16-Oxoserratriol and 16-Oxolycoclavanol: Lycopodium Triterpenoids

By Y. TSUDA,* T. FUJIMOTO, and K. KIMPARA
(*Showa College of Pharmaceutical Sciences, Setagaya-ku, Tokyo, Japan*)

Summary The structures of two new triterpenoids, 16-oxoserratriol (obtained from *L. serratum*) and 16-oxolycoclavanol (obtained from *L. clavatum*), are (Ia) and (IIa), respectively.

TRITERPENOIDS of the 16-oxoserratene group occurring in Lycopodium plants are easily characterizable spectroscopically by their conjugated ketone system,[1] and they show negative o.r.d. peaks at 370—380 nm and seven *C*-Me groups (or its equivalent) in an n.m.r. spectrum. Here we report two further examples of this group of triols, 16-oxoserratriol (Ia), $C_{30}H_{48}O_4$, m.p. 294—298°, and 16-oxolycoclavanol (IIa), $C_{30}H_{48}O_4$, m.p. 328—333°. The latter was isolated from *L. clavatum* (tentatively designated C_2)[2] and the former was recently isolated from *L. serratum* (in addition to 16-oxoserratenediol[1] and the previously described serratenediol,[3,4] 21-episerratenediol,[5] serratriol,[5,6] tohogenol,[5,7] and tohogeninol[7]). They are well characterized as their acetates (Ib) m.p. 309—311°, and (IIb) m.p. 245—247°.†

The n.m.r. spectra of the acetates indicated that each compound has an axial $CH_2{\cdot}OAc$ group and two secondary acetoxy-groups which in (Ib) are both equatorial and in (IIb) both axial.

On reaction with 2,2-dimethoxypropane in *NN*-dimethylformamide in the presence of toluene-*p*-sulphonic acid, (Ia) easily formed an *OO*-isopropylidene derivative (Ic), m.p. 291—294°, while (IIa) gave, with some difficulty, an analogous acetonide (IIc), m.p. 245—249. Their n.m.r. spectra indicated that (Ic) has stereochemistry (A) and (IIc) stereochemistry (B) as already discussed.[2,6] Jones oxidation of these acetonides yielded, with simultaneous loss of the isopropylidene functions, the same keto-aldehyde (III), m.p. 255—257° from either compound, thus proving that (Ia) and (IIa) are stereoisomeric at the secondary hydroxy-groups. Sodium borohydride reduction of (III) regenerated (Ia) (identified as its acetate) in almost quantitative yield as expected.

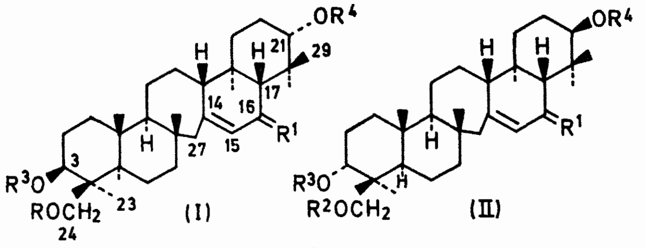
By continuously changing the solvent from $CDCl_3$ to benzene in the n.m.r. measurements[8] on the acetates, two methyl-group signals showed marked downfield shifts—in (Ib) the methyls at δ1·18 p.p.m. moved without separation

---

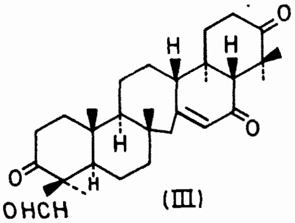
† All compounds described had satisfactory elemental analyses and i.r., u.v., and n.m.r. spectra consistent with the structures assigned.

[$\Delta(CDCl_3 - C_6H_6)$ $-16{\cdot}9$ Hz] and in (IIb) the methyls at 1·23 p.p.m. shifted with an appreciable separation [$\Delta(CDCl_3 - C_6H_6)$ $-16{\cdot}4$ and $-7{\cdot}0$ Hz). These facts indicate that the compounds are 16-oxo-14-enes, C-29 and C-30 are methyl groups, and that the 21-OAc group of (Ib) is equatorial [partial structure (C)] and that of (IIb) is axial [partial structure (D).[1] Difference in the chemical shifts of the 17-H signals of (Ib) and (IIb) also support this conclusion; the peak at δ2·18 p.p.m. for (Ib) supports a 21-equatorial-OAc, and the peak at δ2·52 p.p.m. for (IIb) supports a 21-axial-OAc.[1]

We conclude that these triterpenoids are 16-oxoserrat-14-en-3β,21α,24-triol (Ia) and 16-oxoserrat-14-en-3α,21β,-24-triol (IIa), respectively.

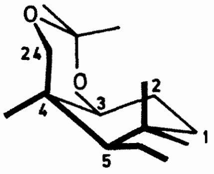


(I) (II)

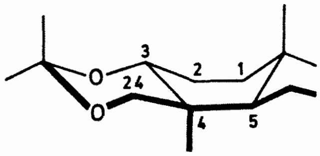


(III)

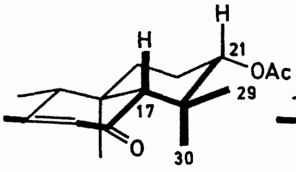
	R¹	R²	R³	R⁴
a	O	H	H	H
b	O	Ac	Ac	Ac
c	O	–CMe₂–		H
d	H₂	Ac	Ac	Ac



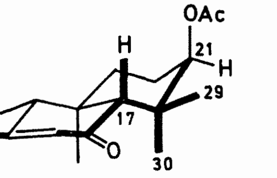
(A)



(B)



(C)



(D)

The structures have been confirmed by synthesis. On oxidation with t-butyl chromate in benzene, serratriol triacetate (Id) and lycoclavanol triacetate (IId) afforded the corresponding 16-oxo-derivatives (Ib) and (IIb), in approximately 20 and 15% yields, respectively. The identities of these compounds were confirmed by comparisons of m.p., t.l.c., i.r., and n.m.r.

(*Received, December 29th,* 1969; *Com* 1955.)

[1] Y. Tsuda and T. Fujimoto, *Chem. Comm.*, 1969, 1042.

[2] Y. Tsuda and M. Hatanaka, *Chem. Comm.*, 1969, 1040.

[3] Y. Inubushi, Y. Tsuda, H. Ishii, M. Hosokawa, and T. Sano, *J. Pharm. Soc. Japan*, 1962, **82**, 1339; Y. Inubushi, Y. Tsuda, H. Ishii, T. Sano, M. Hosokawa, and T. Harayama, *ibid.*, 1964, **84**, 1108.

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

[5] Y. Inubushi, Y. Tsuda, T. Sano, and R. Nakagawa, *Chem. and Pharm. Bull.* (*Japan*), 1965, **13**, 104.

[6] Y. Tsuda, T. Sano, A. Morimoto, and Y. Inubushi, *Tetrahedron Letters*, 1966, 5933.

[7] Y. Inubushi, Y. Tsuda, and T. Sano, *Chem. and Pharm. Bull.* (*Japan*), 1965, **13**, 750.

[8] M. Hashimoto and Y. Tsuda, International Symposium on N.M.R., Preliminary Report, M-2-13, Tokyo, Sept. 1, 1965.