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DEFENSIVE MECHANISMS OF ARTHROPODS. XXIII. AN ALLENIC SESQUITERPENOID FROM THE GRASSHOPPER ROMALEA MICROPTERA

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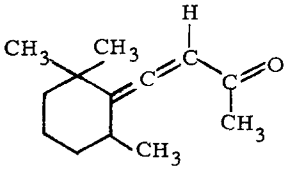
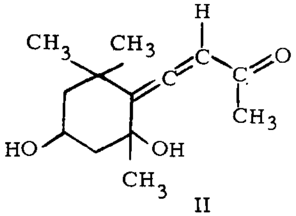
The large flightless grasshopper, Romalea microptera, responds to disturbance by emitting a froth from the anterior respiratory openings (spiracles) on its thorax (1). The froth is a mixture of respiratory air and brownish secretion produced by gland cells that beset the walls of the respiratory tubes leading inward from the spiracles. The secretion has a repellent effect on ants and possibly other predators. Details concerning the cytology of the cells, the mechanism of froth production, and the function of the secretion, will be published elsewhere. We here report the characterization of a new conjugated allenic ketone that constitutes a major component of the secretion.

Secretion was collected from over 1, 000 adult grasshoppers by causing them to discharge their froth into glass capillaries held against their spiracles. The "milkings" of both sexes were initially kept separate, but on extraction with methylene chloride, followed by chromatography of the resultant extract on silica gel, both samples yielded the same colorless, crystalline compound, mp 128 - 128. 5°. In its infrared spectrum, this compound showed characteristic absorption at 2. 9, 5. 15 and 6. 00 μ, associated with hydroxyl, allene, and conjugated carbonyl functions, respectively. While the material could not itself be purified by g. l. c. without decomposition, conversion to a trimethylsilyl derivative could be accomplished in the usual way (2), and this derivative was readily purified by g. l. c. techniques. The high resolution mass spectrum (3) of the purified derivative established the molecular formula to be $C_{19}H_{36}O_3Si_2$ (m/e 368. 2201), corresponding to the bis-trimethylsilyl derivative of a $C_{13}H_{20}O_3$ diol.

The conjugated carbonyl function detected in the infrared spectrum of the original unknown could also be seen in its ultraviolet absorption spectrum, which showed a single strong band at 232 mμ (ϵ = 12,500). While there are very few references to the spectral characteristics of conjugated keto-allenes in the literature, the closely analogous absorption reported for the model compound I (maximum at 230 mμ; ϵ = 16,000) (4) provides an excellent basis for including this chromophore in the structure of the unknown.



I

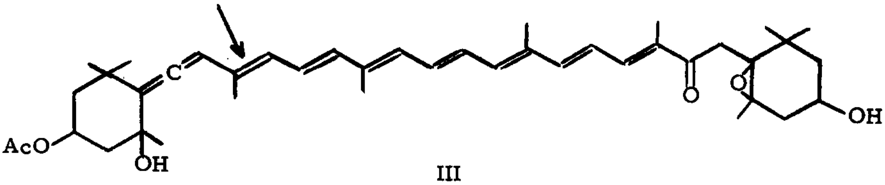


II

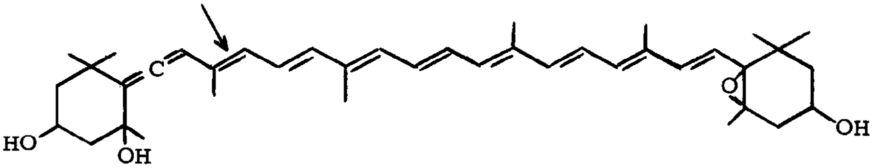
Thus far, the three oxygen atoms have been defined as two hydroxyl groups, and a carbonyl group which appears to be conjugated with an allenic system. The molecular formula $C_{13}H_{20}O_3$ requires structures with a total of four double bond plus ring equivalents. Since the ultraviolet chromophore accounts for three of these, the unknown must be either monocyclic, or acyclic with one undetected double bond. The evidence obtained from the n. m. r. spectrum permitted characterization of most of the twenty protons, and led to the monocyclic alternative II, which we now propose as the structure of this novel natural product. The key features of the n. m. r. spectrum ($CDCl_3$ solution; 100 Mc) were three sharp, three-proton singlets at 1.16, 1.36 and 1.40 ppm (three isolated methyl groups), a three-proton singlet at 2.15 ppm (methyl ketone), a one-proton singlet ($w_{1/2}$ 2 cps) at 5.80 ppm (isolated olefinic proton), a broad multiplet ($w_{1/2}$ ~32 cps) at 4.28 ppm (axial proton α to a hydroxyl group), and two protons exchangeable with D_2O at 1.40 - 1.55 ppm (hydroxyl protons).

A detailed analysis of these data not only provides strong support for structure II (once the hypothesis that we are dealing with a degraded sesquiterpene is made), but also indicates that the two hydroxyl functions are probably trans to one another, with the secondary hydroxyl group occupying an equatorial position (5). The configuration of the allenic group remains undetermined, however, and further work will be required to elucidate this stereochemical detail.

While naturally occurring allenes are far from common, the recently characterized carotenoid pigments fucoxanthin (III) (6) and neoxanthin (IV) (7) provide very close analogies for structure II. In particular, it may be noted that oxidative fission of the appropriate double bond in III or IV (indicated by an arrow above each formula) would lead directly to the formation of II or its monoacetate. In view of the wide distribution of these allenic pigments in the plant kingdom (6, 7), it appears likely that II is produced in the grasshopper by degradation of these or closely related carotenoids.



III



IV

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References and Notes

1. See Fig. 2G in: T. Eisner and J. Meinwald, *Science*, **153**, 1341 (1966).
2. For an excellent leading reference, see J. Diekman, J. B. Thomson and C. Djerassi, *J. Org. Chem.*, **32**, 3904 (1967).
3. We are indebted to Mr. Paul de Montellano for carrying out these mass spectral measurements on the double focusing MS-9 instrument at Harvard University.

4. T. Miki and Y. Hara, Pharm. Bull. (Japan), **4**, 89 (1956).

5. We hope to publish these arguments in full detail, along with the results of related synthetic work which is now in progress.

6. R. Bonnett, A. K. Mallams, J. L. Tee, B. C. L. Weedon and A. McCormick, Chem. Commun., 515 (1966).

7. A. K. Mallams, E. S. Waight, B. C. L. Weedon, L. Cholnoky, K. Györgyfy, J. Szabolcs, N. I. Krinsky, B. P. Schimmer, C. O. Chichester, T. Katayama, L. Lowry and H. Yokayama, Chem. Commun., 484 (1967).