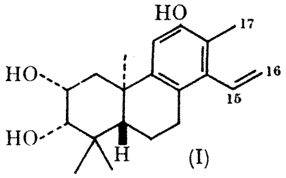
Cleistanthol, a Novel Diterpene from *Cleistanthus schlechteri* (Euphorbiaceae)

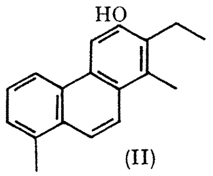
By E. J. McGarry and K. H. Pegel*
(*Chemistry Department, Natal University, Durban, South Africa*)
and L. Phillips and E. S. Waight
(*Chemistry Department, Imperial College, London, S.W.7*)

Summary The aromatic diterpene cleistanthol presents a new type of diterpene skeleton.

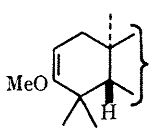
We have isolated from *Cleistanthus schlechteri* a novel aromatic diterpene which we name cleistanthol and formulate as (I) on the basis of the following and much additional evidence to be reported elsewhere.



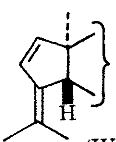
(I)



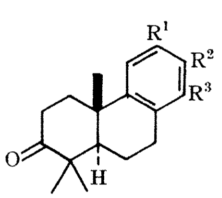
(II)



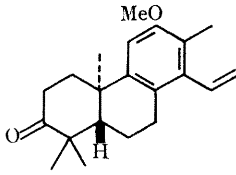
(III)



(IV)



(V) R^1=OMe, R^2=CHMe$_2$. R^3=H
(VI) R^1=H, R^2=OMe, R^3=CHMe$_2$



(VII)

Cleistanthol (I),† $C_{20}H_{28}O_3$, m.p. 193—194°, $[\alpha]_D$ −40° (EtOH throughout) forms a triacetate, $C_{26}H_{34}O_6$, m.p. 146—147°, $[\alpha]_D$ − 53°, is reduced to 15,16-dihydrocleistanthol, $C_{20}H_{30}O_3$, m.p. 225°, $[\alpha]_D$ − 59°, reacts with one mole of periodic acid, and gives a green colour with ferric chloride. The n.m.r. spectrum of cleistanthol triacetate shows the presence of one aromatic proton, one aromatic vinyl group, and one aromatic methyl group (τ 3·24, 3·47 q, and 4·68 sextet, and 7·74 resp.).

Chromic acid oxidation of the triacetate of 15,16-dihydrocleistanthol followed by alkaline hydrolysis yielded the 7-oxo-2,3,12-trihydroxy-8,11,13-triene, $C_{20}H_{28}O_4$, m.p. 239—240°, λ_{max} (EtOH) 236 nm. (log ϵ 4·0), 288 (3·8). The u.v. spectrum of this compound is typical of the *p*-hydroxyphenyl ketone moiety,[1] thus establishing that the aromatic hydroxy-group is situated at C-12.

Selenium dehydrogenation of cleistanthol produced a phenanthrol, $C_{18}H_{18}O$, m.p. 138—139°, indistinguishable in its u.v., i.r., n.m.r., and mass spectra from the phenanthrol (II), m.p. 164°, obtained from methyl vinhaticoate;[2] the structural difference of the two phenanthrols was demonstrated by their different chromatographic mobilities. Such close resemblance of two phenanthrols is only possible if the overall substitution pattern is essentially identical and this can be achieved by interchanging the C-1 methyl and C-2 ethyl groups in (II).

The configuration and placement of the vicinal diol grouping in cleistanthol has been established by the conversion of the 12-methoxy-8,11,13-trien-2,3-diol dimesylate, $C_{23}H_{36}O_7S_2$, m.p. 188°, under reflux with sodium iodide in acetone, into a mixture of the 12-methoxy-2,8,11,-13-tetraen-3-ol mesylate (III), $C_{23}H_{32}O_4S$, m.p. 135°, and the 3-isopropylidene-12-methoxy-A-nor-1,8,11,13-tetraene (IV), $C_{21}H_{28}O$, m.p. 88—89°, $[\alpha]_D$ −21°. Compound (III) is obtained by concerted elimination of the axial 2-mesylate group and the axial 3-hydrogen, while formation of (IV) is initiated by the well known neopentyl ring A contraction of 3(equatorial)-hydroxy-4,4-dimethyl terpenoids followed by elimination of the 2-mesylate group with a proton from C-1. Together with the above results we interpret a shift difference of 0·8 p.p.m. between the C-2 and C-3 proton signals (τ 4·58 q and 5·38 d, resp.) for dihydrocleistanthol triacetate as being due to a 2-axial–3-equatorial relationship of the two vicinal acetate groups with an anisotropic effect caused by the equatorial acetate carbonyl.

Comparison of the specific rotation of the 3-oxo-12-methoxy-8,11,13-triene (VII), $C_{21}H_{30}O_2$, m.p. 112°, $[\alpha]_D$ − 96° with those of the methyl ethers of hinokione (V),[3] $[\alpha]_D$ + 119° and totarolone (VI),[4] $[\alpha]_D$ + 99°, indicates an antipodal relationship and thus the complete structure (I) for cleistanthol.

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† The composition of all compounds is based on high-resolution mass spectrometry and/or combustion analysis. Spectroscopic support has been obtained for all compounds.

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[3] "Dictionary of Organic Compounds," vol. 3, ed. G. Harris, Eyre and Spottiswoode, London, 1962.

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