Clavatol: a Novel Triterpenoid of the Bisnoronocerane Type Isolated from *Lycopodium clavatum*

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Summary A new triterpenoid, clavatol, isolated from *L. clavatum* is 3α,8β,14α,21β-tetrahydroxy-26,27-bisnoronocerane.

A NUMBER of triterpenoids have been isolated from club-moss, *Lycopodium clavatum* and their structures clarified.[1] We now report a new triterpenoid, clavatol (I) (m.p. 277—279°; acetate, m.p. 257—259°), as a minor constituent.

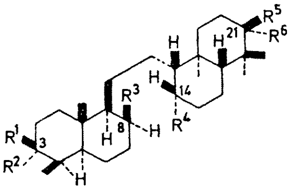
The high-resolution mass spectrum of the acetate (II) did not exhibit a molecular-ion peak, but showed a highest peak at 558·393 corresponding to M^+ — AcOH (558·392 calc. for $C_{34}H_{54}O_6$). Observation of a hydrocarbon peak at 378·328 due to M^+ — 4AcOH (378·329 calc. for $C_{28}H_{42}$) confirmed that clavatol is a tetracyclic bisnortriterpenoid tetraol. The n.m.r. spectra of clavatol derivatives demonstrate that clavatol possesses four secondary hydroxy-groups, six(tertiary) *C*-methyls, no double bond, and more importantly, a symmetrical structure, presumably the bisnoronocerane skeleton. The only unsymmetrical derivative we obtained (by partial acetylation) was a triacetate (IV), m.p. 210—213°, which clearly indicated that the ratio of OAc : *C*-Me is 1 : 2 and the ratio of *CH*·OAc : *CH*·OH is 3 : 1. Oxidation of (IV) gave a keto-triacetate (IX), m.p. 165—169°.

Oxidation of clavatol with Jones' reagent gave a ketone, m.p. 206—208°, which was identical (i.r., t.l.c., m.p., and mixed m.p.) with the tetraketone (VI) prepared by Barton and Overton from α-onocerin,[2] thus confirming clavatol to be 3,8,14,21-tetrahydroxy-26,27-bisnoronocerane.

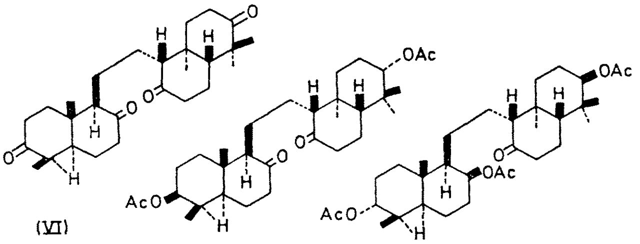
All hydroxy-groups in clavatol are axial since, protons geminal to the acetoxy-groups of the tetra-acetate (II) appeared as broad singlets at δ 4·75 (3-H, 21-H) and 5·31 (8-H, 14-H). Clavatol tetra-acetate was different from 3β,8β,14α,21α-tetra-acetoxy-26,27-bisnoronocerane (V), m.p. 202—204°, which was obtained by sodium borohydride reduction followed by acetylation of the known 8,14-diketo-derivative (VII)[2] (C-8 and C-14 are hindered[3]).

Partial hydrolysis of clavatol tetra-acetate with 5%

methanolic potassium hydroxide solution gave a diacetate (III), m.p. 256—259°. Jones' oxidation of this afforded a diketone (VIII), m.p. 203—206°, which was identical with 8β,14α-diacetoxy-26,27-bisnoronocerane-3,21-dione (i.r., t.l.c., m.p., and mixed m.p.) derived from α-onocerin. Partial hydrolysis (5% KOH—MeOH) of the tetra-acetate (V) and Jones' oxidation of the resulting diol-diacetate gave the expected diketo-diacetate (VIII).



	R^1	R^2	R^3	R^4	R^5	R^6
(I)	H	OH	OH	OH	OH	H
(II)	H	OAc	OAc	OAc	OAc	H
(III)	H	OH	OAc	OAc	OH	H
(IV)	H	OAc	OAc	OH	OAc	H
(V)	OAc	H	OAc	OAc	H	OAc
(VIII)	O		OAc	OAc	O	



(VI)

(VIII)

(IX)

Hence, clavatol is 3α,8β,14α,21β-tetrahydroxy-26,27-bisnoronocerane (I). This is the first example of a bisnoronocerane derivative found in Nature.

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