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PHEROMONES. III. IDENTIFICATION OF trans, trans-10-HYDROXY-3,7-DIMETHYL-2,6-DECADIENOIC ACID AS A MAJOR COMPONENT IN "HAIRPENCIL" SECRETION OF THE MALE MONARCH BUTTERFLY[1]

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Many butterflies and moths possess extrusible brushlike structures that serve for pheromone dissemination during courtship.[3] In the subfamily Danainae, the structures are called "hairpencils,"[4] and are present in the posterior abdomen of males only. In previous papers of this series,[5] we reported the identification of a pyrrolizidinone and two straight chain acetate esters from the hairpencils of the neotropical danaine, *Lycorea ceres ceres*. As part of a program designed to clarify the evolution of a chemical communicative system in a group of related animals, we now report the identification of the major component of the hairpencils of another danaine, the well known monarch butterfly, *Danaus plexippus*.

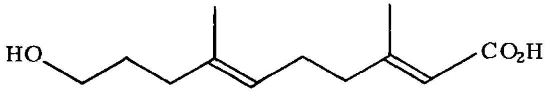
The tufts of hairs from hairpencils of 6,500 male monarchs were individually removed with forceps and extracted with methylene chloride.[6] Room temperature evaporation *in vacuo* afforded a yellow, viscous oil, the infrared spectrum of which showed absorption (CH_2Cl_2) at 2.76, 2.84, 2.94 - 4.17 (w), 5.78, 5.90, and 6.08 μ. Thin layer chromatography (on Mallinckrodt Silic AR TLC-7GF) revealed the presence of one main, highly polar component, which was isolated from a preparative plate as a colorless oil (190 mg) comprising about 80% of the non-lipid material. The remaining 20% of material is at present being investigated. No evidence for the presence of the pyrrolizidinone or the acetates found in *Lycorea ceres ceres*[5] was obtained.

The isolated major component showed infrared bands at 2.76, 2.88, 3.02 - 4.17 (w), 5.77, 5.89, and 6.07 μ (CH_2Cl_2), suggesting the presence of hydroxyl and α, β-unsaturated carboxyl groups. In diethyl ether, the carbonyl region showed bands only at 5.80 and 6.06 μ; the extra carbonyl absorption in the former solvent was assigned to carboxylic acid dimers. An ultraviolet maximum (cyclohexane) at 224.5 mμ (log ε 4.00, based on a molecular weight of 212 derived from mass spectral data) provided further support for the presence of a conjugated carboxyl grouping.

The mass spectrum exhibited a very small parent ion at m/e 212 ($C_{12}H_{20}O_3^+$)[7] accompanied by a large M-18 ion at m/e 194 ($C_{12}H_{18}O_2^+$). Diazomethane esterification of the acid afforded a methyl ester [infrared (CH_2Cl_2): 5.83 and 6.07 μ], the mass spectrum of which exhibited the expected parent ion at m/e 226. Further treatment with pyridine/acetic anhydride yielded an acetoxy methyl ester [infrared (CH_2Cl_2): 5.78, 5.82, and 6.06 μ; ultraviolet $\lambda_{max}^{cyclohexane}$ 223 mμ (log ε 3.99)]. Hydrogenation of this derivative over 5% palladium-charcoal in ethanol gave a saturated product [infrared (CH_2Cl_2): 5.78 μ] with a mass spectral molecular weight of 272. This was consistent with hydrogenation of two double bonds.

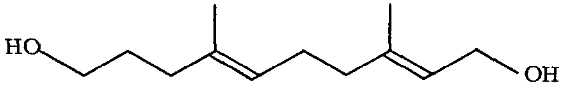
The NMR spectrum ($CDCl_3$) of the original unknown greatly reduced the number of structural possibilities; it revealed two olefinic absorptions at τ 4.28 (singlet) and τ 4.86 (broad), the former being suggestive of the deshielded environment of the α-proton of an α,β-unsaturated acid; the latter absorption indicated a trisubstituted double bond. The acidic and alcoholic protons appeared together at τ 3.02 as a broad signal (two protons) which readily disappeared with deuterium oxide addition. A two-proton triplet at τ 6.35 (J = 6 Hz) was assigned to a primary alcoholic methylene group adjacent to an additional methylene, while a singlet at τ 8.37 (three protons) indicated a vinyl methyl group. In addition, a two-proton multiplet at τ 8.73 corresponded to a normal chain methylene, leaving a poorly resolved absorption band at τ 7.80 (nine protons) to be assigned to six allylic methylene protons plus three allylic methyl protons deshielded by a *cis*-oriented carboxyl group.

These data, along with mass spectral fragmentations and previous results obtained with the queen butterfly (*Danaus gilippus berenice*)[8] suggested that the hydroxy acid had a degraded sesquiterpenoid skeleton; in particular *trans, trans*-10-hydroxy-3,7-dimethyl-2,6-decadienoic acid (I) seemed the most satisfactory structure. Support for this assignment was obtained by reducing the original acid with lithium aluminum hydride or aluminum hydride. The product



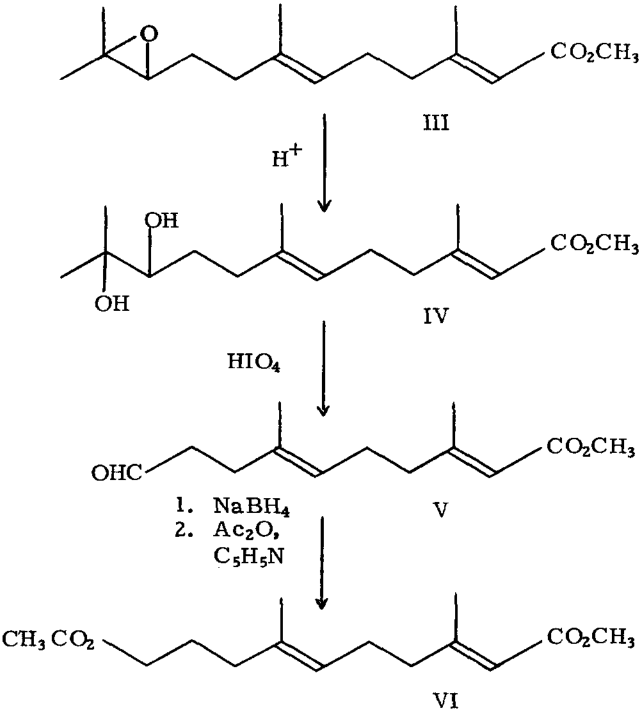
I

proved identical to an authentic sample of the *trans*, *trans* diol II, synthesized recently in this



II

Laboratory.[8] Finally, the reaction sequence outlined below was used to prepare an authentic sample of the *trans*, *trans* methyl ester acetate VI.[9] This synthetic material was



indistinguishable from that derived from the butterfly secretion on the basis of t. l. c., g. c., infrared, and mass spectral comparisons.

Compound I appears to be a special product of the glandular tissue associated with the wall of the stalk of the hairpencils. Thin layer chromatography of blood (including blood drained from the hollow stalks of the hairpencils), and of gut contents, failed to reveal traces of the compound. In view of the proven ability of insects to carry out the biosynthesis of farnesol[10] and several terpene aldehydes,[11] it is not at all unlikely that I is synthesized by the monarch.

References

1. This is the first paper of the series formally designated with a series heading. The previous two papers are given under reference 5, below. The study was supported by Grant AI-02908 from the National Institutes of Health, and by a gift from Hoffman-La Roche, Inc.
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6. We thank Mr. L. J. Friesen for sending us the butterflies live from Santa Barbara, Calif.
7. Satisfactory mass analyses were obtained on an MS-902C double focussing mass spectrometer for all ions mentioned. We wish to express our gratitude to Dr. S. Shrader and the Cornell High-Resolution Mass Spectrometer Facility, supported in part by the National Institutes of Health (Grant No. FR-00355), for invaluable help in this connection.
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9. We are indebted to Professor E. E. van Tamelen and Mr. John McCormick for supplying us with a sample of the epoxy ester III, as well as with procedures for its conversion to VI.
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