Triterpenoids of *Lycopodium clavatum*: the Structure of 21-Episerratriol

By Y. TSUDA*

(*Showa College of Pharmaceutical Sciences, Setagaya-ku, Tokyo, Japan*)

and M. HATANAKA

(*Faculty of Pharmaceutical Sciences, Osaka University, Toyonaka, Osaka, Japan*)

Summary 21-Episerratriol (serrat-14-ene-3β,21β,24-triol) is one of the triterpenoids isolated from club-moss (*Lycopodium clavatum*).

THE neutral fraction of the extract of club-moss, *Lycopodium clavatum*, was found to give a number of triterpenoids as minor components along with the known α-onocerin,[1,2] lycoclavanol,[1] and lycoclavanin.[1] They were conveniently separated by repeated chromatography of their acetates, followed by dry chromatography of the corresponding alcohols, and finally purified as their acetates. The triterpenoids so far isolated are listed in Table 1, where A_5, A_4, A_3, and A_2 are known compounds from other plants[3-6] (identified by direct comparison) while B_5, B_4, B_3, B_2, and C_2 are new triterpenoids.

This communication is concerned with the structure and stereochemistry of the triol B_2. The n.m.r. spectrum of B_2 acetate (XIII) Table 2) suggests that the parent alcohol is a trihydroxyserratene with one primary and two secondary hydroxy-groups. The primary hydroxy-group is an axial CH_2OH. Of the two secondary OH groups, one is equatorial and the other is axial. Thus the compound is presumably a stereoisomer of serratriol (I)[7] and lycoclavanol (II).[7]

The compound, B_2, when heated with 2,2-dimethoxypropane in dimethylformamide and a catalytic amount of toluene-*p*-sulphonic acid, formed an *OO*-isopropylidene derivative (V), m.p. 242—244°, involving the primary OH and a secondary hydroxy-group, as evidenced by its n.m.r. spectrum, $Me_2C(O\cdot)O\cdot$, δ 1·37 (3H) and 1·41 (3H); $C\cdot CH_2\cdot O\cdot$, two doublets at 3·15 and 3·97 (J 12 Hz.); $>CH\cdot O\cdot C$ and $>CH\cdot OH$, 3·45 (2H, broad s.). Comparison of its n.m.r. spectrum with those of *OO*-isopropylidene-serratriol (VI)[7] and -lycoclavanol (VII)[7] revealed that the acetonide had formed between 3β- and 24-hydroxy-groups (serratriol type) rather than between 3α- and 24-hydroxy-groups

TABLE 1

Triterpenoids of Lycopodium clavatum

	Alcohols	M.p.†	Acetates	M.p.
A_5	Serrateneolone (Serraten-21-ol-3-one)		Monoacetate	305—307°
A_4	Diepiserratenediol	295—296°	Diacetate	240—242°
A_3	21-Episerratenediol	286—287°	"	225—227°
A_2	Serratenediol	287—290°	"	336—338°‡
A_1	α-Onocerin	238—239°	"	223—225°
B_5	16-Oxoserratenediol*	294—297°	"	308—309°
B_4	16-Oxodiepiserratenediol*	318—323°‡	"	272—275°
B_3	16-Oxoepiserratenediol*	300—304°	"	242—245°
B_2	21-Episerratriol	330—333°‡	Triacetate	248—249°
B_1	Lycoclavanol	308—310°‡	"	197—198°
C_2	16-Oxolycoclavanol*	328—330°‡	"	245—247°
C_1	Lycoclavanin	344—346°‡	Tetra-acetate	238—240°

* The structures of these compounds will be reported elsewhere.
† M.p.s were determined on a hot-stage (Yanagimoto melting point apparatus).
‡ These m.p.s were determined in open capillary.

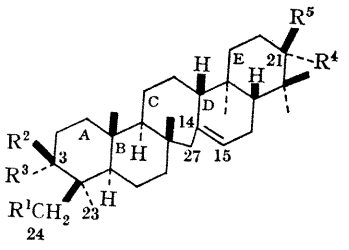
TABLE 2

N.m.r. spectra of serrat-14-ene-3,21,24-triol triacetates

(p.p.m. 60 Hz., in $CDCl_3$)

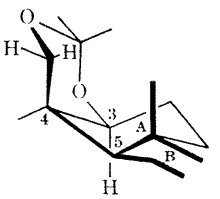
Compounds	C–Me*	–OCOMe*	C–C*H*$_2$–OAc†	> C*H*–OAc	C=C*H*‡
(I) Triacetate	0·70(1) 0·85(3) 0·90(1) 1·00(1)	2·03(1) 2·05(2)	4·24 δ19 *J* 12 Hz.	4·51 (2H,m.)	5·35
(II) Triacetate (IX)	0·70(1) 0·85(3) 0·95(2)	2·05(1) 2·08(2)	4·09 δ18 *J* 12 Hz.	4·70 (1H, broad s.)	5·37
(III) Triacetate (XIII)	0·70(1) 0·86(3) 0·95(1) 1·00(1)	2·02(1) 2·04(1) 2·07(1)	4·22 δ19 *J* 12 Hz.	4·50 (1H,m.) 4·67 (1H, broad s.	5·34
(IV) Triacetate (XV)	0·70(1) 0·84(3) 0·91(1) 0·95(1)	2·05(2) 2·08(1)	4·10 δ17 *J* 11 Hz.	4·53 (1H, m.) 4·96 (1H, broad s.)	5·37

* Numbers in parentheses denote number of methyl groups.
† Signal appears as AB quartet of 2H.
‡ Signal appears as multiplet of 1H.

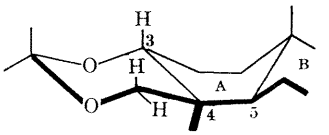


	R^1	R^2	R^3	R^4	R^5
(I)	OH	OH	H	OH	H
(II)	OH	H	OH	H	OH
(III)	OH	OH	H	H	OH
(IV)	OH	H	OH	OH	H
(IX)	OAc	H	OAc	H	OAc
(X)	OH	H	OAc	H	OAc
(XI)	OAc	H	OH	H	OAc
(XII)	OAc	O		H	OAc
(XIII)	OAc	OAc	H	H	OAc
(XIV)	OAc	H	OAc	O	
(XV)	OAc	H	OAc	OAc	H

(lycoclavanol type). Oxidation of the acetonide with chromium trioxide–pyridine complex gave a ketone (VIII), m.p. 212—214°, which was identical (i.r., t.l.c., and m.p.) with the corresponding ketone derived from serratriol (I). Hence, B_2 is 21-episerratriol (III; serrat-14-ene-3β,21β-24-triol).



(V) R^4=H, R^5=OH
(VI) R^4=OH, R^5=H
(VIII) R^4, R^5=O



(VII) R^4=H, R^5=OH

The structure (III) was further confirmed by partial synthesis from lycoclavanol (II). As reported already, partial methanolysis of lycoclavanol triacetate (IX) gives 3,21-diacetate (X) as a major and 21,24-diacetate (XI) as a minor product.[7] Jones oxidation of the latter diacetate, and lithium aluminium hydride reduction of the resulting keto-diacetate (XII) gave the C-3-epimer of lycoclavanol,

whose triacetate (XIII) was identical with B_2 triacetate in all respects.

For comparison, the fourth stereoisomer, serrat-14-ene-3α,21α,24-triol (IV), was prepared by hydride reduction of the keto-diacetate (XIV) derived from lycoclavanol. The corresponding triacetate (XV), m.p. 209—211°, (n.m.r. Table 2), was apparently different from 21-episerratriol triacetate.

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