Albocerol, a New Macrocyclic Sesterterpene

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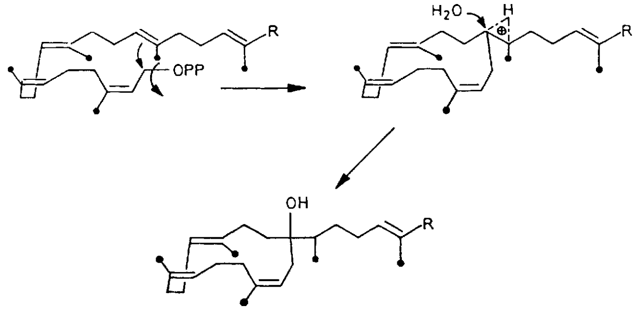
Summary The isolation and structural elucidation of albocerol (**1**), a novel macrocyclic sesterterpene from the insect wax *Ceroplastes albolineatus* are reported.

We have already described the isolation of several sesterterpenes (C_{25} isoprenoids) from the insect wax *Ceroplastes albolineatus*.[1] We now report on the structure elucidation of a new sesterterpene, albocerol (**1**).

The structure of albocerol (**1**) represents a new fundamental cyclization of geranylfarnesyl pyrophosphate, which could give rise to a macrocyclic system.

Albocerol (**1**) has ν_{max} 3400, 1670, and 840 cm^{-1}, λ_{max} 212 nm (ϵ 5026) indicating the presence of OH groups and unsaturation. Its mass spectrum shows ions at *m/e* 374 (M^+; $C_{25}H_{42}O_2$), 356 ($M^+ - H_2O$), 338 ($M^+ - 2H_2O$), 289 ($M^+ - C_5H_9O$), 229 ($M^+ - 2H_2O - C_8H_{13}$), and 109 (C_8H_{13}, 100%) suggesting the presence of an aliphatic C_8H_{13} chain. Its n.m.r. spectrum shows signals at δ 0·88 (3H, d, sec.-Me), 1·60 (9H, s, 3 × C=CMe), 1·72 (3H, s, C=CMe), 2·05 (m, CH_2), 3·96 (2H, s, CH_2OH), and 4·9—5·5 (4H, m, 4 × =CH–) and its acetate (**2**) has ν_{max} 3500 and 1750 cm^{-1} and signals at δ 4·41 (2H, s, =CCH_2OAc) and 2·0 (3H, s, AcO).

Hydrogenation of (**1**) in EtOH with PtO_2 gives the alcohol (**3**), $C_{25}H_{50}O$ (mass spectrometry). Ozonolysis of the 3,5-dinitrobenzoate of albocerol (**4**) afforded the 3,5-dinitrobenzoate of hydroxyacetone (compared spectroscopically with an authentic sample), m.p. 140—142°.



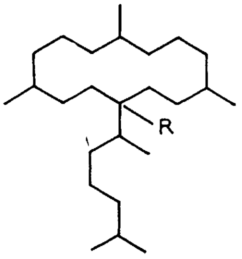
(**1**); R=CH_2OH
(**2**); R=CH_2OAc
(**4**); R=3,5-$(NO_2)_2C_6H_3CO_2CH_2$

From its empirical formula, spectroscopic data for (**1**), (**2**), and (**3**), and from the products obtained by ozonolysis of the *p*-nitrobenzoate (4) we decided that albocerol is a monocyclic sesterterpene with four trisubstituted double bonds, one, in the side chain, containing the primary OH group. It contains another OH group, which was shown to be tertiary.

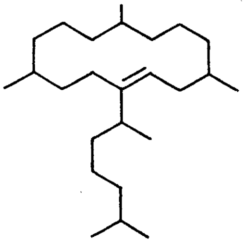
On the assumption that albocerol arises in nature from geranylfarnesyl pyrophosphate (the normal sesterterpene precursor[2]) by a single cyclization, then several structures are possible.

We propose structure (**1**) from the following evidence. Dehydration of tertiary alcohol (**3**) yielded an olefin (**5**) as the main product; λ_{max} 212 nm (ϵ 1392); δ 5·2, (1H, m, $C{=}C\mathit{H}CH_2$); *m/e* 348 (M^+; $C_{25}H_{48}$) and 264 ($M^+ - C_6H_{12}$).

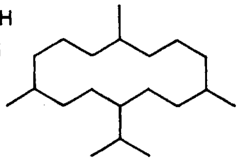
Hydrogenation of (**5**) in EtOAc with PtO_2–H_2 gives the hydrocarbon (**6**) $C_{25}H_{50}$, *m/e* 350 (M^+). The mass spectrum of (**6**) is especially informative and the fragmentation can be assumed to commence with the formation of ions A (*m/e* 264; $M^+ - C_6H_{14}$) and B (*m/e* 236; $M^+ - C_8H_{18}$, 100%) by loss of the side chain, showing the size of the ring of albocerol (**1**). The remainder of the spectrum is very similar to the mass spectrum of cembrane (**7**) previously reported.[3]



(**3**); R=OH
(**6**); R=H



(**5**)



(**7**)

The geometry of the four trisubstituted double bonds in albocerol shown in structure (**1**) was deduced by biogenetic reasoning and n.m.r. data. The geranylfarnesol isolated from the same source has $\Delta^{2,3}$ *cis*.[2]

The n.m.r. spectra of albocerol and its derivatives show one methyl group in a *cis* arrangement. The stereochemistry of the OH group remains to be elucidated.

Thus, albocerol is one of the simplest compounds possible which can be formed from geranyl farnesyl pyrophosphate by C(1)–C(14) cyclization (followed by hydration).

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[1] T. Rios and F. Colunga, *Chem. and Ind.*, 1965, 1184; T. Rios and L. Quijano, *Tetrahedron Letters*, 1969, 1317; T. Rios and F. Gómez, *ibid.*, p. 2929; T. Rios, L. Quijano, and J. Calderon, *J.C.S. Chem. Comm.*, 1974, 728.

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

[3] V. D. Patil, U. R. Nayak, and S. Dev, *Tetrahedron*, 1973, **29**, 341.