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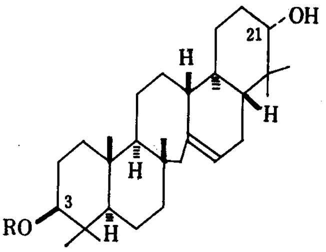
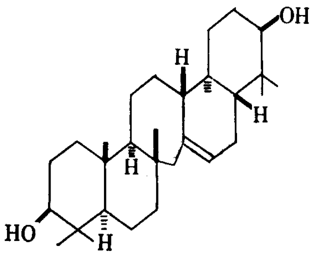
21-Episerratenediol, Isolation and its Structure

This communication is concerned with the constitution and stereochemistry of a triterpene-diol, 21-episerratenediol, which we have isolated from *Lycopodium serratum* THUNB. var. *Thunbergii* MAKINO (Lycopodiaceae) along with serratenediol, serratenediol-3-acetate and two new triterpenoids.

The structure of serratenediol and its 3-acetate, two major triterpenoid constituents, were already elucidated as formulated by I and II, respectively.[1,2]



I : R=H
II : R=$COCH_3$



III

Separation of minor triterpenoids was conveniently effected by repeated chromatography of derived acetates over silica gel and alumina. The physical constants of the three new triterpenoids and their acetates are listed in the Table. The nuclear magnetic resonance spectrum*[1] of A-diacetate indicated the presence of a trisubstituted

	Alcohol		Acetate
(A) 21-Episerratenediol	$C_{30}H_{52}O_2$,	m.p. 289~290°	$C_{34}H_{56}O_4$, m.p. 225~229° $[\alpha]_D$ −29° (c=2.06, $CHCl_3$)
(B) Serratriol	$C_{30}H_{50}O_3$,	m.p. 335~336°	$C_{36}H_{56}O_6$, m.p. 245~247° $[\alpha]_D$ +21° (c=1.9, $CHCl_3$)
(C) Tohogenol	$C_{30}H_{52}O_3 \cdot \frac{1}{2}H_2O$,	m.p. 242~244°	$C_{34}H_{56}O_5$, m.p. 305~306° $[\alpha]_D$ +28° (c=1.6, $CHCl_3$)

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*[1] NMR spectra were taken on Varian A-60 machine in $CDCl_3$ with Me_4Si as an internal standard by Mr. T. Shingu, Kyoto University, to whom we are indebted.

1) Y. Inubushi, T. Sano, Y. Tsuda: Tetrahedron Letters, No. 21, 1303 (1964).

2) Y. Tsuda, T. Sano, K. Kawaguchi, Y. Inubushi: *Ibid.*, No. 20, 1279 (1964).

double bond at 4.65 τ (1H, broad). The C-methyl region of the spectrum was almost superimposable with that of serratenediol diacetate but the acetate methyls of the A-diacetate were appeared separately at 7.91 τ (3H) and 7.95 τ (3H) in contrast to serratenediol diacetate in which the acetate methyls appeared as an overlapped single peak 7.97 τ (6H). Moreover, a broad multiplet at 5.52 τ (1H) and a sharp triplet at 5.31 τ (1H), both are attributable to geminal protons to acetoxyl groups, suggest that the former corresponds to an axial proton, the latter corresponding to an equatorial one.[3]

Chromium trioxide-pyridine complex oxidation of the diol (A) gave a diketone m.p. 206~208° which was identical with serratenedione in all respects. Hence the diol (A) must be an epimer of serratenediol in respect to the stereochemistry of either one or two hydroxyl groups. Then, the diol (A) was partially acetylated by heating the compound with acetic anhydride and pyridine for 8 minutes to a monoacetate, $C_{32}H_{52}O_3$, m.p. 317~319°; $[\alpha]_D$ −44° (c=1.3, $CHCl_3$), IR ν_{max}^{Nujol} cm^{-1} : 3584 (OH), 1730, 1239 (OAc), in about 10% yield, which was apparently different from serratenediol 3-acetate (II). In the nuclear magnetic resonance spectrum of this mono-acetate, a broad multiplet at 5.55 τ (1H) suggested that the presence of an axial proton geminal to an acetoxyl group and a sharp triplet at 6.55 τ (1H) showed the presence of an equatorial proton geminal to a hydroxyl group.

Oxidation of the mono-acetate with chromium trioxide-pyridine complex afforded a keto-acetate m.p. 306~307°. The identity of this with serrateneolone acetate[2] (3β-hydroxy-serrat-14-en-21-one acetate) was rigidly confirmed by direct comparisons of the both samples (m.p., mixed m.p., IR, ORD and TLC). Therefor, the diol (A) was established to be 21-epi-serratenediol (III) (serrat-14-ene-3β,21β-diol).*2

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*2 According to the private communication, Dr. J. W. Rowe isolated episerratenediol (diacetate, m.p. 236~237°, $[\alpha]_D$ −18°), but because of insufficient amounts available the stereochemistry of hydroxyl groups has not been established. The compound is probably identical with 21-episerratenediol, although the direct comparison was not available. cf. J. W. Rowe : Tetrahedron Letters, No. 34, 2347 (1964).

3) H. Vorbrüggen, S. C. Pakrashi, C. Djerassi : Ann., **668**, 57 (1963).