Triterpenoids of *Lycopodium clavatum*: the Structures of Three New Triterpenoids Containing Conjugated Ketone Groups

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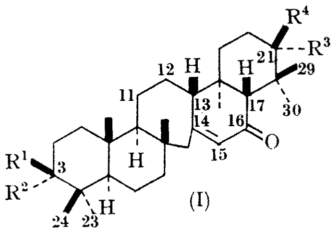
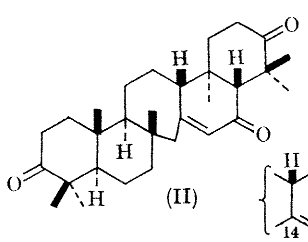
Summary Three new triterpenoids are identified as 16-oxoserrat-14-ene-3,21 diols.

WE report on the structures and stereochemistry of three triterpenoids, B_3 (Ic; $C_{30}H_{48}O_3$, m.p. 300—304°), B_4 (Ie; $C_{30}H_{48}O_3$, m.p. 318—323°), and B_5 (Ia; $C_{30}H_{48}O_3$, m.p. 294—297°), which we have isolated from *Lycopodium clavatum*.[1] Spectroscopic data listed in Tables 1 and 2 indicate that they are secondary diols and contain a keto-group conjugated with a trisubstituted double bond. They contain the same carbon skeleton (they show similar o.r.d. curves with negative peaks at 370—380 nm.) and probably belong to the serratane group (seven C–Me groups). Chromium trioxide–pyridine oxidation of each diol gave the same triketone (II) [$C_{30}H_{44}O_3$, m.p. 278—281°, ν_{max} (KBr) 1715 and 1665 cm.$^{-1}$] *i.e.* they are epimeric diols. Inspection of the chemical shifts and the shapes of the n.m.r. signals due to >C*H*–OAc of the corresponding diacetates revealed that the hydroxy-groups are likely to be at C-3 and C-21, which are both equatorial for B_5 (Ib), both axial for B_4 (If), and equatorial–axial for B_3 (Id), since the signals are almost identical in shapes and shifts with the corresponding signals of serratenediol diacetate (IIIb), diepiserratenediol diacetate (IIIf), and 21-episerratenediol diacetate (IIId), respectively. Sodium borohydride reduction of the triketone (II) at 10° exclusively yielded B_5 (Ia).

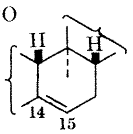


(I)

	R1	R2	R3	R4
(a)	OH	H	OH	H
(b)	OAc	H	OAc	H
(c)	OH	H	H	OH
(d)	OAc	H	H	OAc
(e)	H	OH	H	OH
(f)	H	OAc	H	OAc



(II)



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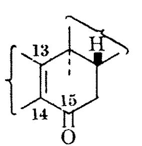

(IV)

The singlet peaks at δ2·2—2·5 were assigned to the methine group (17-H) attached to carbonyl; the neighbouring carbon should be fully substituted. Assuming that the compounds have the serratane skeleton, the conjugated system therefore should be either 16-oxo-14-ene or 11-oxo-12-ene. When the solvent for n.m.r. measurements was changed from $CDCl_3$ to benzene, the two methyl-group signals (marked * in Table 2) of each compound showed marked down-field shifts, indicating that the compounds contain two methyl groups in front of the plane at right angles to the carbonyl.[2] Thus they are 16-oxo-14-enes; for 11-oxo-12-ene only one methyl (at C-10) should shift down-field.

Thus, B_5 is 16-oxoserrat-14-ene-3β,21α-diol (16-oxoserratenediol) (Ia) and B_4 is 16-oxoserrat-14-ene-3α, 21β-diol (16-oxodiepiserratenediol) (Ie).

The stereochemistry of the 21-OAc (or OH) group can be elucidated by n.m.r. evidence. (i) The 17-H methine signal appears at δ 2·2 when 21-OAc is equatorial and at δ 2·4—2·5 when it is axial, apparently indicating the presence of field-direct interaction between 17-H and 21-OAc in the latter case. (ii) By continuously changing the ratio of benzene to $CDCl_3$,[3] the methyl hydrogens at C-29 and C-30 (marked * in Table 2) moved down-field without separation, showing the same shift values (and shapes) when 21-OAc is equatorial, but showed considerable difference in the case of 21-axial-OAc [Δ($CDCl_3$ — benzene) = — 18·3 Hz. for (Ib), and —16·3 and —6·6 Hz. for (If)], the signal due to the protons of a methyl (C-30) in diaxial position with respect to OAc being shifted up-field, thus causing the separation from the 29-H signal.

The 17-H signal of B_3 acetate appeared at δ 2·45 p.p.m. and two methyl hydrogen signals (30-H_3 and 29-H_3) shift separately on changing the solvent from $CDCl_3$ to benzene [Δ($CDCl_3$ — benzene) = — 16·2 and —6·8 Hz. for (Id)]; both indicate that the 21-OAc group of this compound is axial. Hence, B_3 is 16-oxoserrat-14-ene-3β,21β-diol (16-oxoepiserratenediol) (Ic).

Confirmatory evidence was provided by partial syntheses of each compound. When serratenediol diacetate (IIIb) was oxidized with t-butyl chromate in benzene, 16-oxoserratenediol diacetate (Ib; B$_5$-Ac) was produced in approximately 17% yield, accompanied by 15-oxo-derivative (IVb)[4] as expected. Analogously, 21-episerratenediol diacetate (IIId) gave 16-oxoepiserratenediol diacetate (Id; B$_3$-Ac) (*ca.* 18%) and the 15-oxo-13-ene (IVd), m.p. 314—318°, (*ca.* 22%).

TABLE 1

Spectroscopic characterization of 16-*oxoserratene derivatives*

	M.p.	I.r. (cm.$^{-1}$)	U.v. λ_{max} nm. (ϵ)	N.m.r. olefinic proton (1H, broad s.) δ (p.p.m.)
(Ib)	308—309°	1670 s 1625 m	245 (14,000)	5·74
(Id)	242—245°	1671 s 1625 m	245 (13,000)	5·75
(If)	272—275°	1668 s 1623 m	245 (13,000)	5·74

TABLE 2

N.m.r. spectra of the acetates

	C–Me†	–OCOMe†	> C*H*–OAc	17-H (1H, s)
(Ib)	0·83(1), 0·86(4), 1·19*(2)	2·06(1) 2·08(1)	4·50(2H, m.) $w_{\frac{1}{2}}$ 15 Hz.	2·18
(Id)	0·82(1), 0·87(3), 0·91(1), 1·19*(2)	2·05(1) 2·09(1)	4·56(1H) 4·62(1H)	2·45
(If)	0·82(1), 0·87(2), 0·90(1), 0·92(1), 1·19*(2)	2·06(1) 2·08(1)	4·61(2H, b.s.) $w_{\frac{1}{2}}$ 7 Hz.	2·48

* 24-H and 30-H; see text.

† Numbers in parentheses denote number of methyl groups.

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[4] Y. Inubushi, Y. Tsuda, T. Sano, K. Konita, S. Suzuki, H. Ageta, and Y. Ootake, *Chem. and Pharm. Bull.* (*Japan*), 1967, **15**, 1153.