Male Produced Volatiles from Coreid Bug *Leptoglossus australis* (Heteroptera)

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Z. Naturforsch. 40c, 142—144 (1985);
received August 27, 1984

*Leptoglossus australis*, Heteroptera, Male Volatiles, Benzyl Alcohol, 2-Phenyl Ethanol, Ventral Abdominal Scent Gland

From the ventral abdominal gland VII—VIII in male adult *Leptoglossus australis*, five volatiles have been identified by GC and MS data in comparison with authentic standard materials. Benzyl alcohol (31%) and 2-phenyl ethanol (42%) together accounted for over 70% of the total scent. The remaining materials identified were 2-octenyl propionate (19%), (£)$\_1$(£)$\_2$-2,4-hexadienyl acetate (6%) and (E)-2-hexenol (2%).

Introduction

*Leptoglossus* defines a genus of relatively large coreid bugs with distinctive leaf-like hind tibiae (leaf-footed bugs) [1]. Adults in both sexes possess a ventrally placed metathoracic scent gland for defense [2, 3]. Male adults exclusively possess in addition a scent gland which opens ventrally through intersegmental membrane between abdominal sternites VII and VIII [2, 4—6]. Chemical studies on the secretion from this ventral scent gland in several North American species within the genus *Leptoglossus* have been reported but the function remains as yet unknown [2, 5, 6]. Here, we should like to report for comparison with its North American relatives the results of an investigation on the composition of the secretion from the ventral abdominal scent gland of male adults of *Leptoglossus australis* (F.) from Nigeria. The work forms part of wider investigation into the chemical ecology of Heteroptera from tropical West Africa.

Materials and Methods

The ca. 22 mm long adults of *Leptoglossus australis* were collected in Kano state, Nigeria, from a variety of flowering plants from at least four different families (Cucurbitaceae, Compositae, Leguminosae, Rutaceae). Excision of the VII—VIII ventral abdominal scent glands from male adults was effected under 200 mM NaCl and for extraction of the scent volatiles ca. 5 μL of acetone was used. Extracts were stored at low temperature in sealed glass sample tubes. The analytical work was later carried out in Cardiff.

Gas chromatography (GC) was performed with a Varian Vista 6000 instrument equipped with flame ionization detector. Conditions were as follows: column, 28 m OV 101 capillary; splitless injection; oven temperature 70° to 200° C at 4 °C/min; injector 200° C; helium carrier 5 ml/min. Peak areas were measured using a Shimadzu C-E1B integrator.

Gas chromatography-mass spectrometry (GC-MS) was performed using a VG 7070E mass spectrometer. Mass spectra were recorded in the EI mode at 70 eV and 200 μA ionizing current. The separations were achieved with a DANI 3800 gas chromatograph; column, 6 ft x 2 mm i.d. 3% OV 225 on 100—120 mesh Gas Chrom Q; oven temperature 70° isothermal for 8 min and then temperature programmed to 200° C at 6°/min; injector and separator 180° C; helium 8 ml/min; interface and MS source 180° C. Mass spectra were initially identified from published sources [7].

For comparative GC and GC-MS, the following authentic materials were available; (E)-2-hexenol (Aldrich), (£)$\_1$(£)$\_2$,2,4-hexadienyl acetate (Dr. D. W. Knight, Nottingham), benzyl alcohol (B.D.H.) and 2-phenyl ethanol (B.D.H.). Identities of all standard materials were confirmed by (1H) NMR. 2-Octenyl propionate was obtained from 2-octenyl acetate (PPF International: a mixture of (£)- and (E)-isomers) by alkaline hydrolysis followed by subsequent re-esterification with propionic acid using the method of Hassner and Alexanian (1978).

Results and Discussion

A reconstructed ion current trace is shown in Fig. 1. Peak assignments and their corresponding mass spectra are given in Table I. The greater part of the volatile material consisted of two aromatic alcohols; benzyl alcohol (peak 4, 31% total) and 2-phenyl ethanol (peak 5, 42% of total). The remainder consisted of two aliphatic esters, 2,4-hexadienyl acetate, 2-octenyl propionate, and an alcohol,

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Table I. Composition of scent from ventral abdominal scent gland VII–VIII from *Leptoglossus australis*, and mass spectra of the scent components. Component numbers correspond to peaks 1 to 5 in Fig. 1.

<table>
<thead>
<tr>
<th>Component No.</th>
<th>Identity</th>
<th>Composition [%]</th>
<th>Mol. Wt.</th>
<th>Masses of fragment ions (% abundance) in order of decreasing abundance&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(E)-2-hexenol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2</td>
<td>100</td>
<td>57(100), 41(32), 43(19), 82(19), 44(18), 67(18), 55(8), 71(8)</td>
</tr>
<tr>
<td>2</td>
<td>(E,E)-2,4-hexadienyl acetate&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6</td>
<td>140</td>
<td>43(100), 79(33), 41(18), 80(15), 81(13), 140(M+), 98(8), 53(7)</td>
</tr>
<tr>
<td>3</td>
<td>2-octenyl propionate&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>19</td>
<td>184</td>
<td>57(100), 41(45), 43(38), 55(35), 68(19), 81(19), 110(7), 95(7)</td>
</tr>
<tr>
<td>4</td>
<td>benzyl alcohol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>31</td>
<td>108</td>
<td>79(100), 108(89,M+), 107(68), 77(52), 51(23), 91(15), 53(12), 63(8)</td>
</tr>
<tr>
<td>5</td>
<td>2-phenyl ethanol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>42</td>
<td>122</td>
<td>91(100), 92(73), 122(M+), 65(22), 51(8), 77(4), 105(4), 63(4)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Significant ions above m/z 40.

<sup>b</sup> Confirmed by mass spectrum and retention time (OV 225) of authentic compound.

<sup>c</sup> Bond geometry not determined.

Fig. 1. Reconstructed ion current trace of ventral abdominal scent gland VII–VIII from *Leptoglossus australis* obtained by El-GC-MS. GC conditions: 6 ft x 2 mm i.d. glass column packed with 3% OV 225 on 100–120 mesh Gas Chrom Q; injection temperature 180 °C; oven 70 °C for 8 min and then temperature programmed to 200 °C at 6 °C min.

2-hexenol. Retention tests (GC, OV 101) were in agreement with identifications from mass spectral data.

These results on *L. australis* conform to a pattern previously established for the genus *Leptoglossus* (6 species investigated) in N. America [2]. The secretions from the ventral abdominal VII–VIII gland, although dominated by aromatic materials [2, 5], are specifically distinct. Benzyl alcohol it seems is the one predictable component in the genus. It is common to all 7 species of *Leptoglossus* now studied although ranging in amount from 31% (*L. australis*) to 100% (*L. oppositus*). 2-Phenyl ethanol, a major component (42%) in *L. australis* has been recorded previously only in one N. American species (*L. gonagra*, 100%) [2]. The occurrence of aliphatic materials is similarly unpredictable. n-Octanol (23%) was found in *L. corculus* [2]. Variations on this theme extend to other genera of coreid bugs [6]. In a unique small sample of abdominal ventral VII–VIII gland material from *Anoplocnemis curvipes* (F.), we detected benzyl alcohol, hexenyl butanoate and hexanal.

The development of the ventral VII–VIII abdominal scent gland in *Leptoglossus* has been correlated with sexual maturity but under laboratory conditions, in experiments using glandless males, found not to be essential for mating success [5]. A function for the secretion as a long range attractant for females is possible but not proved. Sex biased predation on male bugs by tachnid para-
sitoids (Phasiinae) could be linked with emissions of secretion from the male specific ventral abdominal VII–VIII gland [2].

Acknowledgements

We thank the Higher Education Division of the British Council and the Research and Higher Degrees Committee, Bayero University, for their financial support. Purchase of GC-MS equipment was assisted by funding from the SERC.