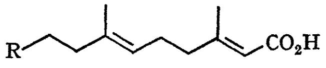
# Identification and Synthesis of *trans,trans*-3,7-Dimethyl-2,6-decadien-1,10-dioic Acid, a Component of the Pheromonal Secretion of the Male Monarch Butterfly†

By J. MEINWALD,* A. M. CHALMERS, T. E. PLISKE, and T. EISNER

(*Department of Chemistry, and Section of Neurobiology and Behavior, Cornell University, Ithaca, New York* 14850)

EXTRACTION of the hairpencils of *ca.* 6500 male monarch butterflies (*Danaus plexippus*) with methylene chloride as previously described,[1] and repeated t.l.c. of the extract, resulted in the isolation of a colourless solid (11·8 mg., 6% of the non-lipid material), contaminated to a small extent (< 5%) with the previously described acid (II).[1] The i.r. spectrum ($CH_2Cl_2$) of this component showed peaks at 2·75, 2·87, 2·90—4·00m (OH), 5·87 br (CO) and 6·08 $\mu$; in diethyl ether two carbonyl bands (5·74 and 5·80 $\mu$) were observed. The u.v. spectrum [$\lambda_{max}$(n-pentane) 225 m$\mu$ (log $\epsilon$ 4·16, based on a molecular weight of 226 from mass spectral data)] supported the presence of a conjugated carbonyl function as suggested by the i.r. spectral evidence.

The mass spectrum revealed a parent ion at *m/e* 226 $(C_{12}H_{18}O_4)^+$,‡ and prominent ions at 208 $(C_{12}H_{16}O_3)^+$, 127 $(C_7H_{11}O_2)^+$, and 100 $(C_5H_8O_2)^+$; these results will be discussed elsewhere.[2] The n.m.r. spectrum ($CDCl_3$) offered good evidence for structure (I); two olefinic absorptions at $\tau$ 4·17 (s, 1H) and, $\tau$ 4·69br (1H) could be assigned to the deshielded $\alpha$-proton of an $\alpha\beta$-unsaturated acid and the proton of the trisubstituted double-bond respectively. Absorption at $\tau$ −0·19br (2H) corresponded to the two acidic protons, an assignment confirmed by $D_2O$ exchange. The signal at $\tau$ 8·32 (3H) was attributed to an allylic methyl group and poorly resolved absorption at $\tau$ 7·77 (7H) was consistent with four allylic methylene protons plus three allylic methyl protons deshielded by a *cis*-oriented carboxyl-group; finally absorption at $\tau$ 7·54br (4H) was attributed to the two additional methylene groups $\alpha$ and $\beta$ to the saturated carboxyl-group. These assignments are in good agreement with their counterparts in the acid (II).



(I) R=$CO_2H$
(II) R=$CH_2{\cdot}OH$

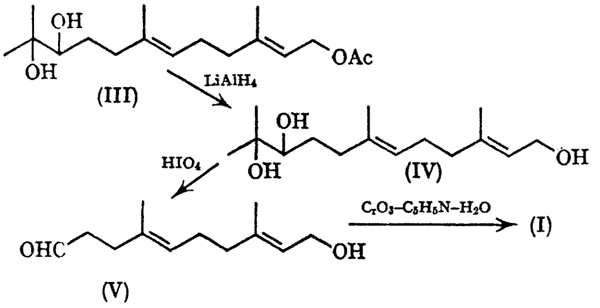
---

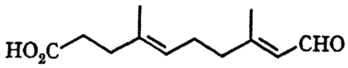
† Part of the series on Pheromones.

‡ Satisfactory mass analyses were obtained on an A.E.I. MS–902 C1 double focussing mass spectrometer for all ions mentioned.

Confirmation of the structure of compound (I) was obtained both by its synthesis from the acid (II) by the Cornforth oxidation method,[3] as well as from the diol (III) as outlined below. The acetoxy-diol (III) had been prepared previously in this laboratory from *trans,trans*-farnesol[4]

The synthetic material, m.p. 93—96°, was identical with the natural product [t.l.c., g.c. (on the derived dimethyl esters), i.r. and mass spectrometric results]. It is of note that the major product from the oxidation of (V) was the acid (VI) i.r. ($CHCl_3$) 5·73, 5·84, 5·99 $\mu$; u.v. $\lambda_{max}$(cyclohexane) 235 m$\mu$ (log $\epsilon$ 3·96); mass spectrum *m/e* 210, 127, and 83] which could be further oxidized to the diacid (I) with silver oxide. However, (I) prepared in this manner was contaminated to a small extent by an unidentified component detectable only by g.l.c.





(VI)

We acknowledge financial support of this research by the National Institutes of Health and by Hoffmann-LaRoche Inc. We thank Dr. S. Shrader and the Cornell High Resolution Mass Spectrometer Facility, supported by the N.I.H., for mass spectra.

(*Received, November 8th,* 1968; *Com.* 1523.)

---

[1] J. Meinwald, A. M. Chalmers, T. E. Pliske, and T. Eisner, *Tetrahedron Letters*, 1968, 4893.

[2] S. Shrader and A. M. Chalmers, unpublished work.

[3] R. H. Cornforth, J. W. Cornforth and G. Popjak, *Tetrahedron*, 1962, **18**, 1351.

[4] J. Meinwald, Y. C. Meinwald, and P. M. Mazzocchi, *Science*, in the press.