The Isolation of Dihydromexicanin E from *Helenium autumnale L.*

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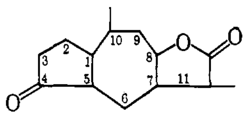
Recently we had occasion to extract a batch of *Helenium autumnale* L. seeking a supply of the sesquiterpene lactone, helenalin, for use in chemical studies.[1] The plants were obtained in late summer, 1963, in the vicinity of Chapel Hill, North Carolina.[2] They were air-dried and 7 kg. of finely ground leaves and stems was extracted in the usual way with methylene chloride.[3] After treatment of an alcoholic solution of the crude extract with aqueous lead acetate, the clarified aqueous alcoholic solution was partially evaporated and extracted with methylene chloride. When attempted crystallization of the dried extract from benzene failed to produce helenalin, as expected, the material was subjected to chromatography in benzene on II–III Activity Woelm neutral alumina. Repeated chromatography of the benzene eluates yielded 14.9 g. of a product which crystallized from ethyl acetate. Repeated crystallization from the same solvent afforded colorless rods, m.p. 133–135°, $[\alpha]^{25}\text{D}$ $-188°$ ($CHCl_3$), $\lambda_{\text{max}}^{\text{EtOH}}$ 222 mμ (ε 10,400), $\lambda_{\text{max}}^{\text{NaOH}}$ 242 mμ; ν^{Nujol} 1760 (γ-lactone), 1700, and 1586 (cyclopentenone) cm.$^{-1}$.

The n.m.r. spectrum,[4] τ 7.80 dd (H-2), 6.25 dd (H-3), 4.60 c (H-8), and 1.23 d and 1.13 d (C-10 and C-11 methyl), suggested a norsesquiterpenoid structure.

Anal. Calcd. for $C_{14}H_{18}O_3$; C, 71.77; H, 7.74. Found: C, 71.79; H, 7.84.

Finally, comparison of published data for dihydromexicanin E[5] pointed to the identification of our substance.



Dihydromexicanin E

Through the courtesy of Dr. J. Romo, University of Mexico, Mexico City, Mexico, a sample of dihydromexicanin E was obtained for direct comparison and proved to be identical by the usual criteria. As far as we know, this represents the first isolation of this substance from plant material. It is interesting that no helenalin could be isolated from this sample of *Helenium autumnale* L. inasmuch as it is usually the principal sesquiterpene component.[6]

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[1] R. A. Lucas, S. Rovinski, R. J. Kiesel, L. Dorfman, and H. B. MacPhillamy, *J. Org. Chem.*, **29**, 1549 (1964).

[2] The plant material was collected and identified by H. E. Ahles, Botany Department, University of North Carolina, Chapel Hill, N. C., to whom our thanks are due.

[3] E. P. Clark, *J. Am. Chem. Soc.*, **58**, 1982 (1936).

[4] This was run in deuteriochloroform solution on a Varian A-60 n.m.r. spectrometer using tetramethylsilane as internal reference; multiplets are described: d, doublet; dd, doublet of doublets; c, complex band whose center is given.

[5] A. Romo de Vivar and J. Romo, *J. Am. Chem. Soc.*, **83**, 2326 (1961); J. Romo, A. Romo de Vivar, and W. Herz, *Tetrahedron*, **19**, 2317 (1963).

[6] E. P. Clark, *J. Am. Chem. Soc.*, **58**, 1982 (1936); **61**, 1836 (1939); **62**, 597 (1940).

Bromination of 6-Benzoyl-2,5-diphenyl-2-phenylglyoxoyl-3,4-dihydro-2H-pyran

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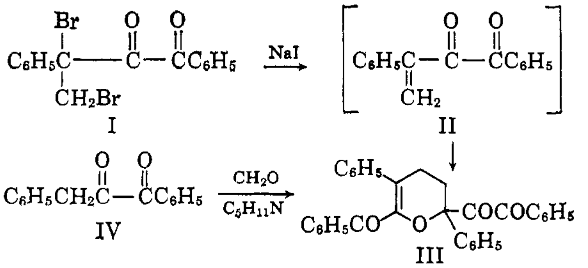
Treatment of 3,4-dibromo-1,3-diphenyl-1,2-butanedione (I) with sodium iodide in acetone previously[2] was reported to produce a dimeric substance which was formulated as 6-benzoyl-2,5-diphenyl-2-phenylglyoxoyl-3,4-dihydro-2H-pyran (III). The structural assignment was based primarily on the elemental analysis,[3] molecular weight of the material, and the analogy to other dimers of similar and proven structure.[3] Presumably III arose *via* the dimerization of 1,3-diphenyl-3-butene-1,2-dione (II) although II could not be isolated. Additional support for this view was obtained by the production of III from the reaction of 1,3-diphenyl-1,2-propanedione (IV) with formaldehyde in the presence of a catalytic amount of piperidine.



Treatment of III with 1 equiv. of bromine in dry carbon tetrachloride provided hydrogen bromide and a yellow solid (V, $C_{32}H_{22}O_4$) in 74.6% yield. The same substance could be generated from III using excess bromine or N-bromosuccinimide.

The ultraviolet spectrum of V, λ_{max} 250 mμ (ε 30,550), 357 (16,500), indicated considerable unsaturation; however, no tractable hydrogenation product could be obtained. Although oxidation of V with periodic acid or ozone provided no information as to the nature of V, treatment of the substance with alkaline hydrogen peroxide provided 2 equiv. of benzoic acid and a high melting acid (VI, $C_{18}H_{14}O_4$).

The dibasic nature of VI was confirmed by the formation of a dimethyl ester (VII) when VI was treated with excess diazomethane. Hydrogenation of VII provided a mixture of diastereoisomers. Decarboxylation of VI was accomplished smoothly using a copper–quinoline catalyst at 220°. Chromatography of the product provided *trans*-1,4-diphenyl-1,3-butadiene (VIII), identical in all respects with an authentic sample. On the basis of these conversions, the bromination product (V) can be formulated as 1,3,6,8-tetraphenylocta-3,5-diene-1,2,7,8-tetraone.

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[1] Abstracted in part from a dissertation by R. L. Smith submitted to the University of North Carolina in partial fulfillment of the requirements for the Ph.D. degree, June, 1962.

[2] C. L. Stevens and R. G. Hiskey, *J. Org. Chem.*, **24**, 32 (1959).

[3] K. Alder and E. Ruden, *Ber.*, **74**, 920 (1941); C. Mannich, *ibid.*, **74**, 557 (1941); H. Fiesselmann and F. Meisel, *ibid.*, **89**, 657 (1956).