molecular ions of the first- and second-eluting isomers (3  $\alpha$  and  $\beta$ , Table I) suggest that these are the conjugated isomers (E and Z), although the retention time of the last-eluting (3  $\gamma$ ) suggests the opposite. In any case, these appear to be three of the four possible olefinic isomers of 3 and it seems unlikely that any represent the isomer with unsaturation at the terminal position of the side chain since this would be expected to show an abundant ion representing cleavage between the benzyl and allyl carbons ( $m/z$  191).

The spectra of the following peaks on the chromatogram appeared quite puzzling until mass measurement of several ions in the peak eluting at  $166^\circ\text{C}$  showed the presence of two oxygen atoms in the pyrazine (Table I, compound 5). Thus, while the molecular ion at  $m/z$  278 exhibited the typical loss of  $\text{C}_4\text{H}_8$ , the resulting abundant ion at  $m/z$  222.1371 was established as  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2$  (222.1368). This ion then lost CO to form  $m/z$  194.1392 ( $\text{C}_{11}\text{H}_{18}\text{N}_2\text{O}$  req. 194.1419) and then another  $\text{C}_4\text{H}_8$  to form  $m/z$  138.0788 ( $\text{C}_7\text{H}_{10}\text{N}_2\text{O}$  req. 138.0793).

Assuming the  $\text{C}_4\text{H}_8$  side chain loss, the molecular formula of 5 is  $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_2$  (The signal from the molecular ion itself was too weak to measure). Retention of oxygen, first by the ion at  $m/z$  222 then by  $m/z$  138 shows that the oxygens are not in the butyl portions of the (presumed) isopentyl side chains while loss of 28 from  $\text{M}^{+}$  and CO from  $m/z$  222 strongly imply the presence of a ketone. The formula then requires that the remaining oxygen be present as either a hydroxyl or an ether linkage. The presence of an ion at  $m/z$  261 ( $\text{M}^{+}-\text{OH}$ ) indicated the former and



structure 5 was suggested. Comparison with a synthetic sample (see experimental) confirmed the assignment.

Two related compounds, eluting shortly after at 174°C and 176°C, are isomers with identical mass spectra and have molecular ions two mass units higher than the keto alcohol 5, along with the typical  $M^+ - C_4H_8$  peak at  $m/z$  224 (Table I, compounds 6a, 8). This loss of  $C_4H_8$  is followed by loss of  $C_4H_9$  to provide the abundant side-chain-free ion formulated as c at  $m/z$  167 and it is clear that these are the corresponding meso and erythro diols 6. Again, comparison with synthetic samples showed that this assignment was correct, although we are not able at this time to assign their respective stereochemical configurations.

The corresponding monoalcohol 7 could also be identified eluting earlier at 158°C (Table I, compound 7). The typical loss of  $C_4H_8$  from its molecular ion at  $m/z$  264 is again followed by loss of  $C_4H_9$  to form the abundant even-electron ion at  $m/z$  151. It is apparent that loss of a side chain by McLafferty rearrangement takes preference even over the usually facile hydroxyl-assisted benzylic cleavage. Comparison with a synthetic sample prepared by partial catalytic hydrogenolysis (Pd-on-C) of the synthetic diol 6 (see experimental) confirmed the structure.

From the retention times of the above compounds it is apparent that replacement of a ketone by a hydroxyl increases the retention temperature by ca. 5°C, so that by examining the chromatogram in the appropriate region before elution of the keto alcohol 5, it was possible to detect a small peak containing diketone 8. As expected, it showed a molecular ion at  $m/z$  276 (Table I, compound 8) and losses of CO and  $C_4H_8 + CO$  to form ions at  $m/z$  248 and 192 respectively. A second loss of the same moieties produces the simple dimethylpyrazine ion at  $m/z$  108. Comparison with both synthetic 8 and a sample prepared by  $MnO_2$  oxidation of the keto alcohol 5 (see experimental) confirmed this assignment. Loss of CO from the molecular ions of the above compounds is interesting and suggests that the isobutyl group as well as a hydrogen may be capable of migrating to the nitrogen<sup>4</sup> in a structure analogous to a. Subsequent loss of CO from a ketene-like side chain would then be straightforward.

A compound isomeric with this diketone was found in some extracts eluting at 166°C just before the keto alcohol 5. Its spectrum is very similar to that of 8 (Table I, compound 8), but its molecular ion at  $m/z$  276 is relatively much more intense. Weak peaks are seen for losses of 17 and 19 m.u. from  $M^+$ , a feature not seen in the diketone 8 but noted in the keto alcohol 5. We speculate therefore that this is an unsaturated keto-alcohol and further that it is 9 rather than 10 since it exhibits an ion at  $m/z$  83 representing the unsaturated ketone side chain (see next).

Finally, a peak eluting shortly after 6, again not seen in all extracts, proved to be the unsaturated diketone (Table I, compound 11) on the basis of a molecular ion at  $m/z$  274, the typical CO losses from  $M^+$ , and the  $M^+ - C_4H_8CO$  ion at  $m/z$  190. A peak at  $m/z$  83 representing the unsaturated side chain is now its base peak.

#### CONCLUSIONS

The source of the isopentyl side chains of these 2,5-dimethylpyrazines is not immediately apparent but the presence of isovaleric acid in the extract suggests that direct alkylation of the dimethylpyrazine nucleus is a possibility. On the other hand, this may merely represent a side pathway from a C5C2 (or double dimethylation of a C3C2) polyketide route.<sup>5</sup> The appearance of both isomers of diol 6 is peculiar, suggesting lack of stereospecificity in the reduction of the ketones.<sup>5</sup> In different species evidence has been presented for absorption of the pyrazines from plants; in other species direct biosynthesis seems involved.<sup>6</sup> However, since these predatory ants, in common with other ponerine species, do not feed on plants, we assume that the pyrazines are synthesized de novo by Mesoponera.

While a related 2,5-diisobutyl-3,6-dioxopiperazine is part of the red pigment pulcherrimin found in Candida pulcherrima,<sup>7</sup> and 2-methoxy-3-isopropylpyrazine occurs in Metiorrhynchus rhipidus,<sup>8</sup> we are aware of no reports of tetrasubstituted pyrazines in insects. However,

recently Tecle, *et al.*<sup>9</sup> have reported the existence of several 5-methyl-2,3-(diisopentyl and pentenyl)pyrazines in the heads of *R. metallica*, an Australian ponerine ant.

The pyrazines in general seem to serve both as trail-laying pheromones<sup>10</sup> and alarm pheromones<sup>11</sup> in ants. Recently evidence has also been obtained implicating their use by insects as warning substances against bird predators.<sup>6</sup>

TABLE I

Compound	Mass Spectrum ( <i>m/z</i> , (Structure, Intensity))
1	178( $M^+$ , 1), 163( $M-CH_3$ , 9), 149(3), 135(11), 122( <u>a</u> , 100), 107(2), 80(4), 54(3)
3alpha	246( $M^+$ , 100), 231( $M-CH_3$ , 43), 203(15), 190( <u>b</u> , 11), 189(81), 175(65), 173(16), 160(15), 147(10), 135(9), 122(8), 91(21), 77(15), 65(15), 53(40)
3beta	246( $M^+$ , 17), 231( $M-CH_3$ , 39), 203(17), 190( <u>b</u> , 100), 189(14), 175(41), 173(9), 160(12), 147(6), 135(33), 122(22), 91(17), 77(15), 65(7), 53(29)
3gamma	246( $M^+$ , 4), 231( $M-CH_3$ , 25), 203(21), 190( <u>b</u> , 100), 189(30), 175(92), 173(14), 160(18), 147(6), 135(10), 122(6), 91(16), 77(15), 65(12), 53(28)
4	248( $M^+$ , 2), 233( $M-CH_3$ , 8), 205(7), 192(dihydro <u>b</u> , 100), 187(5), 149(9), 136(54), 135(67), 121(4), 109(3), 93(5), 82(3), 80(4), 66(8), 57(9), 53(14), 43(11), 42(11)
5	278( $M^+$ , 4), 263( $M-CH_3$ , 19), 261( $M-OH$ , 4), 250(8), 235(10), 222(100), 221(24), 208(18), 194(48), 180(17), 165(18), 151(28), 138(44), 137(31), 135(13), 103(15), 101(22), 95(11), 87(8), 85(19), 80(12)
6	280( $M^+$ , 0.1), 265( $M-CH_3$ , 0.5), 263( $M-OH$ , 1), 247(0.5), 237(4), 224(56), 223(22), 167(100), 151(7), 138(17), 109(4), 80(4), 69(6), 56(9), 55(7), 43(15), 42(18), 41(31), 39(14)
7	264( $M^+$ , 0.5), 249( $M-CH_3$ , 4), 247( $M-OH$ , 1), 231(1), 221(11), 208(86), 207(19), 152(26), 151(100), 149(7), 135(7), 122(8), 121(7), 80(6), 69(6), 67(7), 66(5), 53(13), 43(13), 42(17), 41(29)
8	276( $M^+$ , 6), 261( $M-CH_3$ , 11), 248(11), 233(5), 220(6), 219(4), 206(13), 192(100), 164(17), 150(11), 149(16), 136(19), 122(10), 108(27), 85(11), 80(12), 67(15), 57(65), 53(12)
9	276( $M^+$ , 40), 261( $M-CH_3$ , 15), 259( $M-OH$ , 5), 248(7), 219(9), 206(10), 192(100), 164(18), 149(19), 136(32), 122(14), 108(52), 83(35), 80(24), 67(27), 57(58), 55(35), 53(20)
11	274( $M^+$ , 9), 259( $M-CH_3$ , 11), 246(13), 231(11), 204(9), 190(50), 185(11), 172(10), 171(8), 157(6), 107(5), 83(100), 77(10), 70(13), 57(14), 55(48), 53(12)

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