

An interesting consequence of this model building is that face centered cubic close packing of the noble gases and metals is predicted because of the cubic nature of the closed shell structures. This is in distinct contrast to quantum mechanical calculations which incorrectly predict HCP crystallization⁴. In summary, both the shell structure of the atom and the shell structure of the nucleus can be rationalized in terms of the geometrical structures which arise due to the singlet pairing of adjacent like-fermions. Previously, geometrical arguments have been used to rationalize both electron structure⁵⁻⁸ and nuclear structure⁹⁻¹². Each, however, has been a model uniquely applicable to one system or the other. On the other hand, the models for both electron and nuclear structure described above are derived from a single principle of particle interaction.

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Ceralbol, a new sesterterpene alcohol isolated from insect wax¹

J.S. Calderon, L. Quijano and T. Rios²

Instituto de Química de la Universidad Nacional Autónoma de México, México 20 (D.F., México), 19 August 1977

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

The insect wax *Ceroplastes albolineatus* (Coccidae) was previously shown to contain a number of closely related terpenes containing 25 carbon atoms (Sesterterpenes), all of which are characterized by C₅-C₈-C₅ ring system³⁻⁵.

More recently the insect wax has provided 2 sesterterpenes, albocerol and albolineol, monocyclic and bicyclic respectively^{6,7}.

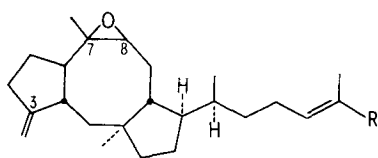
Examination of the more polar fractions of the neutral part, after saponification of this wax, has now led the isolation of a new alcohol. Here we report structural determination of this new substance, which we called ceralbol (1).

Ceralbol (1) is a viscous liquid, has: $[\alpha]_D + 47^\circ$; ν_{\max} 3420, 1650 and 875 cm⁻¹; λ_{\max} 207 nm (ϵ 5800) indicating the presence of OH groups and unsaturation. Its mass spectrum shows molecular ion at m/e 372 (C₂₅H₄₀O₂). Its NMR shows signals at δ (Me₄Si) 0.8 (3H, d, J = 6.5, sec-Me), 0.76 (3H, s, C-Me), 1.16 (3H, s, -O-C-Me), 1.62 (3H, s, -C=C-Me), 2.10 (1H, s, OH), 3.98 (2H, s, -CH₂-OH), 5.32 (1H, t, J = 7, =CH-) and 4.82 (2H, s, =CH₂) and its

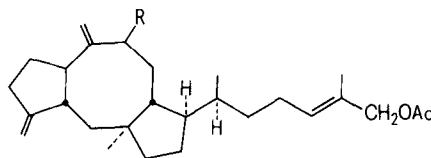
acetate (1a) has ν_{\max} 1735 cm⁻¹, the fact that the IR spectrum of 1a does not show OH bands suggests that the 2nd oxygen atom of ceralbol (1) belongs to an epoxy group. Furthermore the mass spectrum exhibits an ion at m/e 398 (M⁺-16).

From its empirical formula, spectroscopic data for 1, 1a as well as by biogenic considerations, we decided that ceralbol must be a tricyclic compound with an epoxy group, with 2 double bonds, 1 being a terminal methylene group and the 2nd located in the side chain containing the alcohol group. We propose structure 1 from the following evidences.

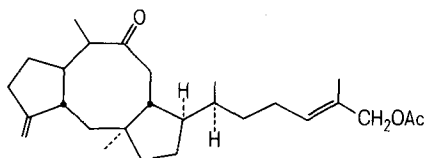
Oxidation of ceralbol (1) with CrO₃/pyridine yielded an $\alpha\beta$ unsaturated aldehyde (1b) C₂₅H₃₈O₂ (M⁺, m/e 370) ν_{\max} 1680, 1630 and λ_{\max} 230 nm (ϵ 13700) whose NMR-spectrum was almost identical to that of the parent compound apart from the signals for the proton of the aldehyde group (9.4) and the β proton on the unsaturated carbonilic system (6.37).



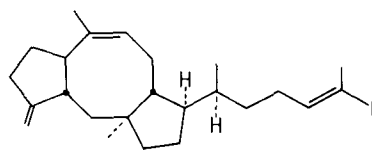
1- R = -CH₂OH
1a- R = -CH₂OAc
1b- R = -CH=O



2- R = -OH
2a- R = -O



3



4- R = -CH₂OH
4a- R = -CH=O

Treatment of acetate **1a** with p.toluen sulfonic acid in acetone afforded an alcohol **2** which showed absorption at 207 nm (ϵ 4100) in the ultraviolet and 3400, 1735 and 1640 cm^{-1} in the infrared spectrum indicating the presence of an unsaturated alcohol group. The NMR-spectrum of this compound showed the low field singlet of a new exocyclic methylene group (4.98), and a triplet (4.28, $J = 7$), due to a methine proton on the carbon atom bearing an allylic hydroxyl group.

Compound **2** oxidated with Jones reagent gave the conjugated ketone **2a** ν_{max} 1695 cm^{-1} ; this compound showed UV absorption at 225 nm (ϵ 6000) for the $\alpha\beta$ unsaturated ketone. The NMR-spectrum of **2a** shows 2 signals at 4.96 and 5.07 for the exocyclic methylene conjugated with the ketone group.

Reduction of ketone **2a** with aluminium amalgam yielded a dihydroderivative **3** which does not show high absorption at 207 nm in the UV. Its IR-spectrum has a band at 1690 cm^{-1} . The NMR-spectrum of **3** does not show the low field 2 signals (4.96, 5.07) of the exocyclic methylene protons of **2a**, a doublet observed ($J = 7.5$ Hz) centered at 1.22 corresponds to a secondary methyl group α to the ketone.

The IR-spectrum of **3** indicate that the ketonic group is found as a substituent in an 8-membered ring, this fact

indicates that the exocyclic methylene group in ceralbol is attached to C-3 and therefore the epoxy group is linked at C-7 and C-8.

Ceroplastol I (**4**), whose molecular structure and absolute configuration have been determined by X-ray method, was correlated with ceralbol (**1**) in the following manner:

Ceroplastol I (**4**) was oxidated with CrO_3/Py yielding the aldehyde (**4a**) and, after a selective epoxidation of the double bond between C₇-C₈ of this compound with 3 chloroperbenzoic acid in benzene, afforded the epoxide aldehyde that was identical with the aldehyde obtained from natural ceralbol (**1b**).

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- 2 This work was supported by a grant from Syntex laboratories, S.A., Mexico, D.F.
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Structure and stereochemistry of attenuol, a new lignan from *Knema attenuata* (Wall.) Warb.¹

B.S. Joshi, K. R. Ravindranath and N. Viswanathan²

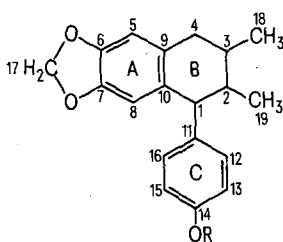
Ciba-Geigy Research Centre, Goregaon, Bombay 400063 (India), 31 May 1977

Summary. A new lignan attenuol has been isolated from the bark of *Knema attenuata* (Wall.) Warb. Its structure (**I**) is deduced on the basis of analytical and spectral data. The compound has been assigned the absolute configuration as 2S,3R-dimethyl-1S-(p-hydroxyphenyl)-6,7-methylenedioxytetralin (**III**).

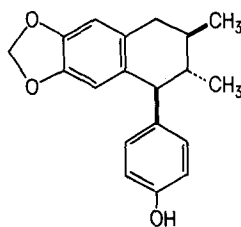
By hexane extraction of the bark of *Knema attenuata* (Wall.) Warb. (Myristicaceae), collected at the Khandala Ghats, we isolated attenuol $\text{C}_{19}\text{H}_{20}\text{O}_3$ (**I**), as colourless needles m.p. 160–1 °C [α_{D}^{25} -20.52° (C, 1.16, CHCl_3), ν_{max} (KBr), 3400, 2970, 1600 cm^{-1} and λ_{max} (EtOH), 223 (sh), 287 and 294 (sh) nm (log ϵ , 4.16, 3.69 and 3.63). In its NMR-spectrum (CDCl_3 , 100 MHz), it exhibited signals at δ 0.9 (3H, d, $J = 6$ Hz, $-\text{CH}-\text{CH}_3$), 1.1 (3H, d, $J = 6$ Hz, $-\text{CH}-\text{CH}_3$), 1.2–1.8 (2H, m, H-2, H-3), 2.7 (2H, m, Ar- CH_2), 3.42 (1H, d, $J = 10$ Hz, H-1), 5.05 (1H, exchanged with D_2O , Ar-OH), 5.81 (2H, s, O- CH_2 -O), 6.15 (1H, s, H-8), 6.55 (1H, s, H-5), 6.75 (2H, d, $J = 9$ Hz, H-13, H-15), 6.98 (2H, d, $J = 9$ Hz, H-12, H-16) in accordance with the unique structure (**I**). The natural abundance Fourier transform ^{13}C -NMR-spectrum of attenuol was in conformity with the proposed structure showing the following chemical shifts (in ppm in CDCl_3 at 25.155 MHz vs. tetramethylsilane; assignments are tentative) C-14, 153.1

(s); C-6, C-7, 145.5, 145.3 (s); C-11, 139.0 (s); C-10, 133.8 (s); C-12, C-16, 130.5 (d); C-9, 130.1 (s); C-13, C-15, 115.2 (d); C-5, 109.7 (d); C-8, 107.6 (d); C-17, 100.4 (t); C-1, 54.1 (d); C-2, 44.0 (d); C-3, 39.5 (d); C-4, 35.5 (t); C-19, C-18, 19.9, 17.1 (q each).

Attenuol afforded a monoacetate (**II**), m.p. 110–1 °C, and its analytical and spectral data supported this formulation. The stereochemistry of attenuol could be derived from its ORD curve (figure) which showed a negative first Cotton effect indicating that the aryl group (ring C) should have a β -configuration³. The C-1, C-2 hydrogens are trans to each other as seen by the large coupling^{4,5} ($J = 10$ Hz) of H-1.



I; R = H
II; R = COCH_3



III

