

CITRONELLYL CITRONELLATE AND CITRONELLYL GERANATE  
IN THE EUROPEAN HORNET, Vespa crabro (HYMENOPTERA: VESPIDAE)

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Abstract: Citronellyl citronellate and citronellyl geranate, new insect natural products, have been identified in the van der Vecht's gland of the European hornet.

Gas chromatographic-mass spectrometric analysis<sup>1</sup> of excised seventh sternal glands (also called the van der Vecht's gland) of the European hornet,<sup>2</sup> Vespa crabro, indicated the presence of two terpenoid components in addition to the normal straight chain acids and odd-carbon-containing alkanes. These compounds, with apparent molecular weights of 308 and 306, both exhibited base peaks at  $m/z$  69 with other important ions at  $m/z$  41(88), 55(38), 81(42), 95(35), 109(28), 123(25), 138(18), 152(6), 153(5), 170(1), 171(0.6) and 308(0.5) for 1 and  $m/z$  41(93), 55(20), 81(30), 82(28), 95(24), 100(5), 109(8), 123(31), 138(15), 151(18), 168(1), 169(1), 306(0.5) for 2. Attempted silylation indicated no hydroxyl groups.

Hydrogenation of the mixture (after removal of the acids) gave a single compound 3 (with an integrated GC area comparable to that of 1 plus 2) that showed  $m/z$  41(60), 43(100), 57(80), 70(82), 85(35), 87(12), 97(15), 111(20), 140(30), 155(5), 157(3), 173(18), 227(4) and 312(0.5). It thus appeared that 1 contained two reducible sites and that 2 contained three reducible sites. The ion at  $m/z$  155 was attributed to the acyl group  $C_9H_9C\equiv O^+$  and that at  $m/z$  173 to the protonated acid fragment  $C_9H_9CO_2H_2^+$ . The ion at  $m/z$  140, attributed to an alkyl fragment  $C_{10}H_{20}^+$ , further indicated that the reduced compound was an ester, similar to esters previously isolated from bee Dufour's glands.<sup>3</sup> The ions at  $m/z$  152, 153, 170 and 171 in 1 indicated one double bond in the acid fragment and the ion at  $m/z$  138 indicated one double bond in the alcohol portion. The ions at  $m/z$  151, 168 and 169 in 2 indicated two double bonds (or a triple bond) in the acid portion of 2 while the ion at  $m/z$  138 showed only one double bond in the alcohol fragment. Hydrolysis of the crude extract gave citronellool. Hydrogenation of citronellyl decanoate gave a compound with a molecular weight of 312 which was different from 3.

These data suggested that 1 and 2 might be esters of terpenoid acids and alcohols, compounds previously unknown in animals. Citronellyl citronellate, citronellyl geranate and citronellyl nerate were prepared from citronellool and the appropriate acid chlorides.<sup>4</sup> Their infrared and nuclear magnetic resonance spectra were in accord with the assigned structure. The retention times and mass spectra of citronellyl citronellate and citronellyl geranate were identical to those of the hornet compounds 1 and 2; no trace of the nerate was found. Hydrogenation of each of the synthetic materials gave a compound identical to 3. The ratio of 1 to 2 in the hornet extract

was 1:2 and these esters represented <5% of the total volatiles. The amount per individual is estimated at <0.1  $\mu\text{g}$ . This is the first chemical isolated from the seventh sternal gland, an exocrine gland unique to social vespids. The function of the gland is unknown.



Citronellyl citronellate has been reported in the essential oil of *Eucalyptus citriodora*<sup>5</sup> and citronellyl geranate is a constituent of Bulgarian rose oil.<sup>6</sup> Neither of these compounds has been found previously in an animal source.<sup>7</sup>

#### REFERENCES AND NOTES

1. A Finnigan 3200 E GC-MS utilizing 1.6 m 3% OV-17 on Supelcoport 60/80 column was used, temperature programmed from 50<sup>o</sup>-300<sup>o</sup>C at 12<sup>o</sup>/min.
2. Specimens, collected by net in College Park, MD. and at the Howard University property at Beltsville, MD., were placed individually in glass shell vials. These were kept in an ice chest, transported to the lab and dissected within 48 hrs. The seventh sternal glands were excised from 50 workers and extracted with methylene chloride. The solution, filtered through anhydrous sodium sulfate, was reduced to 300  $\mu\text{l}$  with nitrogen gas. Five extracts and a control extract of exoskeleton were analyzed.
3. R. M. Duffield, A. Fernandes, C. Lamb, J. W. Wheeler and G. C. Eickwort, *J. Chem. Ecol.*, 1981, 7, 319; A. Fernandes, R. M. Duffield, J. W. Wheeler and W. E. LaBerge, *J. Chem. Ecol.*, 1981, 7, 453.
4. Citronellic and geranic acids were prepared by oxidation of citronellal and citral with silver oxide. The acid chlorides were prepared using excess thionyl chloride (2:1) and the acids at room temperature with ether as solvent; E. Campaigne and W. M. LeSeur, *Org. Syn.*, 1963, Coll. Vol. 4, 919.
5. M. L. Sharma and K. L. Handa, *Indian Soap J.*, 1963, 29, 160.
6. C. Mann and T. Smith, *Int. Congr. Essent. Oils*, 1979, 7, 458.
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