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CHEMISTRY OF AUSTRALIAN PONERINE ANTS: 2,5-DIMETHYLCHROMONE FROM *RHYTIDOPONERA METALLICA*

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ABSTRACT.—Investigation of the CH_2Cl_2 extract of the body of the ant *Rhytidoponera metallica* has led to the identification of the previously unknown 2,5-dimethylchromone [**1**] along with the known isogeraniol and a series of C13–C17 *n*-alkanes and *n*-alkenes.

Members of the genus *Rhytidoponera* have provided an interesting array of both new and known compounds. For example, a series of new pyrazines representing the most structurally complex compounds of this class to be isolated from an animal source to date have been identified in the head of *Rhytidoponera metallica* F. Smith (Formicidae) (1). Although this work on the pyrazines was not carried out at the glandular level, precedent would suggest that these compounds arise in the mandibular glands of these ants. More recently the extractives from the heads of *Rhytidoponera victoreae* have been examined and a similar set of complex pyrazines noted.[2]

In addition to pyrazines, various species of *Rhytidoponera* have also yielded a variety of aromatic compounds. For example, mellein (3,4-dihydro-8-hydroxy-3-methylisocoumarin) has been identified from the gaster of *Rhytidoponera chalybaea* (2,3) and 2-hydroxy-6-methylacetophenone (4) from the body of *Rhytidoponera aciculata*. These two compounds have also been reported from the mandibular glands of carpenter ants (5,6) and from the anal glands of various *Hypoclinea* species (7), respectively. In addition, methyl 2-hydroxy-6-methylbenzoate has been found in the mandibular gland of the related *Gnamptogenys pleuradon* (8).

As part of our continuing interest in this genus we now report our results from a chemotaxonomic investigation of the extractives from the bodies of *R. metallica*.

RESULTS AND DISCUSSION

A gc trace of the CH_2Cl_2 extract of the gasters and thorax of *R. metallica*, following removal of the acids, is presented in Figure 1. Most of the extract is accounted for as hydrocarbons with *n*-heptadec-8-ene, *n*-tridecane, and *n*-pentadecane being the major components. In assigning the position of the unsaturation unit in the alkenes, the oxymercuration technique (9) was used. Thus, the methoxy compounds derived from peak 6 showed prominent peaks in the mass spectrum at *m/z* 143, 157, and 171, while the products derived from peak 11 showed prominent peaks at *m/z* 129, 143, 157, and 171. These results fix the olefinic bond at C-7 and C-8 in peaks 6 and 11, respectively.

Further assignments were readily made to peaks 1, 13, and 14. Peak 1 was identified on the basis of its mass spectrum as isogeraniol, a terpene alcohol previously identified from the pygidial gland of *R. metallica*, along with heptadecene, heptadecane, and *m*-hydroxybenzaldehyde (10). It has been also suggested that this latter compound may function as a recruitment pheromone (11), but while collection locations were not given in the previous work, it is, perhaps, noteworthy that *m*-hydroxybenzaldehyde was not detected in the present extracts. The latter two components (peaks 13 and 14) were identified as dibutyl phthalates and are considered to be artifacts.

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[2]C.-M. Sun, J.J. Brophy, and R.F. Toia, unpublished results.

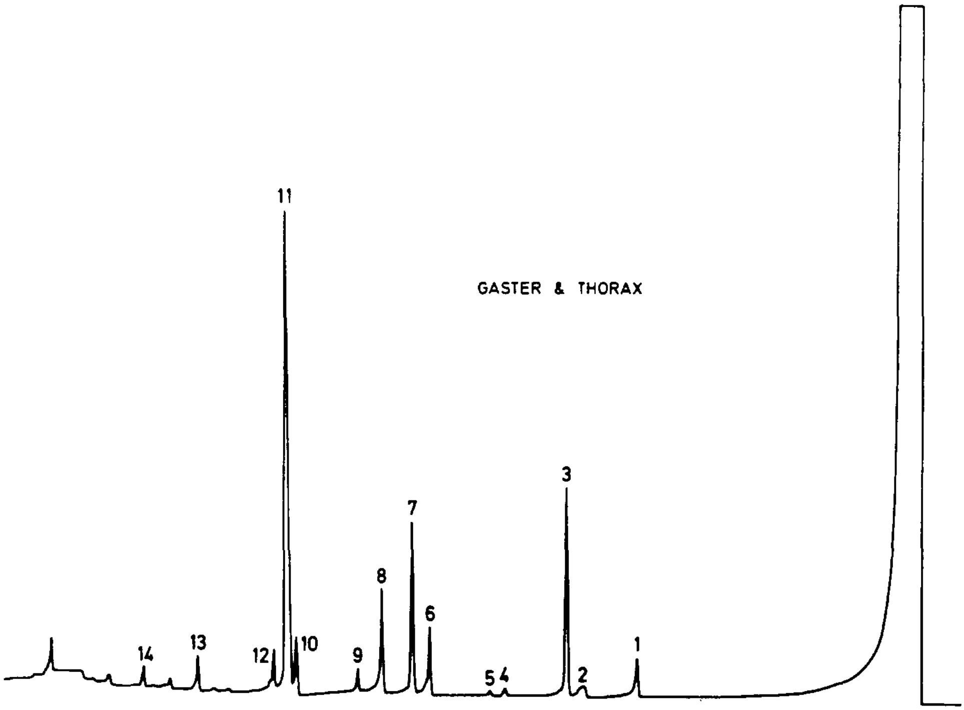
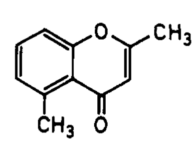


FIGURE 1. Gc trace of the volatiles from the bodies of *Rhytidoponera metallica*. Peak identifications: 1, *iso*-geraniol; 2, *n*-tridecene; 3, *n*-tridecane; 4, *n*-tetradecene; 5, *n*-tetradecane; 6, *n*-pentadec-7-ene; 7, *n*-pentadecane; 8, 2,5-dimethylchromone; 9, *n*-hexadecane; 10, *n*-heptadecadiene; 11, *n*-heptadec-8-ene; 12, *n*-heptadecane; 13, diisobutylphthalate.

The mass spectrum of the one remaining peak in the gc trace (peak 8) indicated a mol wt of 174, which was shown by hrms to be consistent with the molecular formula $C_{11}H_{10}O_2$ and a fragmentation pattern that was consistent with a chromone as one possibility. Initial comparison was made with the commercially available 2,6-dimethylchromone having a similar, although not identical, mass spectrum and gc retention time. Reconsideration of possible substitution patterns for the chromone, based on plausible biosynthetic routes to the compound, suggested the 2,5-dimethyl derivative. Supporting evidence was obtained from the nmr spectrum of the partially purified extract from the ant, which indicated a 1,2,3-substituted benzene ring and two aromatic-type methyl groups.

Proof of structure was obtained by unambiguous synthesis of 2,5-dimethylchromone [**1**], which, when comparisons were made, proved to be identical in all respects to the naturally occurring material. An examination of the literature indicated that although this compound had been mentioned once previously by name (2), it had been neither synthesized nor isolated from a natural source.

The occurrence of the compound is also of interest from the biogenetic point of view because it is closely related to the other aromatics identified from other species of



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Rhytidoponera. In particular, assuming a polyketide pathway to **1**, it represents the addition of one further malonate unit to 2-hydroxy-6-methylacetophenone, the biosynthesis of which was recently reported in *R. aciculata* (13).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mass spectra were obtained on an AE1 MS12 mass spectrometer coupled to a Shimadzu GC6 AMP gas chromatograph. Separations were effected on support coated open tubular (SCOT) columns, either (A) OV1 (30 m×0.5 mm) programmed from 90° to 250° at 5°/min or (B) free fatty acid phase (FFAP) (85 m×0.5 mm) programmed from 80° to 225° at 5°/min with He as carrier gas. The mass spectrometer was operated at 8000 V and 70 eV ionizing voltage. Spectra were acquired on a VG Digispec Display system. Accurate mass measurements were obtained on an AEI MS902 mass spectrometer under chemical ionization conditions (isobutane reagent gas) using the chart timing method (14). Nmr spectra were recorded for $CDCl_3$ solutions on either a Perkin-Elmer EM360 (60 MHz) or a Bruker CXP300 (300 MHz) spectrometer. Uv spectra were measured in EtOH solution on a Varian 635 spectrometer. Chromatographic separations were carried out using radial centrifugal chromatography on a chromatotron using 1-mm Si gel (GF254) layers. Microanalyses were carried out by the School of Chemistry, University of New South Wales, Microanalytical Unit. Methoxymercuration of the crude ant extract was carried out according to the method of Blomquist *et al.* (9). The reaction product, after workup, was examined directly by gc-ms under the same conditions on column A as used for the original extract.

ISOLATION OF THE NATURALLY OCCURRING CHROMONE FROM THE BODIES OF *R. METALLICA*.—Specimens of *R. metallica* (ca. 100 ants) were collected in Centennial Park, Randwick, New South Wales. A voucher specimen has been lodged with the Australian National Insect Collection, CSIRO, Division of Entomology, Canberra. The heads were removed, and the bodies (gaster and thorax) were ground with anhydrous Na_2SO_4. The mixture was extracted with CH_2Cl_2 in a Soxhlet apparatus for 15 h. The crude extract was washed with aqueous 10% $NaHCO_3$ solution and dried over $MgSO_4$, and the solvent was evaporated to give a pale yellow oil. A sample of the extract was examined by gc and gc-ms. The remainder of the extract was chromatographed on Si gel, whence the uv-active material (0.7 mg) was isolated and its nmr and uv spectra recorded.

SYNTHESIS OF 2,5-DIMETHYLCHROMONE [**1**].—A solution of 2-hydroxy-6-methylacetophenone (100 mg) in dry Et_2O (50 ml) was added slowly to a suspension of excess NaH (80 mg, in 50% oil suspension) in the same solvent (50 ml). After stirring at room temperature for 30 min, excess dry EtOAc (100 μl) was added slowly and the mixture stirred overnight at room temperature. The reaction was quenched by the addition of cold H_2O, and the mixture neutralized with 5% HCl. Work-up in the normal manner gave a yellow oil that was purified by Si gel chromatography to yield 1-(2-hydroxy-6-methyl)phenylbutan-1,3-dione (35 mg) as an amorphous solid. Ms *m/z* (%) 192 (33), 177 (40), 135 (100), 134 (64), 106 (20), 105 (10), 78 (16), 77 (21); nmr (60 MHz) δ 12.5 (1H, s), 7.5–6.8 (3H, m), 2.98 (2H, s), 2.70 (3H, s), 2.21 (3H, s). The diketone (above) (30 mg) was dissolved in concentrated HCl (1 ml) to give a yellow solution, and H_2O (8 ml) was added. 2,5-Dimethylchromone [**1**] subsequently crystallized as colorless needles (12 mg), mp 67–69°; Found: C 75.5%, H 5.5%; $C_{11}H_{10}O_2$ requires C 75.8%, H 5.8%; ms *m/z* (%) 174 (100), 173 (24), 159 (6), 146 (8), 145 (20), 134 (16), 106 (11), 105 (7), 78 (7), 77 (6); ^{1}H nmr (300 MHz) δ 7.45 (1H, m), 7.25 (1H, d, J=8 Hz), 7.09 (1H, d, J=8 Hz), 6.08 (1H, s), 2.85 (3H, s), 2.33 (3H, s); uv λ max (ε) 224 (19,200), 240 (9600), 246 (9600), 265 (4900), 299 (5800).

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