N,N-DIMETHYL-β-PHENYLETHYLAMINE AND BORNYL ESTERS FROM THE HARVESTMAN

Sclerobunus robustus (ARACHNIDA: OPILIONES)

O. Ekpa, J.W. Wheeler*  J.C. Cokendolpher  R.M. Duffield
Department of Chemistry  Department of Biological Sciences  Department of Zoology
Howard University  Texas Tech University  Howard University
Washington, D.C. 20059  Lubbock, Texas 79409  Washington, D.C. 20059
USA  USA

Abstract: The defensive secretion of Sclerobunus robustus contains camphene, limonene, bornyl acetate, bornyl propionate, nicotine and N,N-dimethyl-β-phenylethylamine, a new natural product, as the major component.

The defensive secretions of daddy long-legs (harvestmen) contain a variety of low molecular weight organic compounds including either quinones and/or phenols, or short-chain acyclic ketones and alcohols.

Gas chromatographic-mass spectroscopic analysis of methylene chloride extracts of the defensive secretions of Sclerobunus robustus showed four major peaks and two minor ones for both males and females (Figure 1). The chief component (50% of volatiles present) exhibited a mass spectrum having a cluster of small peaks at m/z 149, 148, 147 and 146 with additional peaks at m/z 133, 132, 118, 117, 116, 105(0.5), 104(0.5), 103(0.6), 91(2), 77(2), 65(2), 58(100), 51(2), 42(10). The base peak at m/z 58 and peaks at 65, 77, 91 and 105 suggested either a tertiary or secondary aromatic amine. The mass spectrum of the unknown was similar to that of commercially available ephedrine (M.W. 165) but the m/z 77 peak was much stronger and the GC retention time was longer. N,N-Dimethyl-β-phenylethylamine was prepared from 2-phenylethylamine, formaldehyde and formic acid by the method of Icke et al. The unknown's mass spectrum was identical in all respects to that of the synthetic compound and the two samples coeluted on both columns, establishing the structure of the major component as 2.

A second nitrogen-containing compound (5%) exhibited a strong molecular ion at m/z 162, an intense M-1 ion with additional ions at m/z 133(20), 130(5), 109(8), 92(5), 84(100) and 42(28). Comparison of the mass spectrum with published spectra and coinjection with an authentic sample identified this material as nicotine.

1315
The remaining two major components appeared to be a terpenoid acetate (20%) and the related propionate (20%) on the basis of their mass spectra. The acetate exhibited a molecular ion at m/z 196(0.5) with other ions at m/z 154(8), 136(28), 121(30), 108(20), 95(85), 80(20), 43(100) and 41(43). The M-42 and M-60 peaks suggested an acetate and the peaks at m/z 93, 121 and 136 appeared terpenoid. The other GC peak exhibited a molecular ion at m/z 210(2) with other ions at m/z 154(7), 136(33), 121(32), 109(23), 108(21), 95(82), 93(48), 57(100) and 41(57). The losses of 56 and 74 suggested a related propionate. Comparison of the mass spectrum of the acetate with reported spectra of bornyl and isobornyl acetates\(^7\) indicated that this might be the bornyl series. Synthesis of bornyl and isobornyl acetates and propionates and comparison of their retention times and mass spectra established these two peaks as bornyl acetate (4) and bornyl propionate (5). The remaining two minor components of the secretion were identified as camphene (6) (2%) and limonene (7) (3%) by comparison with published spectra\(^6\) as well as spectra and retention times of authentic samples.

Compounds 2-7 are new natural products isolated from the defensive secretions of opilionids. Camphene and limonene have been reported in ants\(^8\) and limonene in termites.\(^9\) Bornyl acetate, bornyl propionate, nicotine and N,N-dimethyl-\(\beta\)-phenylethylamine are unknown in arthropods, although bornyl acetate and bornyl propionate have recently been shown to be sex pheromone mimics for the American cockroach.\(^10\)

This is the first chemical study of a member of the superfamily Travunioidea (family Triaenonychidae), thought to be the most primitive of the laniatorid superfamilies.\(^11\)
secretion of *Sclerobunus* is very different from the quinones and phenols secreted by other laniatorids (superfamily Gonyleptoidea - families Gonyleptidae, Cosmetidae and Stygnommattidae).

It appears that the defensive secretions of members of the Travunioidea may prove to be a diverse source of opilionid natural products.

![Figure 1](image_url)

*Figure 1.* Gas chromatogram of a methylene chloride extract of *Sclerobunus robustus* secretion. Numbered peaks are identified in the discussion. Drawing from the original.

**REFERENCES AND NOTES**


3. Opilionids were collected in Lincoln, Otero and Grant Counties, New Mexico (elevation 6,500-9,000 ft.) during March and August, 1980. Secretions were absorbed onto filter paper squares which were then extracted in methylene chloride. The specimens and filter paper squares were handled with forceps.

4. A Finnigan 3200E combined gas chromatograph-mass spectrometer (EI) with 1.8 meter x 1 mm
10% SP-1000 and 3% OV-17 columns was used.


(Received in USA 3 November 1983)