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PHEROMONES. VII. AFRICAN MONARCH: MAJOR COMPONENTS OF THE HAIRPENCIL SECRETION

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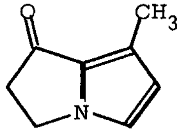
Male danaid butterflies have characteristic brushlike glandular organs called hairpencils, which are extruded from the posterior end of the abdomen and play an important role in courtship.[1] In order to elucidate the intricacies of a chemical communicative system in a group of related animals, we have been studying the substances that can be extracted from these brushes. To date, we have identified the major components of the hairpencils of three New World species: Lycorea ceres ceres from Trinidad [2], and Danaus gilippus (the Queen) and D. plexippus (the Monarch) from the U.S.A. [3-5] (see Table 1). In the case of D. gilippus, electrophysiological [6] and behavioral [7] studies indicate that the heterocyclic ketone I serves as a pheromone. The role(s) of the other compounds in Table 1 remain(s) unknown. We now report on the chemistry of D. chrysippus (the African Monarch), an Old World member of the subfamily Danainae.

Hairpencils were obtained from 67 males captures in Sierra Leone. Upon exhaustive extraction with methylene chloride, 12.8 mg. of a yellow oil was obtained. Thin layer chromatography (Silica gel G, 1% methanol in methylene chloride) revealed the presence of two major components which were then isolated by preparative TLC. The less polar of these (5.5 mg) was shown to be identical, by TLC, GLC, and IR, to the heterocyclic ketone I. The other (3.5 mg) resembled the terpene diol IV in TLC and IR. The NMR spectrum ($CDCl_3$) of this component showed: δ 5.38(t, 1, J = 6.5 Hz, C = C-H), 4.12(d, 2, J = 6.5 Hz, C = C-CH_2-O), 3.43 (d, 2, J=5.5 Hz, CH_2-O), 2.74 (s, 2OH, exchangeable with D_2O), 2.00(m, 2, CH_2-C = C), 1.64 (s, 3, C = C-CH_3), 1.37 (m, 5, 2CH_2, CH), 0.89(d, 3, J = 6.0 Hz, CH_3-C). The mass spectrum of the bis-trimethylsilyl derivative revealed a parent ion at m/e 316, corresponding to a $C_{10}H_{20}O_2$ diol.

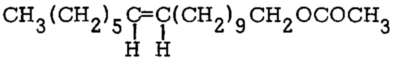
Lycores ceres ceres



I

$CH_3(CH_2)_{14}CH_2OCOCH_3$

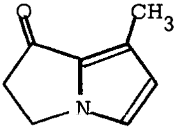
II

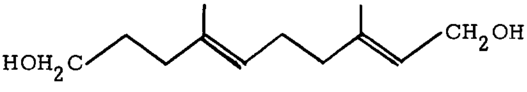


$CH_3(CH_2)_5\underset{H}{C}=\underset{H}{C}(CH_2)_9CH_2OCOCH_3$

III

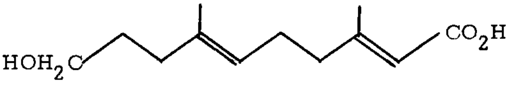
Danaus gilippus



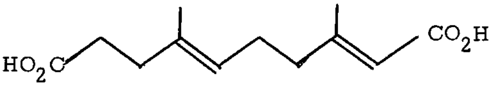


IV

Danaus plexippus



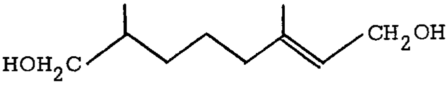
V



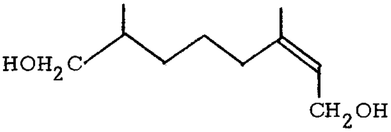
VI

Table 1

From these data, and in light of the similarity to IV, the molecule appeared to be 3,7-dimethyloct-2-en-1,8-diol. The two possible geometric isomers of this diol, E-(VII) and Z-(VIII), were prepared as described below.

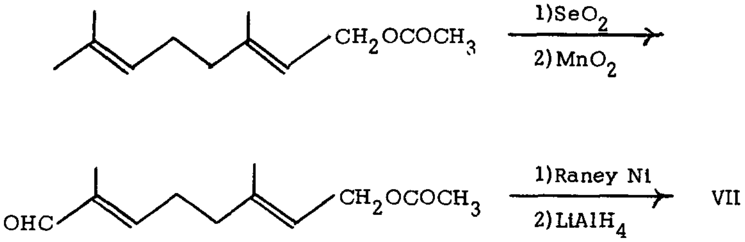


VII



VIII

The key step in these syntheses was based on reports of the selective selenium dioxide oxidation of a terminal allylic methyl group in polyunsaturated systems.[8,9,10] Oxidation of geranyl acetate with selenium dioxide (refluxing 95% ethanol, 9 hr.) gave an orange oil which was freed from selenium by steam distillation. The material thus obtained was a mixture of the desired doubly unsaturated alcohol acetate and the product of further oxidation, IX. After completion of the oxidation with manganese dioxide (pentane, 0°, 30 min.),IX was reduced with W-2 Raney nickel (95% ethanol, 2 atm. H_2, 15 min.) to a mixture of the mono-unsaturated aldehyde acetate and the corresponding alcohol acetate. Treatment of this mixture with excess lithium aluminum hydride gave VII in an overall yield of 16% (<u>Anal.</u> Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.88; H, 11.85).



IX

The NMR spectra of natural and synthetic VII were in excellent agreement, as were the mass spectra of the corresponding bis-trimethysilyl derivatives. (If the selenium dioxide reaction had resulted in oxidation of the C_3-methyl group rather than that at C_7, the NMR spectrum of the final product would have shown two allylic methyl absorptions and no methylene resonance adjacent to both an oxygen and a double bond.) The bis-α-naphthylurethane derivatives of both the natural and synthetic diols, after recrystallization from aqueous ethanol, had a melting range of 146-148°, and the mixture melting range was undepressed. The bis-trimethylsilyl derivatives of natural and synthetic materials behaved identically in GLC (5' 20% Carbowax 20 M on base-washed Firebrick, 176°, R_t 13.6 min.).

The Z-isomer (VIII) was also synthesized as outlined above, starting with neryl acetate. That it was not identical to the natural material was shown by its 60 MHz NMR spectrum (allylic methyl protons shifted downfield by 4.5 Hz from those of the natural material), and the GLC behavior of its bis-trimethylsilyl derivative (same column and conditions, R_t 11.5 min.).

When hairpencils from African Monarchs raised in the laboratory (normal food plant)[11] were extracted and examined in the same manner, the extracts were found to contain the normal complement of VII, but no detectable amount (<30 ng per animal) of I. A similar observation has been made in the case of the Queen.[7] The absence of I in laboratory-reared individuals, as well as the function of the oxygenated terpenes (IV, V, VI, VII), remains an intriguing mystery. While VII has not been found in nature previously, it is of interest to note that the closely related 10-hydroxygeraniol has recently been shown to be a key intermediate in the biosynthesis of loganin and the indole alkaloids.[12,13]

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Footnotes and References

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