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. $300-304^\circ$), B_4 (Ie; $C_{30}H_{48}O_3$, m.p. $318-323^\circ$), and B_5 (Ia; $C_{30}H_{48}O_3$, m.p. $294-297^\circ$), 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 ketogroup 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) $[C_{30}H_{44}O_3, \text{m.p. }278-281^\circ, v_{max}$ (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 >CH-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 B₅ (Ib), both axial for B₄ (If), and equatorial-axial for B₃ (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).

The singlet peaks at $\delta 2 \cdot 2 - 2 \cdot 5$ 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 CDCl₃ 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-3 β ,21 α -diol (16-oxoserratenediol) (Ia) and B_4 is 16-oxoserrat-14-ene-3 α , 21 β -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 $\delta 2.2$ when 21-OAc is equatorial and at $\delta 2.4$ —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 CDCl₃³ 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 (CDCl₃ – 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 B₃ acetate appeared at δ 2:45 p.p.m. and two methyl hydrogen signals (30-H₃ and 29-H₃) shift separately on changing the solvent from CDCl₃ to benzene [Δ (CDCl₃ - benzene) = -16.2 and -6.8 Hz. for (Id)]; both indicate that the 21-OAc group of this compound is axial. Hence, B₃ is 16-oxoserrat-14-ene-3 β ,21 β -diol (16oxoepiserratenediol) (Ic).

Confirmatory evidence was provided by partial syntheses

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of each compound. When serratenediol diacetate (IIIb) was oxidized with t-butyl chromate in benzene, 16-oxoserratenediol diacetate (Ib; B5-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; B₃-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. $\lambda_{\max} nm. (\epsilon)$	N.m.r. olefinic proton (1H, broad s.) δ (p.p.m.)
(Ib)	308—309°	1670 s	245 (14,000)	5.74
(Id)	242—245°	1625 m 1671 s 1625 m	245 (13,000)	5.75
(If)	272—275°	1625 m 1668 s 1623 m	245 (13,000)	5.74

TABLE 2

N.m.r. spectra of the acetates

	C-Me†	-OCOMe†	>CH-OAc	17-Н (1Н, s)
(Ib)	0.83(1), 0.86(4), 1.19*(2)	2.06(1) 2.08(1)	4.50(2H, m.)	2.18
(Id)	0.82(1), 0.87(3), 0.91(1) $1.19*(2)$	2.05(1) 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)	2.00(1) 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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