Albolineol, A Sesterterpene with a Novel Bicyclic Skeleton

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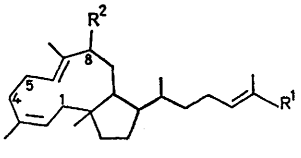
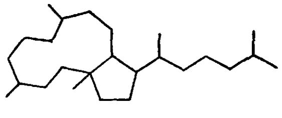
Summary The isolation and structural elucidation of albolineol (**1**), a novel bicyclic sesterterpene from the insect wax *Ceroplastes albolineatus* are reported.

WE have reported the isolation[1] of the sesterterpenes ceroplastols I and II and albolineol, C_{25} isoprenoids from the insect wax *Ceroplastes albolineatus*, and the structural characterization[2] of ceroplastols I and II. Though a number of sesterterpenes are known, only five skeletal types have been found so far. We now report the structure of albolineol (**1**), representing a new fundamental cyclization of geranyl farnesyl pyrophosphate, which could give rise to the cyclic system of the ceroplastanes.

Albolineol has m.p. 114—115°, $[\alpha]_D$ $-23{\cdot}4°$, λ_{max} 208 nm, (ϵ 4663), ν_{max} 3600, 1670, and 840 cm^{-1}, indicating the presence of OH groups and unsaturation, and gives analytical data consistent with the formula $C_{25}H_{42}O_2$ (previously reported as $C_{13}H_{22}O$). Its mass spectrum shows no molecular ion but has ions at *m/e* 356 ($M^+ - H_2O$), and 229 (80%; $M^+ - 2H_2O - C_8H_{13}$) suggesting the presence of an aliphatic C_8H_{13} chain. Its n.m.r. spectrum shows signals at δ (Me_4Si) 0·88 (overlapping 3H, d, sec.-Me, and 3H, s, tert.-Me), 1·63 (6H, s, 2 × C=CMe), 1·66 (3H, s, C=CMe), 4·0 (2H, s, =CMeCH$_2$OH), 4·48 (1H, t, *J* 6 Hz, =CMe-C*H*OH), and 5·4 (3H, m, 3 × =CH), and its diacetate (**2**) has signals at δ 4·25 (2H, =CCH$_2$OAc) and 5·25 (1H, >CHOAc). Hydrogenation of (**1**) in EtOAc–HClO$_4$ with PtO$_2$–H$_2$ gives the hydrocarbon (**6**), molecular formula $C_{25}H_{48}$ (mass spectrometry).

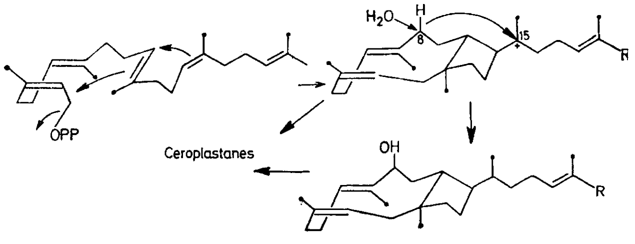


(1); R¹ = CH$_2$OH, R² = OH
(2), R¹ = CH$_2$OAc, R² = OAc
(3), R¹ = CH=O, R² = OH
(4), R¹ = CH=O, R² = OAc
(5), R¹ = CH=O, R² = O



(6)

From its empirical formula, spectroscopic data for (**1**), (**2**), and (**6**), and from the products obtained by ozonolysis of the p-nitrobenzoate of (**1**)[1] we decided that albolineol is a bicyclic sesterterpene with three trisubstituted double bonds, with one in the side chain containing the primary OH group ($CH_2CH{=}CMeCH_2OH$). It also contains another OH group, which was shown to be secondary and allylic.



SCHEME

The ceroplastanes are considered to be produced from geranyl farnesyl pyrophosphate or its biochemical equivalents, which, in turn, might be constructed by condensation of five isoprene units. The C_5–C_8–C_5 ring system of ceroplastanes might be constructed by successive two-step cyclizations, in which the first step was assumed to be a solvolytic cyclization leading to the C_5–C_{11} skeleton.[3] Thus, albolineol is a possible intermediate in the biosynthetic route to ceroplastanes as in the Scheme,† and we suggest that it has the structure (**1**).

Structure (**1**) for albolineol is supported by biogenetic evidence and also the following. Oxidation of (**1**) with MnO_2 gave an $\alpha\beta$-unsaturated hydroxy-aldehyde (**3**), m.p. 105—107°, ν_{max} 3500, 1680, and 1620 cm^{-1}, λ_{max} 231 nm (ϵ 17,000); δ 4·5 (1H, C=CCHOH) 6·5 (1H, CHC=CH=O), and 9·26 (1H, CH=O), M^+ 372 ($C_{25}H_{40}O_2$) (by mass spectrometry).

With Ac_2O– pyridine, (**3**) yields an acetate (**4**) and on further oxidation with MnO_2 (specific for allylic alcohols) it yields the $\alpha\beta$-unsaturated ketone (**5**), m.p. 88°, λ_{max} 232 (ϵ 3600) and 206 (ϵ 4450), ν_{max} 1685 and 1625 cm^{-1} ($\alpha\beta$ unsaturated CO groups and unsaturation), m/e 370 (M^+; $C_{25}H_{38}O_2$), δ 1·91 (3H, =CMeCO), and 5·82 (1H, (C*H*=CC=O).

The ketone function in (**5**) was located from its n.m.r. spectrum, which suggested the presence of the –CCH=CMe-COC– unit, and the multiplet at δ 5·82 was assigned to 6-H (β to CO). This eliminates the allylic C-4 or C-5 positions for the secondary OH since if this were the case one C=C-C*H*$_2$CO signal would appear. Finally C-1 for the OH was likewise discarded because a signal from an α proton in the $\alpha\beta$ unsaturated ketone system was not observed.

The location of the OH group at C-8 is in accord with the hypothesis of Canonica *et al.*,[4] for the biosynthesis of ophiobolins, in which they propose hydride ion transfer from C-8 to C-15, leaving a positive charge on C-8. Neutralization of this charge with water could give either albolineol or, following further cyclization, all the derivatives of ceroplastane.

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† A similar scheme was proposed for the biogenetic synthesis of a hypothetical intermediate from which all the ophiobolins could be derived.[4]

[1] T. Rios and F. Colunga, *Chem. and Ind.*, 1965, 1184.

[2] Y. Iitaka, I. Watanabe, I. T. Harrison, and S. Harrison, *J. Amer. Chem. Soc.*, 1968, **90**, 1092; T. Rios and L. Quijano, *Tetrahedron Letters*, 1969, 1317.

[3] T. Rios and S. Pérez, *Chem. Comm.*, 1969, 214.

[4] L. Canonica, A. Fiecchi, M. Galli Kienle, B. M. Ranzi, and A. Scala, *Tetrahedron Letters*, 1967, 3371.