trans-4-Phenyl-3-buten-2-one from the African Harvester Ant Messor galls (Mayr)
(Hymenoptera: Formicidae)

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By gas chromatography mass spectrometry and synthesis of authentic standard, trans-4-phenyl-3-buten-2-one for the first time as well as known hydrocarbons have been identified in the Dufour’s gland secretion of the African harvester ant Messor galls (Mayr).

Introduction

The Formicine ants to which the harvester ant Messor galls (Mayr) belongs, constitutes one of the most conspicuous ant taxa in the African tropics particularly south of the Sahara. Messor galls is among the commonest species found in the soil fauna of shrub-savanna in Northern Nigeria.

The study of exocrine gland secretions as well as their functions in relation to behavioural patterns in social insects, particularly ants and bees has attracted the attention of numerous scientists for the last two and half decades. In ants, these volatile secretion play leading roles in alarm behaviour, attraction, defence, trail marking, group raiding and in numerous processes involved in the care of broad and establishments of new colonies. The glandular origin of ants pheromones varies considerably from sub-family to sub-family. The most common sources are the hind gut contents, Pavan’s, venom, tibial and Dufour’s glands [1].

A number of organic compounds such as alkanes, alkenes, alkanols, alkanals, alkanones, alkaloids and terpenes have been identified as chemical components of the secretions from these glandular sources [2]. The possible pheromonal roles of some of these organic compounds have also been determined [2].

In this discussion, the result of a chemical study of one of Africa’s economically important Formicid species M. galls (Mayr) is presented with a view of expanding the catalogue of chemicals used as signals by social insects.

Materials and Methods

Workers ants of Messor galls (Mayr) were collected at night from their colonies in open field, on the campuses of Bayero University, Kano, Institute for Agricultural Research of Ahmadu Bello University, Kano station and Abubakar Tafawa Balewa University, Bauchi. They were immediately transported to the laboratory where they were chilled prior to the isolation of scent materials. Dufour’s gland was excised under a 200 mM NaCl solution and the scent volatiles extracted in chromatography and freshly distilled ether. Extracts (sample volume ca. 5 μl) were stored at low temperatures in sealed ampoules. The secretion components were examined by gas chromatography (GC) and coupled gas chromatography-mass spectroscopy (GC-MS). Identification of the components was tentatively based on mass spectral and confirmed by comparison of the GC retention data and fragmentation patterns with those of authentic samples. In some cases GC identity were corroborated by chromatography with authentic standards.

Analysis of the scent volatiles were carried out on a Packard Model 427 gas chromatograph equipped with a flame ionization detector and glass capillary column (2 m x 2 mm) packed with 5% OV-225 and 100–120 mesh gas chrom G. The flow rate of the carrier gas (nitrogen) was 30 ml/min. The oven temperature was 70 °C isothermal for 15 min, then programmed to 270 °C at 6 °C/min. Mass spectra were measured in electron impact (EI) modes at 70 eV and 100 μA ionizing current using a KRATOS MS25 mass spectrometer interfaced to a CARLO-ERBO-FRACTOVAP 4200 gas chromatograph. Separations were achieved using a silicon OV column 2 m x 2 mm, 5% OV-225 on 100–120 mesh gas chrom Q, 30 ml/min, 70 °C isothermal for 15 min. and then temperature programmed to 200 °C at 6 °C/min.

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Data was acquired using KRATOS DS55 data system and chromatograms were numbered consecutively for purposes of identification. Authentic standards from Fluka and BDH chemicals were used where possible for comparative GC and GC-MS purposes. Melting points were determined in open capillaries on a Gallenkamp melting point apparatus and uncorrected. Infrared spectra were recorded using Beckman Acculab TM10 spectrophotometer. ¹H NMR spectra were obtained at 90 MHz on a Perkin-Elmer R-32 spectrometer with tetramethylsilane as an internal standard. All boiling points were uncorrected.

The synthesis of **trans**-4-phenyl-3-buten-2-one was achieved by stirring a mixture of freshly distilled benzaldehyde (0.50 mol), acetone (0.50 mol) and 500 ml 0.1 M NaOH in ethanol, 50 ml, and ether, 250 ml, at 5 °C for 30 min and was further stirred at room temperature for 72 h. The ether layer was separated and repeatedly washed with water and dried (MgSO₄). The yellow oil obtained after evaporation was distilled to yield **trans**-4-phenyl-3-buten-2-one, 50 g (68%), as colourless oil b.p. 259–260 °C (Lit. b.p. 260–262 °C) [3] which solidified on cooling to a crystalline mass m.p. 40 °C (Lit. m.p. 39–41 °C) [3]. IR (neat) 1608, 1680 cm⁻¹. ¹H NMR (CDCl₃) δ 2.4 (s, 3H, CH₃) 6.73, (1H, d, J = 15 Hz): 7.45 (s, 5H, ArH) 7.68, (1H, d, J = 15 Hz): Mass spec. m/z 146 (M⁺ 30), 131 (100), 103 (50), 77 (26), 57 (20), 51 (25), 43 (48), 41 (12).

**Results and Discussion**

Table I shows the composition as well as mass spectral data of scent volatiles from the Dufour's gland of the worker ants of *Messor galla*. Components numbers correspond to peaks 1 to 9, Fig. 1. Peak 1 corresponds to tridecane (2), pentadecane

<table>
<thead>
<tr>
<th>Scent gland Component No.</th>
<th>R.T. [°C]</th>
<th>R.A. [%]</th>
<th>Identification</th>
<th>Mol. wt.</th>
<th>Masses of fragment ions¹, m/z (% abundance) in order of decreasing abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14</td>
<td>15.5</td>
<td>Tridecane</td>
<td>184</td>
<td>43 (100), 57 (95), 71 (80), 41 (65), 85 (55), 55 (30), 99 (20), 113 (10), 127 (10), 141 (5), 155 (3), 184 (M⁺, 5)</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>15.2</td>
<td>Pentadecane</td>
<td>212</td>
<td>43 (100), 57 (98), 71 (85), 41 (80), 85 (70), 55 (40), 99 (18), 113 (15), 127 (10), 141 (7), 155 (5), 169 (3), 183 (2), 212 (M⁺, 5)</td>
</tr>
<tr>
<td>3</td>
<td>18.2</td>
<td>22.5</td>
<td>Pentadecene</td>
<td>210</td>
<td>41 (100), 43 (98), 55 (90), 57 (80), 69 (75), 83 (70), 97 (65), 111 (45), 125 (20), 140 (15), 154 (8), 182 (3), 210 (M⁺, 5)</td>
</tr>
<tr>
<td>4</td>
<td>19.0</td>
<td>2.0</td>
<td>Benzyl alcohol</td>
<td>108</td>
<td>79 (100), 108 (M⁺, 75), 107 (63), 77 (57), 57 (45), 51 (32), 34 (19), 91 (17)</td>
</tr>
<tr>
<td>5</td>
<td>20.5</td>
<td>4.3</td>
<td>Pentadecadiene</td>
<td>208</td>
<td>54 (100), 41 (95), 43 (80), 58 (55), 57 (38), 67 (75), 88 (70), 82 (40), 96 (28), 109 (10), 123 (5), 208 (M⁺, 8)</td>
</tr>
<tr>
<td>6</td>
<td>23.0</td>
<td>2.2</td>
<td>4-Phenyl-3-buten-2-one</td>
<td>146</td>
<td>131 (100), 103 (54), 43 (43), 77 (38), 146 (M⁺, 36), 57 (27), 51 (33), 41 (17)</td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td>17.5</td>
<td>Nonadecane</td>
<td>268</td>
<td>57 (100), 43 (90), 71 (65), 41 (38), 55 (35), 85 (32), 99 (20), 113 (15), 117 (10), 141 (8), 155 (6), 189 (5), 189 (4), 197 (3), 211 (2), 268 (M⁺, 5)</td>
</tr>
<tr>
<td>8</td>
<td>28</td>
<td>12.5</td>
<td>Heneicosane</td>
<td>296</td>
<td>71 (100), 57 (95), 43 (90), 41 (80), 85 (75), 55 (65), 99 (20), 113 (15), 127 (10), 141 (6), 155 (4), 182 (1), 296 (M⁺, 5)</td>
</tr>
<tr>
<td>9</td>
<td>28.7</td>
<td>8.4</td>
<td>Heneicosene</td>
<td>294</td>
<td>57 (100), 47 (90), 55 (85), 69 (72), 82 (70), 97 (68), 111 (50), 125 (40), 139 (30), 153 (25), 181 (15), 209 (10), 223 (5), 237 (3), 294 (M⁺, 2)</td>
</tr>
</tbody>
</table>

Abbreviations: R.T., retention time; % R.A., percent relative amount; m/z, mass/charge; ¹ Significant ions above m/z 40; ² Confirmed by mass spectrum and retention time (OV-225) of authentic sample; ³ bond geometry and position not determined.

Table I. Composition of Scent volatiles from Dufour's gland contents of *Messor galla* and mass spectra of the scent components. Component numbers correspond to peaks 1 to 9 in Fig. 1.
Time [min]

Fig. 1. Reconstructed ion current trace of Dufour's gland scent materials from *Messor galla* obtained by EI-GC-MS. GC conditions: 2 m × 2 mm glass column packed with 5% OV 225 on 100—120 mesh Gas Chrome Q; injection temperature 180 °C; oven temperature 170 °C for 5 min and then temperature programmed to 200 °C at 6 °C per min.

Fig. 2. Mass spectrum of *trans*-4-phenyl-3-buten-2-one from *Messor galla* (Mayr).

The presence of benzyl alcohol (4) and in particular, *trans*-4-phenyl-3-buten-2-one (6) have not been previously reported in any ant secretions. It has been reported that the Dufour's gland secretion of ants are fortified with alkanes and alkenes [4—6]. *trans*-4-Phenyl-3-buten-2-one (6) was identified by co-chromatography with a synthetic sample which gave a retention time and mass spectral fragmentation pattern identical with that of the natural product. The synthesis of 6 was achieved by simple crossed aldol condensation of freshly distilled benzaldehyde with acetone in a two phase solvent system (ether-water) containing 0.1 M NaOH solution. Flash distillation gave 6 as a colourless oil b.p. 259—260 °C (Lit. b.p. 260—262 °C) [3] which solidified on cooling to a crystalline mass m.p. 40 °C (Lit. m.p. 39—41 °C) [3]; IR (neat) 1608 and 1680 cm, ¹H NMR (CDCl₃) ppm, TMS, multiplicity ¹(Hz) 2.40 (s, 3H, CH₃), 6.73 (1H, d, 15 Hz), 7.45 (s, 5H, ArH), 7.68 (1H, d, 15 Hz); mass spec. 70 eV: m/z (relative intensity) 146 (M⁺, 30), 131 (100), 103 (50), 77 (26), 57 (20), 51 (25), 43 (48). The mass spectrum of 6 is shown in Fig. 2.

It is known that ants in the sub-families Dolichoderinae, Ponerinae and five sub-families of Formicidae contain several acyclic and cyclic ketones which elicit defensive and alarm behaviours [4]. The gladular sources of these scent volatiles in these ants sub-families are the oral, mandibular and Dufour's glands respectively. Preliminary investigation suggests that the *α,β*-unsaturated ketones 6 might be an alarm pheromone in *M. galla*.

Undoubtedly, the presence of *trans*-4-phenyl-3-buten-2-one (6) in the Dufour's glands of *M. galla* suggests that the chemistry of Formicids still offers many surprises as testimony to the biosynthetic versatility of these well developed exocrine organs. It is difficult to avoid the conclusion that the great success of the Formicidae ant is highly correlated with the evolution of these social organs which are committed to the synthesis of pheromones, particularly alarm/defence products [7].

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