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Triterpenoid Chemistry. VI.[1] Lycopodium Triterpenoid. (5). The Structures and Stereochemistry of Serratriol, 21-Episerratriol, and Lycoclavanol

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The structures of triterpenoid-triols, serratriol, 21-episerratriol, and lycoclavanol, isolated from *Lycopodium* plants, were established as serrat-14-en-3β,21α,24-triol (**3**), serrat-14-en-3β,21β,24-triol (**36**), and serrat-14-en-3α,21β,24-triol (**22**), respectively. The fourth possible stereoisomeric triol, serrat-14-en-3α,21α,24-triol (**43**), was prepared from lycoclavanol. New method of acetonide formation of 1,3-glycol was reported.

The structural studies of serratenediol (**1**), a representative of Lycopodium triterpenoid, have established its unique structure in which ring C is a seven membered one.[1a] Further investigations of *Lycopodium* plants have revealed that they contained a number of minor triterpenoids of serratane group.[1e,4] Serratriol, 21-episerratriol, and lycoclavanol are three examples of stereoisomeric triol of this group being isolated from several *Lycopodium* plants; serratriol from *L. serratum*,[1d,e,5] 21-episerratriol from *L. clavatum*,[1e,4] *L. cernuum*,[1e] and *L. complanatum*[1e] (Japanese sp.), and lycoclavanol from *L. clavatum*[1e,6] and *L. complanatum*[1e] (Japanese sp.). Their structures have been established in two preliminary communications.[4,7] Here we present a full detail of our investigation in addition with further stereochemical discussions.

Serratriol, 21-episerratriol, and lycoclavanol have the same formulae, $C_{30}H_{50}O_3$, and formed by acetylation with pyridine-acetic anhydride the triacetates, $C_{36}H_{56}O_6$, whose nuclear magnetic resonance (NMR) spectra were listed in Table I.

Serratriol

The NMR spectrum of serratriol acetate indicated the presence of six tertiary C-methyl groups and of three acetyl methyls. One of three acetoxy groups is primary and the other are secondary, since the geminal protons to acetoxy group appeared as an AB quartet at δ 4.24 (2H, J=12, δ_{AB}=19 Hz) and as multiplets at δ 4.51 (2H, $W_{1/2}$=15 Hz).

1) This paper constitutes the part VI of triterpenoid chemistry and the followings are regarded as earlier parts of full papers of this series. *a*) Part I: Lycopodium triterpenoid. (1). Y. Inubushi, Y. Tsuda, T. Sano, T. Konita, S. Suzuki, H. Ageta, and Y. Otake, *Chem. Pharm. Bull.* (Tokyo), **15**, 1153 (1967); *b*) Part II: Y. Tsuda and K. Isobe, *Chem. Pharm. Bull.* (Tokyo), **15**, 797 (1967); *c*) Part III: Lycopodium triterpenoid. (2). Y. Tsuda, T. Sano, and Y. Inubushi, *Tetrahedron*, **26**, 751 (1970); *d*) Part IV: Lycopodium triterpenoid. (3). T. Sano, Y. Tsuda, and Y. Inubushi, *ibid.*, **26**, 2981 (1970); *e*) Part V: Lycopodium triterpenoid. (4). Y. Tsuda, T. Fujimoto, K. Isobe, T. Sano, and M. Kobayashi, *Yakugaku Zasshi*, **94**, 970 (1974).

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4) Y. Tsuda and M. Hatanaka, *Chem. Comm.*, **1969**, 1040.

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

6) Y. Inubushi, Y. Tsuda, and T. Sano, *Yakugaku Zasshi*, **82**, 1083, 1537 (1962).

7) Y. Tsuda, T. Sano, A. Morimoto, and Y. Inubushi, *Tetrahedron Letters*, **1966**, 5933.

Table I. NMR Spectra of Serrat-14-en-3,21,24-triol Triacetates (ppm, 60 MHz, in $CDCl_3$)

Comp.	C–Me[a]	–OCOMe[a]	–Ċ–CH$_2$–OAc[b]	>CH–OAc	–Ċ=CH–[c]
4	0.70(1)	2.03(1)	4.24	4.51	5.35
3β, 21α	0.85(3)	2.05(2)	δ=19	(2H, m.)	
	0.90(1)		J=12Hz		
	1.00(1)				
23	0.70(1)	2.05(1)	4.09	4.70	5.37
3α, 21β	0.85(3)	2.08(2)	δ=18	(1H, b.s.)	
	0.95(2)		J=12Hz	4.94(1H, b.s.)	
37	0.70(1)	2.02(1)	4.22	4.50	5.37
3β, 21β	0.86(3)	2.04(1)	δ=19	(1H, m.)	
	0.95(1)	2.07(1)	J=12Hz	4.67	
	1.00(1)			(1H, b.s.)	
42	0.70(1)	2.05(2)	4.10	4.53	5.37
3α, 21α	0.84(3)	2.08(1)	δ=17	(1H, m.)	
	0.91(1)		J=11Hz	4.96	
	0.95(1)			(1H, b.s.)	

a) numbers in parentheses denote number of methyl groups.
b) signal appears as AB quartet of 2H
c) signal appears as multiplet of 1H

The multiplet at δ 5.35 corresponding to one hydrogen showed the presence of a trisubstituted double bond. These data suggested that serratriol is a hydroxy-serratenediol.

The first chemical evidence that serratriol is one of congeners of serratenediol was obtained from the following reactions. Oxidation of serratriol triacetate (**4**) with sodium dichromate yielded an enone (**5**) (λ_{max} 256 nm, ν_{max} 1643, 1615 cm^{-1}) whose double bond was tetrasubstituted. Further oxidation of this enone with selenium dioxide gave a dienone (**6**) (λ_{max} 249 and 280 nm, ν_{max} 1653, 1625, and 1603 cm^{-1}) which on treatment with zinc in acetic acid was converted with loss of one methyl group to a phenol (**7**) (λ_{max} 282 and 291 nm). These reactions are completely parallel to those of serrat-14-ene and of serratenediol diacetate (**2**).[1a] Molecular rotation changes (Table II) in the above series of compounds were also parallel to those in the corresponding compounds (**8**, **9**, and **10**) derived from serratenediol diacetate;[1a] the fact which strongly suggested that serratriol possesses the same structure with that of serratenediol except one hydroxy-group which is placed at one of the seven methyl groups in serratenediol.

Table II. The Changes of Molecular Rotation

Serratenediol series	$[M]_D$	ΔM_D	Serratriol series	$[M]_D$	ΔM_D
Diacetate (**2**)	+100°	+ 91°	triacetate (**4**)	+ 50°	+ 85°
The enone (**8**)	+191°		the enone (**5**)	+135°	
The dienone (**9**)	+ 64°	−127°	the dienone (**6**)	+ 33°	−102°
The phenol (**10**)	+131°	+ 67°	the phenol (**7**)	+ 63°	+ 30°

Serratriol failed to form an O,O-isopropylidene derivative by the reaction with acetone and *p*-toluenesulfonic acid. (For the acetonide formation the forced condition is required··· see next section). However it easily formed a cyclic carbonate (**11**) under the reaction with phosgene and pyridine. The infrared (IR) absorption at 1746 cm^{-1} of **11** indicated that the carbonate is more than six-membered one. Oxidation of **11** with pyridine-chromium trioxide complex gave a keto-carbonate (**12**) (ν_{max} 1767 and 1720 cm^{-1}). Hydrolysis of this

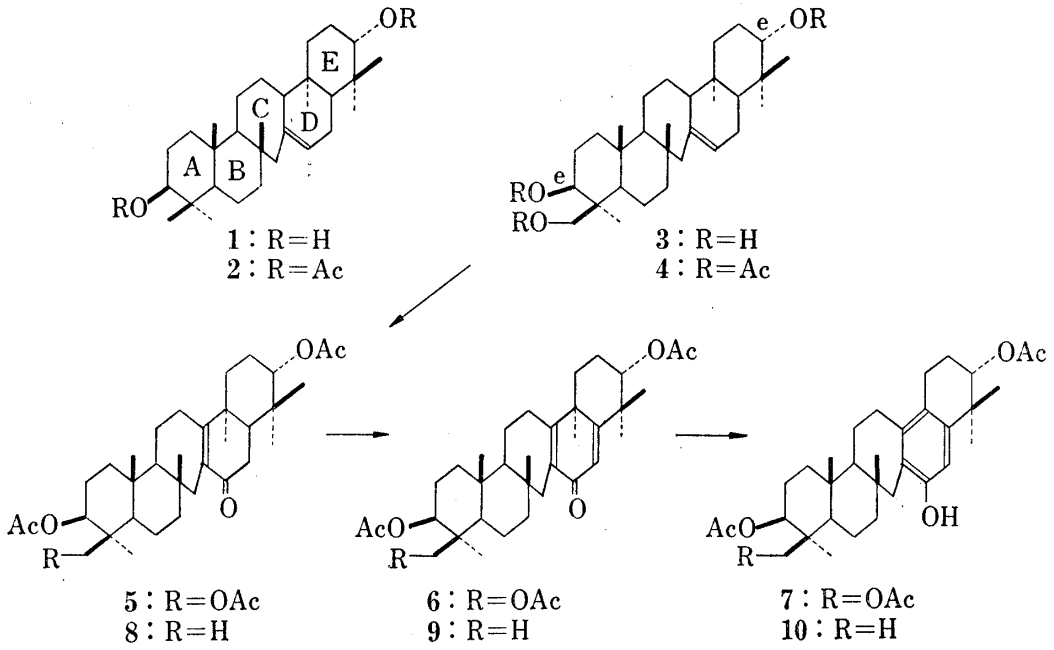

Chart 1

keto-carbonate with 5% methanolic potassium hydroxide, followed by acetylation of the resulting keto-diol (**13**) gave a keto-diacetate (**14**), while partial acetylation of the keto-diol (**13**) under mild condition furnished a keto-monoacetate (**15**), introduction of acetyl group to the primary hydroxy-group being confirmed by its NMR peaks at δ 4.25 (J=12 Hz, δ_{AB}= 16 Hz). Oxidation of **15** yielded a diketo-acetate (**16**).

In the optical rotatory dispersion (ORD) spectra both of the keto-carbonate (**12**) and the keto-diacetate (**14**) exhibited negative Cotton effects very similar to that of serrat-14-en-21-one, and the diketo-acetate (**16**) exhibited weakly negative Cotton effect which was almost identical with that of serrat-14-en-3,21-dione, indicating that serratriol is a derivative of serrat-14-en-3,21-diol and that the cyclic carbonate must be formed between 3-OH and a primary hydroxyl group.

Reduction of the diketo-acetate (**16**) with lithium aluminum hydride (LAH), followed by acetylation regenerated serratriol triacetate (**4**) as expected, confirming that the skeletal change did not occur during above transformations and that the secondary hydroxy groups of serratriol have the equatorial orientations since 3-keto group (and 21-keto-group as well) is known to be reduced to equatorial 3β-hydroxy group by hydride.[1a] In fact, the multiplets at δ 4.51 (2H) for 3-H and 21-H of serratriol triacetate were identical in their shapes and chemical shifts with those of serratenediol diacetate in which two hydroxy groups are in equatorial orientations.

The configuration of -CH_2OH group was assigned to be axial, since the chemical shifts (4.30—4.18 ppm) of the acetylated derivatives of this group are consistent with that for axial-CH_2OAc (4.30—4.08 ppm) rather than equatorial one (3.84—3.77 ppm).[8] Wolff-Kishner reduction of the diketone (**16**) accompanied retroaldol cleavage of this group and gave a nor-hydrocarbon (**17**); the fact which showed the position of this group to be at C_4 since it forms cyclic carbonate between 3β-OH group. Thus serratriol must have the structure (**3**). This conclusion was finally confirmed by transforming serratriol into serratenediol (see the last section).

The 3-keto derivative of serratriol was prepared as follows. Partial hydrolysis of serratriol triacetate (**4**) with 3% ethanolic hydrochloric acid under reflux gave a mixture of several

8) A. Gaudemer, M.J. Polonsky, and E. Wenkert, *Bull. Soc. Chem. France*, 1963, 407.

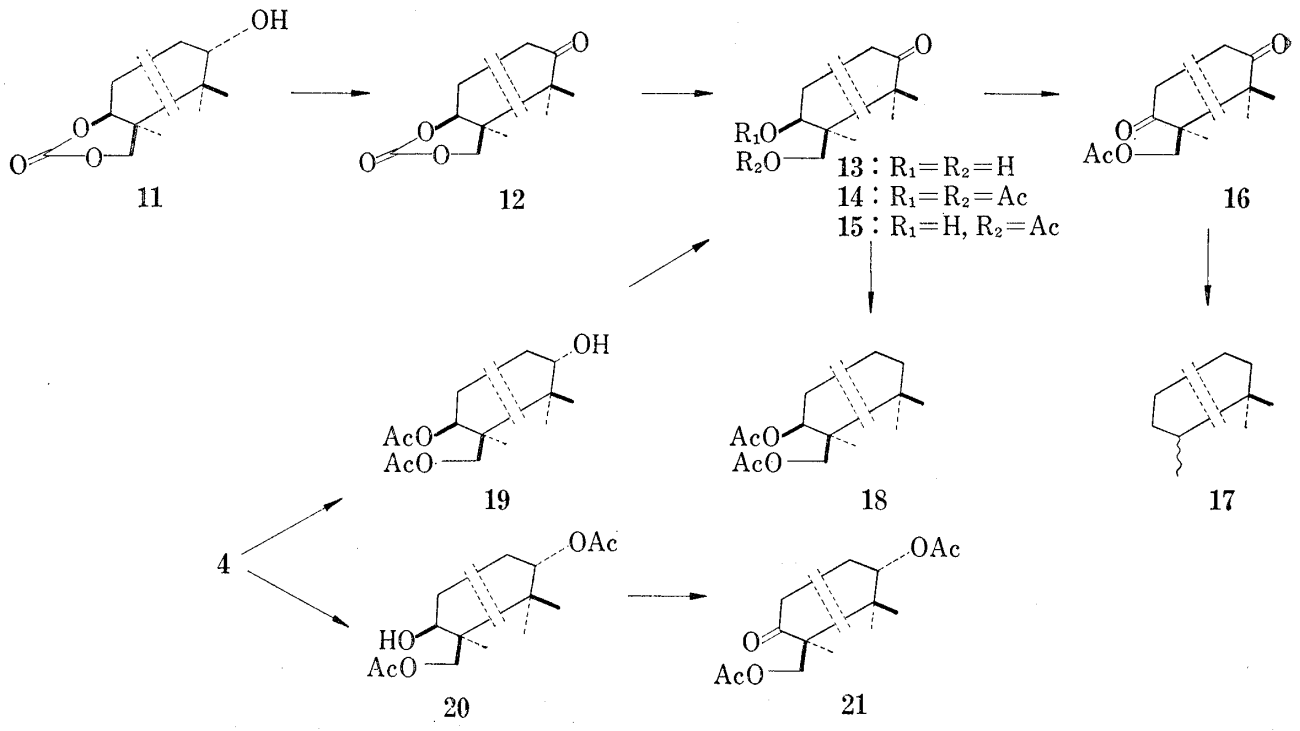

Chart 2

compounds from which two diacetate -a, mp 249—251°, and -b, mp 235—237° were isolated in pure forms. The diacetate-a (**19**) showed the presence of -CH_2-OAc group at δ 4.25 (J=12, δ_{AB}=20 Hz) in its NMR spectrum and gave, on oxidation, the keto-diacetate (**14**) identical with the compound obtained from the carbonate (**12**). Therefore **19** is the 21-hydroxy-compound. The other diacetate-b (**20**) also showed the presence of -CH_2-OAc group at δ 4.23 (J=12, δ_{AB}=18 Hz) in its NMR and gave, on oxidation with pyridine-chromium trioxide complex, a different keto-diacetate (**21**). This is the expected 3-keto derivative, since its ORD spectrum showed a positive Cotton effect as that of serrat-14-en-3-one.[1a] The expected 24-hydroxy compound was not isolated from the mixture. This fact will be explained by easy acetyl migration from 3β-OAc to cis-arranged 4β-CH_2OH group.

Mass Spectra of Serratriol Derivatives

The mass spectra of serratriol derivatives (Table III) supported above structural assignment. As shown in Chart 3, the fragment ions **a**, **b**, and **c** are characteristic of serrat-14-ene.[1a,9] The ion **a** was formed by the retro-Diels-Alder cleavage of ring D. The ions **b** and **c** are derived from the cleavage of ring C and are consisted of ring A/B and ring D/E, respectively. In compounds (**14** and **19**), the mass number of fragment ion **a** (*m/e* 402) and also those of its satelite ions (**a**-AcOH) and (**a**-2×AcOH) clearly indicated that it carries two acetoxy-groups, demonstrating that two of three acetoxy-group are at ring A/B. This was also supported by the mass number of the fragment ion **b** (*m/e* 307).

While the mass number of fragment ion **c** (*m/e* 262) from **21** carried only one acetoxy-group and that (*m/e* 204) from **18** was lacking acetoxy-group as expected.

Lycoclavanol and 21-Episerratriol

The NMR spectrum of lycoclavanol triacetate (**23**) exhibited peaks of six C-methyl groups and three acetyl methyls. An AB quartet at δ 4.09 (J=12 Hz, δ_{AB}=19 Hz) was attributed to a -CH_2-OAc group with an axial orientation. The signals of the geminal protons to secon-

9) J.P. Kutney and G. Eigendrof, *Tetrahedron*, **25**, 3753 (1969).

Table III. Mass Spectra of Serratriol Derivatives (%; relative intensity)

Compound	*m/e* Ion **a**	Ion **b**	Ion **c**
21	358(5) 298(**a**-AcOH; 7.5)	263(12.5) 203(**b**-AcOH; 64)	262(19) 202(**c**-AcOH; 36)
14	402(2) 342(**a**-AcOH; 2) 282(**a**-2AcOH; 8.0)	307(13) 247(**b**-AcOH; 23) 187(**b**-2AcOH; 100)	218(54.5)
19	402(3.9) 342(**a**-AcOH; 6.2) 282(**a**-2AcOH; 14.8)	307(4) 247(**a**-AcOH; 13.3) 187(**a**-2AcOH; 64.9)	220(40.6)
20	342(**a**-OH; 5.9)	247(**b**-OH; 9.8)	262(28.4) 202(**c**-AcOH; 45.1)
18	402(7) 342(**a**-AcOH; 10) 282(**a**-2AcOH; 25)	307(4) 247(**b**-AcOH; 10) 187(**b**-2AcOH; 45)	204(56)
16	358(3.4) 298(**a**-AcOH; 3.9)	263(16.8) 203(**b**-AcOH; 89.7)	218(100)

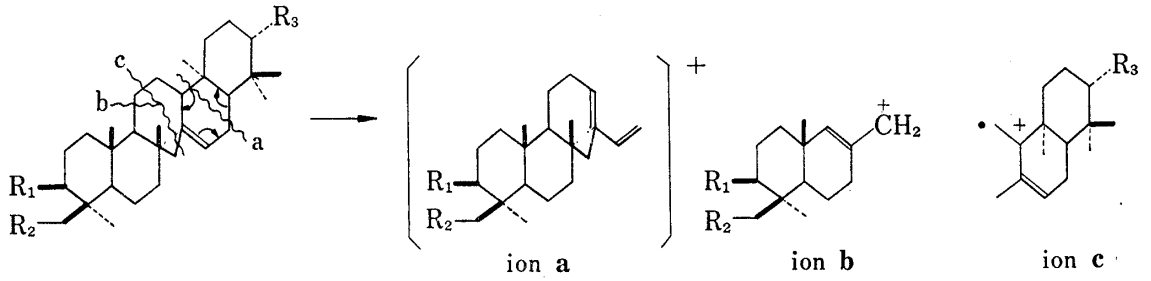

Chart 3

dary acetoxyl groups appeared at δ 4.70 (1H) and at 4.94 (1H) as broad singlets ($W_{1/2}$=5 Hz), suggesting that the both secondary hydroxy groups of lycoclavanol to be axial. Thus lycoclavanol was assumed to be an isomer of serratriol concerning on the stereochemistries of two secondary hydroxy-groups, *i.e.* serrat-14-en-3α,21β,24-triol.

Chemical correlation of serratriol and lycoclavanol was as follows. Partial acetylation of lycoclavanol (**22**) with acetic anhydride in pyridine at 5° for 30 min gave a mono-acetate (**24**), as a major product. Introduction of acetyl group to the primary hydroxy-group was shown by an AB quartet at δ 4.07 (J=12 Hz, δ_{AB}=17 Hz) in its NMR spectrum. Oxidation of **24** with pyridine-chromium trioxide complex gave a diketo-acetate which was identical with the diketone (**16**) derived from serratriol, thus confirming the above assumption. That lycoclavanol and serratriol differ in the stereochemistry of both the hydroxy-groups was chemically proved as follows. In contrast to serratriol, lycoclavanol did not give a cyclic carbonate under the condition with phosgene in pyridine. After several fruitless attempts to prepare the O,O-isopropylidene derivatives from serratriol and lycoclavanol, we found that the forced condition, that is, gentle reflux of the compound in DMF with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid is effective for this purpose. Under this condition serratriol gave the desired acetonide (**25**) in excellent yield within 2 hr. Lycoclavanol was more difficult to react but gave the acetonide (**26**) in about 50% yield after 6 hr. The NMR spectra of **25** and **26** clearly indicated the introductions of O,O-isopropylidene group. Hydrolysis of both acetonides regenerated serratriol and lycoclavanol, respectively, proving that no rearrangement took place during the reaction. Acetylation of the acetonides (**25** and **26**) with pyridine-acetic anhydride gave the corresponding acetates (**27** and **28**). Oxidation of the acetonides (**25** and **26**) with pyridine-chromium trioxide afforded the keto-acetonides (**29** and **30**), respectively, which were different each other, though the both ketones exhibited

the similar negative Cotton effects in the ORD spectra indicating that they are 21-ketones. Thus, the stereochemistry of C_3-hydroxy-group of serratriol and lycoclavanol must be different.

Hence lycoclavanol has diaxially arranged 3α-OH and 4β-CH_2OH, which in the acetonide must have been changed to diequatorial arrangement by converting the ring A into energetically unfavored boat conformation. Therefore, the lycoclavanol is more difficult to form the acetonide than serratriol and the acetonide is more unstable than that of serratriol. It was gradually hydrolysed into lycoclavanol on merely heating the compound in methanol. (Further stereochemical discussions in connection with the NMR spectra of acetonides are given in the accompanying paper).

Partial hydrolysis of lycoclavanol triacetate gave much simpler result than that of serratriol triacetate, since acetyl migration in this case is not possible unless ring A had changed to a boat form. Thus mild methanolysis of lycoclavanol triacetate yielded diacetate-B (**31**)

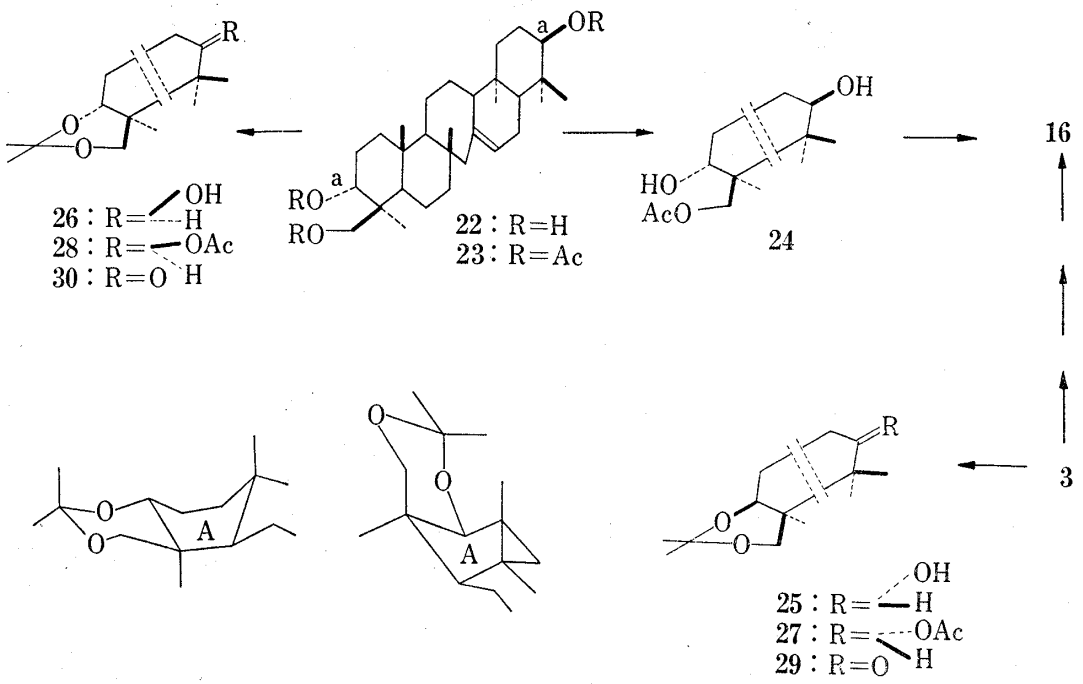

Chart 4

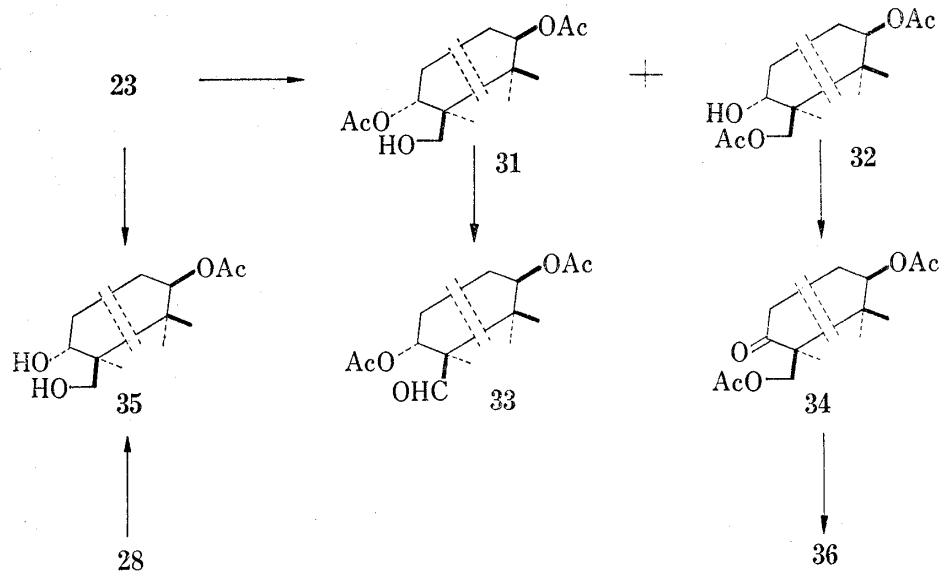

Chart 5

as a major and diacetate-A (**32**) as a minor product. The diacetate-B (**31**) has two secondary acetoxy-groups shown by NMR spectrum. Jones' oxidation of **31** to an aldehyde (**33**) (δ 10.03, 1H, singlet) confirmed the structure. The diacetate-A (**32**) had primary acetoxy-group shown by the NMR spectrum and yielded, on Jones' oxidation, a keto-diacetate (**34**) which exhibited positive Cotton effect in the ORD spectrum indicating that the compound is 3-keto derivative, but it was different from **21** derived from serratriol. Thus, the stereochemistry of C_{21}-hydroxy-group is again different from that of serratriol. Therefore, lycoclavanol is serrat-14-en-3α,21β,-24-triol.

Formation of the diacetate-A (**32**) by partial hydrolysis must require some comments. Its formation suggests the acetyl migration through the boat conformation, though we can not exclude the alternative possibility of ester exchange between the monoacetate (**35**) and methyl acetate being formed in the reaction mixture by methanolysis of acetyl group. In fact, alkaline hydrolysis of lycoclavanol triacetate by 2% methanolic sodium hydroxide for short time under reflux yielded the mono-acetate (**35**) in addition to fully deacetylated compound, lycoclavanol, the structure of **35** being proved by alternative synthesis from the acetonide-acetate (**28**). In either case the higher reactivity of 3α-acetoxy-group to the hydrolytic cleavage than 21β-acetoxy-group will be explained in terms of participation of neighboring $-CH_2OH$ group in diacetate-B (**31**).

21-Episerratriol (**36**) is the third stereoisomer, serrat-14-en-3β,21β,24-triol. The NMR spectrum of the acetate (**37**) showed that the compound is also a trihydroxyserratene with one primary and two secondary hydroxy groups, in the latters one is equatorial and the other is axial since one of geminal protons to secondary acetoxy-group appeared as a broad singlet at δ 4.67 and the other as a multiplet at δ 4.50.

21-Episerratriol, when allowed to react with 2,2-dimethoxypropane under the forced condition described above, formed an acetonide (**38**) in excellent yield as in serratriol. The acetonide had the spectral pattern characteristic of serratriol type (Type **A**···see accompanying paper). Oxidation of this with pyridine-chromium trioxide complex yielded a keto-acetonide, which was identical with the keto-acetonide (**29**) obtained from serratriol.

Hence serratriol and 21-episerratriol differ only in stereochemistry of 21-hydroxy-group.

If our stereochemical assignments of these three triterpenoids are correct, C_3-epimer of lycoclavanol must be identical with 21-episerratriol. This was proved to be the case by reduction of the keto-diacetate (**34**) with lithium aluminum hydride. The triacetate of the product was identical with 21-episerratriol triacetate (**37**).

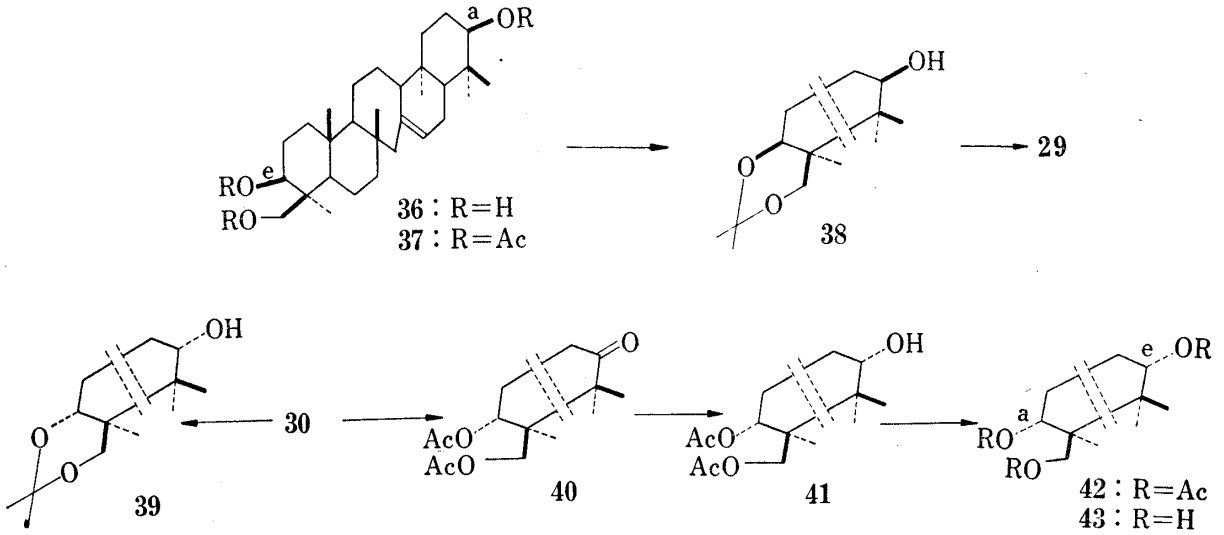

Chart 6

The fourth stereoisomer, serrat-14-en-3α,21α,24-triol, which has 3-axial and 21-equatoriol hydroxy-groups, was prepared from lycoclavanol for comparison. Reduction of the keto-acetonide (**30**) with lithium aluminum hydride yielded the desired acetonide (**39**) having 21α-hydroxy group (equatorial) as a major product. But, since it was rather unstable and slowly decomposed into triol during the purification from the accompanying axial isomer (lycoclavanol acetonide), the following variation was adopted to prepare the pure 21-isomer. The keto-acetonide (**30**) was firstly converted to the keto-diacetate (**40**) by hydrolysis with acetic acid followed by acetylation, which was then reduced to the alcohol by sodium borohydride and rigorously purified. Acetylation of the product (**41**) afforded the desired triacetate (**42**), mp 209—211° in pure form, which was apparently different from the other three triacetates (NMR spectrum is listed in Table I). The corresponding triol (**43**) had mp 318—320° (decomp.).

Correlation of Lycoclavanol to Diepiserratenediol and of Serratriol to Serratenediol

If the conversion of $-CH_2-OH$ to CH_3 succeed, lycoclavanol and serratriol will give the corresponding diols, diepiserratenediol and serratenediol, respectively. These transformations will give final rigid structural proofs to those triols.

Wolff-Kishner reduction of the aldehyde (**33**) obtained from lycoclavanol afforded two products on thin-layer chromatography (TLC). The more mobile compound was a diol, whose diacetate, mp 240—242° was completely identical with diepiserratenediol diacetate (**44**).[1e,4,10]

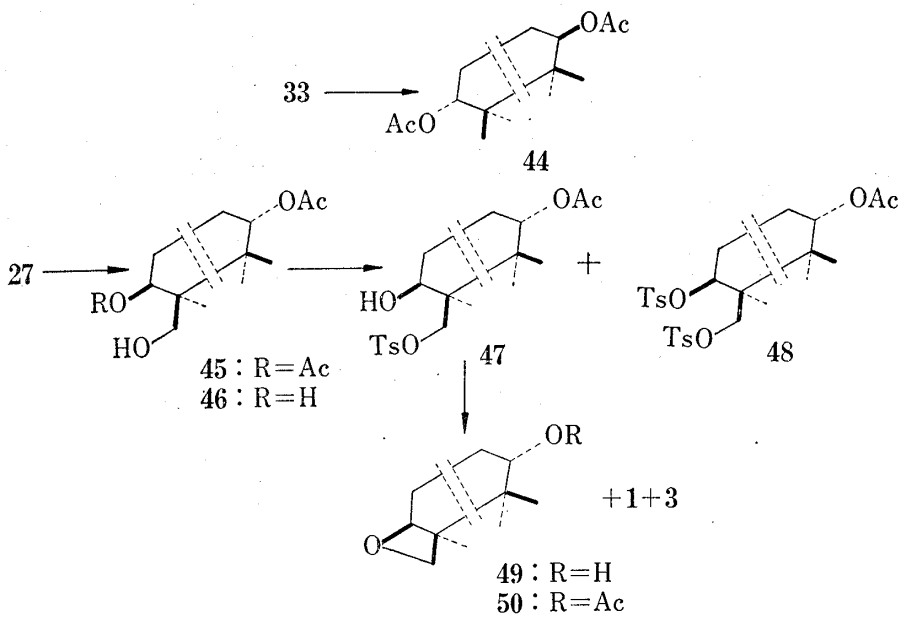

Chart 7

Correlation of serratriol and serratenediol was not simple, since hydrolysis of serratriol triacetate did not give the suitable diacetate (**45**). It was achieved as follows. The acetonide-acetate (**27**) was firstly hydrolysed to the mono-acetate (**46**). Tosylation of this with *p*-toluenesulfonyl chloride in pyridine gave a monotosylate (**47**), together with a ditosylate (**48**). The presence of the $-CH_2-OTs$ group and a secondary hydroxyl group in the monotosylate (**47**) were shown by its NMR signals at δ 4.15 and at 3.22. Lithium aluminum hydride reduction of this monotosylate in tetrahydrofuran (THF) under reflux yielded three compounds A, B, and C, which were separated by chromatography over alumina in yield of 60%, 18%, and 15%, respectively. The compound-A had a composition of $C_{30}H_{40}O_2$ and formed, on acetylation, a monoacetate (**50**), which had no OH band in its IR spectrum. Therefore, the

10) J.W. Rowe, *Tetrahedron Letters*, **1964**, 2347.

second oxygen must be forming an ether linkage. In accord with this, the NMR spectrum exhibited a quartet of 1H at δ 4.60 and an AB quartet at δ 4.30, which were assigned to C_3-H and C_{24}-H respectively. Thus, it is an oxetane (**49**) formed by attack of 3β-hydroxylate to cis-arranged -CH_2OTs group. The compound-B, on acetylation gave a diacetate which was completely identical with serratenediol diacetate (**2**). The compound-C was serratriol, confirmed as the triacetate. (More detailed stereochemical discussions on this reduction will be given in a separate paper).

Experimental

Unless otherwise stated melting points were determined on a Yanagimoto melting point apparatus, NMR spectra were measured in $CDCl_3$, IR spectra were taken on Nujol mull, and ORD's were taken in dioxane solution. Identities were confirmed by IR and by TLC comparisons. Alumina used for chromatography was washed with 2.5% AcOH and reactivated.

The Enone (5)——Serratriol triacetate [1d,5] (490 mg) in benzene (5 ml) was stirred with 15% (v/v) AcOH–H_2SO_4 (40 ml), and the mixture was kept overnight at room temp., then poured into ice-water and extracted with $CHCl_3$. The extract was washed with 5% $NaHCO_3$, water, and dried over $MgSO_4$. Evaporation of the solvent left a solid (430 mg) which was a mixture of isoserratriol triacetate (Δ^{13-14}) and serratriol triacetate as shown by NMR spectrum.

The above solid (300 mg) and sodium bichromate (352 mg) in AcOH (20 ml) was refluxed for 2 hr. The mixture was diluted with water, extracted with $CHCl_3$, and the extract was washed with water, dried over $MgSO_4$, and evaporated to give a residue (312 mg) which was chromatographed in benzene over alumina. Crystallization of the eluate gave **5**, colorless needles, mp >300°. $[\alpha]_D$ +22.3° (c=1.1 in $CHCl_3$). IR cm^{-1}: 1740—1720, 1643, 1615. UV nm(log ε): 256 (3.33). NMR δ: 0.65 (3H,) 0.80 (3H), 0.90 (3H), 0.96 (3H), 1.00 (3H,), 1.07 (3H), 2.02 (3H), 2.05 (3H), 2.06 (3H), 4.24 (2H, ABq. J=11 Hz, δ_{AB}=20.5 Hz), 4.54 (2H, m). *Anal.* Calcd. for $C_{36}H_{54}O_7$: C, 72.21; H, 9.09. Found: C, 72.31; H, 9.34.

The Dienone (6)——The enone **5** (151 mg) and $SeO_2 \cdot 2H_2O$ (179 mg) in AcOH (10 ml) were heated under reflux for 3 hr. After cooling the solvent was removed *in vacuo* and a residue in benzene was chromatographed over alumina. Elution with benzene afforded **6** (72 mg) (needles from *n*-hexane–benzene), mp 267—269°. $[\alpha]_D$ +5.5° (c=0.55 in $CHCl_3$). IR cm^{-1}: 1740—1710, 1653, 1625, 1603. UV nm(log ε): 249, (3.86), 280 (3.32). NMR δ: 0.66 (3H), 0.79 (3H), 1.01 (3H), 1.19 (3H), 1.30 (6H), 2.06 (6H), 2.08 (3H), 4.18 (2H, ABq. J=12 Hz, δ_{AB}=20 Hz), 4.48 (2H, m), 6.32 (1H). *Anal.* Calcd. for $C_{36}H_{52}O_7$: C, 72.45; H, 8.78. Found: C, 72.18; H, 9.08.

The Phenol (7)——To a solution of **6** (88 mg) in AcOH (15 ml), zinc dust (1.5 g) was added and the mixture was refluxed for 4 hr. The cooled mixture was filtrated and the filtrate was concentrated *in vacuo* to dryness. The residue was extracted with $CHCl_3$ and the organic extract was washed with water, dried over $MgSO_4$ and evaporated to give a solid which was passed through alumina in benzene to yield **7** (56 mg) (prisms from $CHCl_3$–MeOH), mp 255—257°. $[\alpha]_D$ +10.7 (c=0.56 in $CHCl_3$). IR cm^{-1}: 1740—1700, 1606, 1595. UV nm(log ε): 282 (3.23), 291 (3.24). NMR δ: 0.65 (3H), 0.79 (3H), 1.00 (3H), 1.25 (6H), 2.05 (9H), 4.25 (2H, ABq. J=12 Hz, δ_{AB}=19 Hz), 4.55 (1H, m), 4.98 (1H, t, J=4 Hz), 6.61 (1H), 5.20 (1H, OH). *Anal.* Calcd. for $C_{35}H_{50}O_7$: C, 72.13; H, 8.65. Found: C, 72.41; H, 8.80.

Serratriol Carbonate (11)——Serratriol (48 mg) in pyridine (10 ml) and $CHCl_3$ (4 ml) was treated at 0° with toluene (20 ml) saturated with $COCl_2$, and the mixture was kept overnight at room temp., then poured into ice-water and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$, and evaporated to dryness. Crystallization of a residue (42 mg) from $CHCl_3$–MeOH afforded **11** as prisms, mp 285—287°. IR cm^{-1}: 3475, 1746. NMR δ: 0.68 (3H), 0.82 (6H), 0.87 (3H), 0.96 (3H), 1.28 (3H), 3.21 (1H, m), 3.86 (d, J=11 Hz), 4.68 (d, J=11 Hz), 5.35 (1H, m).

Acetylation of this (20 mg) with pyridine (1 ml) and Ac_2O (0.5 ml) gave the corresponding acetate (prisms from $CHCl_3$–MeOH), mp >300°. IR cm^{-1}: 1767, 1721. NMR δ: 0.70 (3H), 0.85 (9H), 0.91 (3H), 1.27 (3H), 2.07 (3H), 3.98 (2H, ABq. J=12 Hz, δ_{AB}=49 Hz), 4.50 (1H, m), 5.35 (1H, m). *Anal.* Calcd. for $C_{33}H_{50}O_5$: C, 75.24; H, 9.57. Found: C, 74.79; H, 9.59.

Keto-carbonate (12)——The carbonate **11** (80 mg) in pyridine (2 ml) and pyridine (1 ml)–chromium trioxide (0.1 g) complex were stirred at room temp. for 20 hr. Working up as usual, the product in benzene was chromatographed over alumina. Elution with benzene yielded **12** (40 mg) (prisms from $CHCl_3$–MeOH), mp 266—268°. IR cm^{-1}: 1767, 1720. ORD[ϕ](nm): −2000° (317) (trough), +500° (277) (peak). *Anal.* Calcd. for $C_{31}H_{46}O_4$: C, 77.13; H, 9.61. Found: C, 77.06; H, 9.91.

Hydrolysis of the Keto-carbonate (12)——The keto-carbonate **12** (100 mg) in 5% methanolic-KOH (50 ml) was refluxed for 5 hr and the mixture was poured into water, and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$, and evaporated to give the 21-keto-diol (**13**; 35 mg) (prisms from $CHCl_3$–MeOH), mp 268—270°. IR cm^{-1}: 3370, 1706. *Anal.* Calcd. for $C_{30}H_{48}O_3$: C, 78.89;

H, 10.98. Found: C, 78. 60;H, 10.80.

Acetylation of this gave the 21-keto-diacetate (**14**), (needles from $CHCl_3$–MeOH), mp 245—247°. IR cm^{-1}: 1732, 1707. NMR δ: 0.82 (6H), 0.92 (6H), 1.05 (3H), 1.08 (3H), 2.02 (3H), 2.05 (3H), 4.24 (2H, ABq. $J=12$ Hz, $\delta_{AB}=24$ Hz), 4.50 (1H, m), 5.38 (1H, m). ORD[ϕ](nm): −1200° (315) (trough), +820° (280) (peak). *Anal.* Calcd. for $C_{34}H_{52}O_5 \cdot 3/2H_2O$: C, 71.92; H, 9.75. Found: C, 72.29; H, 9.68.

Serrat-14-en-3β,24-diol Diacetate (**18**)——A mixture of **13** (200 mg), hydrazine hydrochloride (200 mg) and hydrazine (3 ml) in diethyleneglycol (15 ml) was heated at 180° for 5 hr, and KOH (1 g) was added. After removal of excess hydrazine, the mixture was heated at 180° for further 5 hr. After working up as usual, the product (168 mg) was acetylated in Ac_2O (9 ml) and pyridine (15 ml). The product was crystallized from $CHCl_3$–MeOH to give **18** (79 mg) as needles, mp 218—222°.

Partial Acetylation of the 21-Keto-diol (**13**)——To a solution of **13** (150 mg) in pyridine (10 ml) was added acetic anhydride (1 ml) at 0°, and the mixture was kept for 30 min at room temp., then poured into ice-water. The product, after working up as usual, showed 4 spots on TLC, which was separated by preparative TLC. Compound A (30 mg) was identical with 21-keto-diacetate (**14**). Compound B (trace) was not characterized. Compound C (45 mg) was the 21-keto-24-monoacetate (**15**), mp 208—210°, (prisms from MeOH). NMR δ: 0.82 (6H), 0.92 (3H), 1.05 (3H), 1.08 (3H), 1.14 (3H), 2.06 (3H), 3.29 (1H, m), 4.25 (2H, ABq. $J=12$ Hz, $\delta_{AB}=16$ Hz). *Anal.* Calcd. for $C_{32}H_{50}O_4$: C, 77.06; H, 10.11. Found: C, 77.04; H, 10.16. Compound D was the starting material.

The Diketo-acetate (**16**)——21-Keto-24-monoacetate (**15**; 50 mg) in pyridine (1 ml) and pyridine (1 ml)-CrO_3 (0.1 g) complex were mixed and the mixture was allowed to stand overnight at room temp., then poured into ice-water, and extracted with $CHCl_3$. The extract was washed with 5% HCl, water, dried over $MgSO_4$, and evaporated to dryness. Chromatography of the residue in benzene over alumina gave **16** (needles from MeOH), mp 242—244°. IR cm^{-1}: 1735, 1703. NMR δ: 0.88 (3H), 0.94 (3H), 1.05 (6H), 1.09 (3H), 1.15 (3H), 2.00 (3H), 4.30 (2H, ABq. $J=12$ Hz, $\delta_{AB}=40$ Hz), 5.42 (1H, m). ORD[ϕ](nm): −2400° (320) (trough), +120° (290) (peak). *Anal.* Calcd. for $C_{32}H_{48}O_4 \cdot 1/4H_2O$: C, 76.68; H, 9.75. Found: C, 76.60; H, 9.59.

Hydride Reduction of the Diketo-acetate (**16**)——Diketo-acetate (**16**; 20 mg) and LAH (100 mg) in THF (10 ml) were refluxed for 4 hr. After addition of a few drops of water to decompose excess LAH, the mixture was filtered and the residue was washed with $CHCl_3$ several times. The combined organic filtrate was evaporated to dryness and the residue was acetylated with pyridine (1 ml) and acetic anhydride (0.5 ml). The product, obtained by working up, was identical with serratriol triacetate (**4**), mp and mixed mp 245—247°.

Nor-hydrocarbon (**17**)——The diketo-acetate (**16**; 20 mg) and anhydrous hydrazine (1 ml), in triethyleneglycol (5 ml) were heated at 150° for 1 hr then metallic sodium (0.5 g) was added and the mixture was heated at 230—250° for further 4 hr. The cooled mixture was poured into water, extracted with ether which was washed with water, dried over K_2CO_3, and evaporated. The residue in *n*-hexane was passed through alumina and the eluate crystallized from methanol gave a nor-hydrocarbon (**17**), mp 179—182°. Calcd. for $C_{29}H_{48}$: M^+, 286. Found: $m/e=286$.

Partial Hydrolysis of Serratriol Triacetate (**4**)——Serratriol triacetate (672 mg) in EtOH (250 ml) and conc. HCl (9 ml) was refluxed for 30 min. After cooling the mixture was neutralized with 10% $NaHCO_3$ and evaporated *in vacuo*, and the residue was diluted with water, then extracted with $CHCl_3$. The organic extract was dried over $MgSO_4$ and evaporated to give an oil (689 mg) which was chromatographed in benzene over alumina (12×0.8 cm) as follows. i) Elution with benzene (100 ml) gave the starting material (350 mg), mp 246—249°. ii) Further elution with benzene (300 ml) gave a solid (100 mg) which was crystallized from $CHCl_3$–MeOH to give serratriol diacetate-a (**19**) as needles, mp 249—251°. NMR δ: 0.69 (3H), 0.83 (9H), 0.96 (3H), 0.99 (3H), 2.02 (3H), 2.05 (3H), 3.70 (1H, m), 4.25 (2H, ABq. $J=12$ Hz, $\delta_{AB}=20$ Hz), 4.53 (1H, m), 5.35 (1H, m). *Anal.* Calcd. for $C_{34}H_{54}O_5$: C, 75.23; H, 10.03. Found: C, 75.30; H, 10.30. iii) Following elutions with benzene (300 ml) gave a mixture (45 mg) (two spots on TLC) which was separated by preparative TLC into serratriol diacetate-a (16 mg) and serratriol diacetate-b (**20**), the latter on crystallizations from MeOH–$CHCl_3$ afforded prisms, mp 235—237°. NMR δ: 0.69 (3H), 0.84 (3H), 0.90 (3H), 1.12 (3H), 2.03 (6H), 3.21 (1H, m), 4.23 (2H, ABq. $J=12$ Hz, $\delta_{AB}=18$ Hz), 4.50 (1H, m), 5.34 (1H, m). *Anal.* Calcd. for $C_{34}H_{54}O_5$: C, 75.23; H, 10.03. Found: C, 75.45; H, 9.77. iv) Elution with $CHCl_3$ (200 ml) gave a gum (178 mg) which showed several spots on TLC.

The Keto-diacetate-a (**14**)——i) The diacetate-a (**19**; 100 mg) and pyridine (2 ml)-CrO_3 (0.1 g) were stirred overnight at room temp. The mixture was poured into ice-water and extracted with $CHCl_3$. The extract was washed with 5% HCl, H_2O, and dried over $MgSO_4$. Evaporation of the solvent left a crystalline residue, which was chromatographed in benzene over alumina. Elution with benzene and crystallization of the eluate from $CHCl_3$–MeOH gave the keto-diacetate-a (**14**; 85 mg) as needles, mp and mixed mp 245—247°, identical with the 21-keto-diacetate obtained from the keto-carbonate (**12**).

ii) The keto-acetonide (**29**) (see below) was hydrolysed with 70% AcOH as described below. Acetylation of the product with pyridine-Ac_2O gave the keto-diacetate-a (**14**), mp and mixed, mp 245—247°.

The Keto-diacetate-b (**21**)——Similar oxidation of the diacetate-b (**20**; 30 mg) with pyridine (1.5 ml)-CrO_3 (25 mg) complex gave the 3-keto-diacetate (**21**) (20 mg). Crystallizations from $CHCl_3$–MeOH furnished

prisms, mp 252—254°. IR cm^{-1}: 1725. NMR δ: 0.70 (3H), 0.86 (6H), 0.90 (3H), 1.04 (3H), 1.13 (3H), 1.99 (3H), 2.05 (3H), 4.30 (2H, ABq. $J=12$ Hz, $\delta_{AB}=38$ Hz), 4.52 (1H, m), 5.38 (1H, m). ORD[ϕ](nm): +1220° (307) (peak). *Anal.* Calcd. for $C_{34}H_{52}O_5$: C, 75.51; H, 9.69. Found: C, 75.77; H, 9.96.

Partial Acetylation of Lycoclavanol (22)——Lycoclavanol (500 mg) and Ac_2O (1 ml) in pyridine (20 ml) were stirred at 5° for 30 min. The mixture was poured into ice-water and filtered to collect ppt which was washed well with water, dried, then digested with large amount of benzene, and the extract was passed through short column of alumina. i) First benzene eluate gave lycoclavanol triacetate (**23**; 50 mg), ii) elutions with benzene–CH_2Cl_2 gave 21,24-diacetate (diacetate-A) (**32**), mp and mixed, mp 243—245° (100 mg) (see below). iii) Elutions with $CHCl_3$ gave a monoacetate **24** (270 mg) (needles from $CHCl_3$–MeOH), mp 252—254°. NMR δ: 0.69 (3H), 0.82 (6H), 0.88 (3H), 0.94 (3H), 1.05 (3H), 2.04 (3H), 3.46 (1H, b.s), 3.70 (1H, b.s), 4.07 (2H, ABq. $J=12$ Hz, $\delta_{AB}=17$ Hz), 5.33 (1H, m). *Anal.* Calcd. for $C_{32}H_{52}O_4$: C, 76.75; H, 10.47. Found: C, 77.27; H, 10.76.

Oxidation of the Monoacetate (24)——The monoacetate (**24**; 100 mg) in pyridine (1 ml) was stirred with pyridine (1 ml)–CrO_3 (150 mg) for 2 hr at room temp. After keeping the mixture overnight at room temp., it was poured into ice-water and extracted with $CHCl_3$ which was washed with 5% HCl, water, and dried over $MgSO_4$, then evaporated. Chromatography of the residue in benzene over alumina gave the diketone (**16**; 90 mg), mp and mixed mp 242—244°, identical with the diketone obtained from serratriol.

Serratriol Acetonide (25)——Serratriol (1.012 g), *p*-TsOH (85 mg) and 2,2-dimethoxypropane (10 ml) in DMF (20 ml) were refluxed for 2 hr. The cooled mixture was neutralized with $NaHCO_3$ (520 mg), filtered and the filtrate evaporated *in vacuo* to dryness. The residue in benzene was chromatographed over Florisil to yield **25** (1.160 g), (needles from $CHCl_3$–MeOH), mp 250—252°. IR cm^{-1}: 3500. *Anal.* Calcd. for $C_{33}H_{54}O_3$: C, 79.46; H, 10.92. Found: C, 79.45; H, 10.87.

Acetylation of **25** (1.06 g) with pyridine (10 ml) and acetic anhydride (5 ml) at room temp. gave an acetate (**27**; 1.180 g) (needles from $CHCl_3$–MeOH), mp >300°. IR cm^{-1}: 1728, 1252. *Anal.* Calcd. for $C_{35}H_{56}O_4$: C, 77.73; H, 10.44. Found: C, 77.70; H, 10.36.

Treatment of the acetonide (**25**) with warm 70% AcOH quantitatively regenerated serratriol (**3**).

The Keto-acetonide (29)——The acetonide (**25**; 76 mg) was oxidized with pyridine (2 ml)–CrO_3 (0.1 g) as described above. The product in benzene was passed through Florisil to give **29** (needles from acetone), mp 213—215°. IR cm^{-1}: 1703. ORD[ϕ](nm): −2240° (316) (trough), +1166° (280) (peak), ($c=2.13$). *Anal.* Calcd for $C_{33}H_{52}O_3$: C, 79.78; H, 10.55. Found: C, 79.46; H, 10.19.

Lycoclavanol Acetonide (26)——Lycoclavanol (300 mg), *p*-TsOH (200 mg) and 2,2-dimethoxypropane (20 ml) in dimethylformamide (DMF) (10 ml) were refluxed for 6 hr. The cooled mixture was filtered to remove the starting material. Evaporation of the filtrate left a residue which in benzene was passed though a column of Florisil. Crystallizations of the benzene eluate from *n*-hexane–ether afforded **26** (120 mg), mp 212—214°. (lit.[7] mp 200—204°). *Anal.* Calcd. for $C_{32}H_{54}O_3$: C, 79.46; H, 10.92. Found: C, 79.10; H, 10.70.

The compound **26** (20 mg) on acetylation with acetic anhydride (0.5 ml) and pyridine (1 ml) gave an acetate (**28**), mp 168—171°. *Anal.* Calcd. for $C_{34}H_{56}O_4$: C, 77.73; H, 10.44. Found: C, 77.59; H, 10.41.

The compound **26** (10 mg) in $CHCl_3$ (1 ml) was treated with AcOH (1 ml) for 1 hr. The product after acetylation was identical with lycoclavanol triacetate (**23**), mp and mixed mp 193—194°.

The Keto-acetonide (30)——The acetonide **26** (120 mg) was oxidized with pyridine (1 ml)–CrO_3 (0.05 g) complex as described above. The product in benzene was passed through Florisil column to give **30** (90 mg) (prisms from acetone), mp 210—212°. (lit.[7] mp 197—201°). IR cm^{-1}: 1706. ORD [ϕ](nm): −1080° (316) (trough), ($c=1.33$). *Anal.* Calcd. for $C_{32}H_{52}O_3$: C, 79.78; H, 10.55. Found: C, 79.62; H, 10.46.

Methanolysis of Lycoclavanol Triacetate (23)——To a solution of lycoclavanol triacetate (0.5 g) in dry $CHCl_3$ (10 ml) and abs. MeOH (10 ml), 0.2N methanolic sodium methoxide (10 ml) was added and the mixture was kept overnight at room temp. The mixture, after acidification with AcOH, was evaporated to dryness and the residue digested with benzene which was passed through alumina column. First benzene eluate gave the starting material (170 mg). Following benzene, and benzene–CH_2Cl_2 eluate gave a mixture of diacetates. Repeated chromatography of this mixture yielded the diacetate-A (**32**) (35 mg), mp 243—245°, as a more and the diacetate-B (**31**) (see below) as a less mobile compounds. The diacetate-A had two forms: the sample (prisms) crystallized from acetone showed broad IR bands at 1720—1703, while the sample (needles) crystallized from MeOH had sharp bands at 1737 and 1703 cm^{-1}, the latter contained MeOH as shown by NMR spectrum. Melting points of the two samples were identical. The former sample had—NMR δ: 0.69 (3H), 0.82 (9H), 0.92 (3H), 1.05 (3H), 2.05 (3H), 2.09 (3H), 3.73 (1H, b.s), 4.08 (2H, ABq. $J=12$ Hz, $\delta_{AB}=17.5$ Hz), 4.69 (1H, b.s), 5.35 (1H, m). *Anal.* Calcd. for $C_{34}H_{54}O_5 \cdot 1/2H_2O$: C, 74.04; H, 9.98. Found: C, 73.56; H, 10.15.

Following eluates gave the diacetate-B (**31**) (160 mg), mp 225—227° (needles from MeOH). NMR δ: 0.70 (3H), 0.82 (3H), 0.85 (6H), 0.94 (3H), 0.96 (3H), 2.08 (6H), 3.60 (2H, ABq. $J=11$ Hz, $\delta_{AB}=19$ Hz), 4.68 (1H, b.s. $W_{1/2}=6$ Hz), 5.06 (1H, b.s. $W_{1/2}=6$ Hz), 5.36 (1H, m). *Anal.* Calcd. for $C_{34}H_{54}O_5$: C, 72.83; H, 10.07. Found: C, 73.18; H, 10.07.

The Keto-diacetate-A (34)——The diacetate-A **32** (100 mg) in acetone (30 ml) was treated with Jones' reagent at 5° until the mixture does not consume excess reagent. The mixture was diluted with water (100

ml) and extracted with ether which was washed with water, dried over $MgSO_4$, and evaporated. Purification of the product gave **34** (90 mg) (prisms from MeOH), mp 235—237°. IR cm^{-1}: 1725. NMR δ: 0.74 (3H), 0.90 (3H), 0.95 (3H), 1.00 (3H), 1.11 (3H), 1.22 (3H), 2.02 (3H), 2.14 (3H), 4.35 (2H, ABq. $J=12$ Hz, $\delta_{AB}=40$ Hz), 4.77 (1H, b.s), 5.42 (1H, m). ORD[ϕ](nm): −550° (308) (peak), −1660° (274) (trough). *Anal.* Calcd. for $C_{34}H_{52}O_5$: C, 75.51; H, 9.69. Found: C, 75.77; H, 9.48.

The Aldehyde-diacetate (33)——The diacetate-B **31** (100 mg) in acetone (50 ml) was similarly oxidized with Jones' reagent at 0° (about 5 min). Working up as above, the product on chromatography over alumina gave **33** (60 mg), mp 191—195°. IR cm^{-1}: 1738, 1698. NMR δ: 0.69 (3H), 0.80 (3H), 0.88 (6H), 0.91 (3H), 1.07 (3H), 2.05 (6H), 10.03 (1H).

Lycoclavanol 21-Monoacetate (35)——i) To a soln. of lycoclavanol triacetate (100 mg) in MeOH (20 ml) was added 20% NaOH (2 ml) and the mixture was refluxed for 30 min. Water (10 ml) was added to the mixture, cooled, and filtered. The precipitate in $CHCl_3$ were separated by dry column chromatography over alumina to give **35** (25 mg), mp and mixed mp 275—277°, and lycoclavanol (60 mg), mp >300°.

ii) The acetonide-acetate **28** (20 mg) in 80% AcOH (5 ml) was heated on a water bath for 2 hr, then the mixture diluted with water. Crystallization of the precipitate from $CHCl_3$-acetone gave **35** as prisms, mp 275—277°. IR cm^{-1}: 3500, 1700. *Anal.* Calcd. for $C_{32}H_{52}O_4$: C, 76.75; H, 10.47. Found: C, 76.96; H, 10.38.

21-Episerratriol Acetonide (38)——21-Episerratriol[4] (**36**; 30 mg), *p*-TsOH (10 mg), and 2,2-dimethoxypropane (2.5 ml) in DMF (2.5 ml) were refluxed for 1 hr. The solvent was evaporated *in vacuo* and the residue in benzene was chromatographed over Florisil. Benzene eluate (30 mg) was crystallized from acetone to yield **38** as prisms, mp 242—244°. *Anal.* Calcd. for $C_{33}H_{54}O_3$: C, 79.46; H, 10.92. Found: C, 79.36; H, 10.97.

Oxidation of the Acetonide (38)——The acetonide **38** (11 mg) in pyridine (0.5 ml) was treated with pyridine (1 ml)-CrO_3 (30 mg) complex overnight at room temp. Working up as usual, the crystalline product (10 mg) was crystallized from acetone to yield the keto-acetonide as needles, mp 214—216°. The TLC of this was identical with the sample (**29**) obtained from serratriol (see above), but the IR of the two samples were slightly different. Seeding of the anthentic sample to the acetone solution of this afforded colorless needles, mp 212—214°, whose TLC and IR spectrum was completely identical with the anthentic specimen (**29**).

21-Episerratriol (36) **from the Keto-diacetate-A** (34)——The keto-diacetate-A **34** (17 mg) and LAH (40 mg) in THF (20 ml) were refluxed for 2 hr. After adding a few drops of water, the organic layer was dried over $MgSO_4$, and filtered. Evaporation of the solvent left a crystalline residue which was crystallized from MeOH as needles. Acetylation of this with pyridine-Ac_2O gave prisms, mp 235—237° (from MeOH), which was identical with 21-episerratriol triacetate (**37**).

LAH Reduction of the Keto-acetonide (30)——The keto-acetonide **30** (50 mg) and LAH (80 mg) in ether (20 ml) were stirred for 2 hr under reflux. After adding a few drops of water, the organic layer was dried with K_2CO_3 and evaporated to dryness. Chromatography of the crystalline residue in benzene over Florisil gave an oil (5 mg) as the first eluate, whose TLC was identical with the starting material. Following elutions with benzene and several crystallizations of the eluate (40 mg) from *n*-hexane gave an isomeric acetonide (**39**) as needles, mp 212—213°, which had smaller *Rf* than that of lycoclavanol acetonide (**26**).

The 21-Keto-3,24-diacetate (40)——The keto-acetonide **30** (60 mg) in 80% AcOH (10 ml) was heated on a water bath for 2 hr, then diluted with water. The resulting ppt. was filtered and dried, then acetylated in pyridine (6 ml) and Ac_2O (3 ml). Crystallization of the product gave **40** as needles, mp 190—192°. IR cm^{-1} (KBr): 1740, 1710, 1240. NMR δ: 0.83 (6H), 0.93 (6H), 1.05 (3H), 1.08 (3H), 2.05 (3H), 2.07 (3H), 4.09 (2H, ABq. $J=11$ Hz, $\delta_{AB}=17$ Hz), 4.94 (1H, m), 5.40 (1H, m).

Serrat-14-en-3α,21α,24-triol Triacetate (42)——To a solution of **40** (20 mg) was added sodium borohydride (20 mg) at 0° and the mixture was stirred for 1.5 hr at room temp. After decomposition of excess hydride with one drop of AcOH, the mixture was diluted with water, and extracted with ether. The ethereal extract was washed with water, dried over $MgSO_4$, and evaporated. The product when purified by a preparative TLC [20×20 cm, developed with $CHCl_3$–MeOH (20: 1)] gave the mono-ol **41** (10 mg) (prisms from MeOH), mp 235—239°. NMR δ: 0.67 (3H), 0.83 (9H), 0.95 (6H), 2.03 (3H), 2.06 (3H), 3.21 (1H, m), 4.07 (2H, ABq. $J=12$ Hz, $\delta_{AB}=17.5$ Hz), 4.93 (1H, m), 5.36 (1H, m).

The mono-ol (**41**) was acetylated in pyridine (3 ml) and Ac_2O (2 ml). The product in benzene was passed through alumina and crystallized from *n*-hexane–MeOH to give the triacetate (**42**) as needles, mp 209—211°. IR cm^{-1} (KBr): 1742, 1250.

The triacetate (**40**; 10 mg) was hydrolysed with 5% methanolic KOH (5 ml) under reflux for 5 hr. The triol (**43**) obtained was crystallized from MeOH to give prisms, mp 318—320° (decomp.).

Wolff-Kishner Reduction of the Aldehyde-diacetate (33)——The aldehyde-diacetate **33** (50 mg), anhyd. hydrazine (0.5 ml), and hydrazine dihydrochloride (0.1 g) in diethyleneglycol (10 ml) were heated at 180° for 4 hr. Na (0.5 g) was added portion-wise to the mixture, the temp. was raised to 210° and the mixture was kept for 4 hr. The mixture was poured into water, extracted with $CHCl_3$, and the extract was washed with water, dried over $MgSO_4$, and evaporated to dryness. The residue, showed two spots on TLC, was separated by preparative TLC. Stripping of the upper zone and extraction with $CHCl_3$ gave a crystalline solid (diepiserratenediol) which was acetylated with Ac_2O (0.5 ml) and pyridine (1 ml) to give on crystalliza-

tion from MeOH, diepiserratenediol diacetate (**44**) (12 mg), mp and mixed mp 240—242°. The compound of the lower zone was not characterized.

Serratriol 21-Monoacetate (46)——The acetonide-acetate **27** (1.1 g) in benzene (20 ml)–AcOH (15 ml)–water (5 ml) was heated on a water-bath for 1 hr. The solution was concentrated *in vacuo* to remove benzene and diluted with water. The precipitate (994 mg) was collected and crystallized from $CHCl_3$–MeOH to afford **46** (647 mg) as prisms, mp >300°. IR cm^{-1}: 3450, 3250, 1722, 1245. *Anal.* Calcd. for $C_{32}H_{52}O_4$: C, 76.75; H, 10.47. Found: C, 76.73; H, 10.63.

Partial Tosylation of the 21-Monoacetate (46)——The 21-acetate **46** (51 mg) and *p*-TsCl (134 mg) in pyridine (3 ml) were allowed to stand overnight at room temp. The mixture was poured into water and extracted with $CHCl_3$. The extract was washed with 5% HCl, 5% $NaHCO_3$, and water, dried over $MgSO_4$, and evaporated to dryness. The residue in benzene was chromatographed over alumina (3 g). Elution with benzene (20 ml) gave a ditosylate **48** (31 mg) (needles from MeOH), mp 185—186°. IR cm^{-1}: 1728, 1250, 1600. *Anal.* Calcd. for $C_{46}H_{64}O_8S_2$: C, 68.28; H, 7.96. Found: C, 68.33; H, 8.04. Further elutions with benzene (150 ml) gave a monotosylate **47** (32 mg) (needles from MeOH), mp 188—189°. IR cm^{-1}: 3400, 1732, 1270, 1600. NMR δ: 0.70 (6H), 0.80 (3H), 0.86 (3H), 0.92 (3H), 1.11 (3H), 2.08 (3H), 2.49 (3H), 3.22 (1H, m), 4.15 (2H, ABq. J=11 Hz, δ_{AB}=14 Hz), 4.49 (1H, m), 5.35 (1H, m), 7.35 (2H, d. J=9 Hz), 7.80 (2H, d. J=9 Hz). *Anal.* Calcd. for $C_{39}H_{58}O_6S$: C, 71.54; H, 8.93. Found: C, 71.57; H, 9.02.

LAH Reduction of the Monotosylate (47)——To a suspension of LAH (517 mg) in THF (10 ml), a solution of the monotosylate (**47**, 280 mg) in THF (10 ml) was added dropwise during a period of 1 hr. The mixture was refluxed for further 5 hr. After cooling, the excess hydride was decomposed by adding water and the precipitate was filtered and washed with $CHCl_3$. The combined filtrate was dried over $MgSO_4$, evaporated, and a residue (231 mg) in benzene was chromatographed over alumina (4 g). i) Elution with benzene (150 ml) gave an oxetane **49** (71 mg) (prisms from MeOH–$CHCl_3$), mp 254—256°. IR cm^{-1}: 3450. NMR δ: 0.70 (3H), 0.87 (3H), 0.97 (3H), 1.00 (3H), 1.27 (3H), 1.36 (3H), 3.27 (1H, m), 4.30 (2H, ABq. J=7 Hz, δ_{AB}=20 Hz), 4.60 (1H), 5.37 (1H, m). *Anal.* Calcd. for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98. Found: C, 82.10; H, 11.15. Acetylation of **49** (45 mg) with pyridine (1 ml) and Ac_2O (0.5 ml) yielded the acetate (**50**) (needles from *n*-hexane–benzene), mp 273—275°. IR cm^{-1}: 1720, 1248. NMR δ: 0.74 (3H), 0.89 (3H), 0.96 (6H), 1.25 (3H), 1.36 (3H), 2.10 (3H), 4.30 (2H, ABq. J=7 Hz, δ_{AB}=22 Hz), 4.60 (2H, m), 5.36 (1H, m). *Anal.* Calcd. for $C_{32}H_{50}O_3$: C, 79.62; H, 10.44. Found: C, 79.62; H, 10.60. ii) Further elution with benzene (400 ml) gave a mixture (69 mg) which was separated by preparative TLC into **49** (39 mg) (upper zone) and serratenediol (20 mg) (lower zone). iii) Elution with $CHCl_3$ (200 ml) gave another crop of serratenediol (**1**; 13 mg), mp 300°, as identified with the authentic specimen. iv) Elution with $CHCl_3$–MeOH (100 ml) gave serratriol (**3**; 23 mg), mp >300°. Acetylation of serratenediol and serratriol yielded the corresponding acetates, (**2** and **4**), which were identical with authentic specimens, respectively.