Tetrahedron Letters No. 46, 4635 - 4638, 1972 Pergamon Press. Printed in Great Britain.

γ-DODECALACTONE FROM ROVE BEETLES

J. W. Wheeler[1]

Department of Chemistry, Howard University

Washington, D. C. 20001

G. M. Happ[2]

Department of Biology, New York University

University Heights, N. Y. 10453

J. Araujo, J. M. Pasteels

Zoologie Générale, Université Libre de Bruxelles

Bruxelles, Belgique

(Received in USA 18 September 1972; received in UK for publication 10 October 1972)

Many staphylinid beetles possess exocrine glands, yet the secretions of only two species have been identified[3], the principal components being monoterpenes. A more complex molecule has been found in the blood of a staphylinid[4]. The pygidial secretions of two species of staphylinids of the genus Bledius contain, in addition to terpenes, a benzoquinone, undecene, and γ-dodecalactone, which has not been reported previously from insect sources.

Pygidial glands of Bledius mandibularis and B. spectabilis from the Atlantic coasts of the United States and Europe, respectively[5], were excised and immersed in methylene chloride and the resulting extract analyzed by combined gc-ms[6]. This revealed the same five components in both species: The mass spectrum of the first component was similar to reported spectra for 1-undecene[7] and identical to that of an authentic sample. The presence of the terminal double bond was confirmed by an absorption at 11.0 μ in its infrared spectrum and by ozonolysis to decanal, identified from the mass spectrum of the aldehyde and its methoxime[8].

Methyl p-benzoquinone (II) was identified by comparison of its mass spectrum with that of an authentic sample. In addition to the parent peak at m/e 122, it exhibited large peaks at m/e 94,

82, 68, 66, and 54. Within the spectrometer source, a small portion was reduced to the hydroquinone (m/e 124),[9] but this compound was not detected in the primary gas chromatography.

The relative concentrations of the two terpene aldehydes, neral (III) and geranial (IV) approached those of commercial citral (~1:2) and their mass spectra and retention times were identical to those of authentic samples.

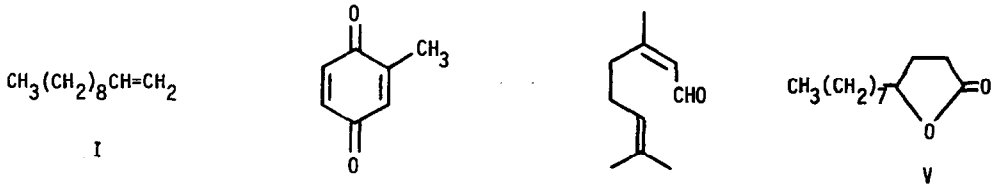
γ-Dodecalactone (V), the major component in the extracts of both species, eluted at 155°C on column A and 200° on column B and showed a base peak at m/e 85 with smaller peaks at m/e 128, 180, 197, 198, and 199. Chemical ionization mass spectroscopy indicated that the molecular ion was m/e 198 exhibiting a quasi-molecular ion at m/e 199[10]. The base peak at m/e 85 is characteristic of γ-lactones[11] and distinguishes them from the isomeric δ-lactones which have a base peak at m/e 99. Preparative gas chromatography (1% OV-17) gave material whose proton magnetic resonance spectrum exhibited intense absorption for the terminal CH_3- at δ0.9 and -CH_2- absorption at 1.2 as well as weak additional absorption at 2.3 and 4.4. The infrared spectrum showed a strong absorption at 5.6 μ. Comparison of the unknown with an authentic sample of γ-dodecalactone[12] indicated identical retention times on both columns as well as identical mass spectra.

Although all five components are present in both species, the proportions differ: B. mandibularis - I, II, III, IV, and V in the ratios 5:6:1:17:70; B. spectabilis 14:1:2:6:77.

At least three distinct biogenetic pathways must be involved in the synthesis of these secretions from the pygidial glands of Bledius. Geranial and neral (neither of which has been found previously in beetles) are probably formed via the mevalonic acid pathway responsible for the production of other insect terpenes[13]. Benzoquinone biosynthesis has been described in tenebrionid beetles[14]. Undecene and γ-dodecalactone may stem from a common precursor, a β, γ-unsaturated C_{12} acid, which either decarboxylates giving undecene or effects addition across the double bond to form the lactone.

γ-Dodecalactone, the first γ-lactone from insect sources has a fruity odor, and has been isolated from various fruits[15] and butterfat[16]. A few other lactones have been reported from exocrine secretions of animals, functioning as queen pheromones in hornets[17], and sex-related recognition pheromones in male black-tailed deer[18]. The deer pheromone, cis-γ-dodec-6-enoic acid lactone differs from the major component of Bledius secretions by only an addition double bond and has also been found in butterfat[18].

When menaced by another Bledius, an ant, or a pair of forceps, Bledius bends the tip of its abdomen forward and applies pygidial secretion to the attacker, suggesting that the secretion serves a defensive function. It is also feasible that one or more components regulate the growth of algae which flourish within the burrows of Bledius and upon which the insects feed[19].



I II III - cis IV - trans V

References and Notes

1. This work was completed during the tenure of a Special Fellowship in the laboratory of Dr. H. M. Fales, National Heart and Lung Institute, National Institutes of Health, Bethesda, Maryland. We thank Dr. Fales and the Public Health Service (Grant CC-00270) for generous support.

2. The partial support of USPHS Grant CC-00343 and NIH Biomedical Sciences Support Grants to New York University is gratefully acknowledged,

3. H. Schildknecht, Zeit. Naturforsch., 23b, 1213 (1968); S. A. Abou-Donia, L. J. Fish, and G. Pattenden, Tetrahedron Lett., 43, 4037 (1971).

4. C. Cardani, D. Ghiringhelli, R. Mondelli, and A. Quilico, ibid., 29, 3537 (1965); T. Matsumoto, M. Yanagiya, S. Maeno, and S. Yasuda, ibid., 60, 6297 (1968).

5. B. mandibularis were excavated from their burrows south of Dewey Beach, Delaware. We thank Dr. L. Hermann for showing us this large population of beetles and each of the following for assisting in the tedious collecting: E. Booker, R. H. Chung, S. K. Oh, W. S. Stewart, C. C. Shroff, Y. N. Vaishnav, D. von Endt, S. J. Uhm, J. B. Wheeler, M. Wheeler, and C. M. Happ. B. spectabilis were obtained in the same manner in September 1971 near Roscoff, Finistere Nord, France.

6. A combined gas chromatograph--mass spectrometer (LKB 9000) was used with two columns: A, 1% OV-17 temperature programmed from 70°C and B, 10% SP-1000 temperature programmed from 40°C at 8°/min. both on Supelcoport 80-100 mesh (Supelco, Bellefont, Pa.).

7. Comparison of mass spectra with known compounds was greatly facilitated through the use of a mass spectra search program written by Dr. S. R. Heller of DCRT, NIH.

8. H. M. Fales and T. Luukkainen, Anal. Chem., 37, 955 (1965); B. S. Middleditch and B. A. Knights, Org. Mass Spectrom., 6, 179 (1972).

9. H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Molecules", Holden Day, San Francisco, 1967, p. 118.

10. We thank Dr. G. W. A. Milne of NHLI, NIH for this measurement.

11. Ref. 9, p. 206.

12. K and K Laboratories.

13. R. B. Clayton, in "Chemical Ecology" (E. Sondheimer and J. B. Simeone, ed.,), Academic Press, New York, 1970, pp. 235-280.

14. J. Meinwald, J. E. Rogers, Jr., and T. Eisner, Abstr. Int. Symp. Chem. Nat. Prod. (1964), pp. 138-139.

15. B. Willhalm, E. Palluy, and M. Winter, Helv. Chim. Acta, 49, 65 (1966); J. J. Broderick Am. Perfumer Cosmet., 81, 43 (1966); C. S. Tang and W. G. Jennings, J. Agr. Food Chem., 16, 252 (1968).

16. G. Jurriens and J. M. Oele, J. Am. Oil Chemist Soc., 42, 857 (1965); D. A. Forss, G. Urbach, and W. Stark, Int. Dairy Conq. Proc. (Munich), 3, 211 (1966).

17. R. Ikan, R. Gottlieb, E. D. Bergman, and J. Ishay, J. Insect Physiol., 15, 1709 (1969).

18. R. G. Brownlee, R. M. Silverstein, D. Müller-Schwarze, and A. G. Singer, Nature, 221, 284 (1969).

19. E. Bro Larsen, Trans. 9th Ent. Int. Congress Entomol., 1, 502 (1952).