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The Structure of Serratenediol.[*3]

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Retropinacol rearrangement of serratenediol established that either terminal ring of this triterpenoid has the partial structure (A). The accumulated chemical and spectroscopic evidences have been summarized in the structure and stereochemistry (1) containing seven-membered ring for serratenediol, which was confirmed by further degradation into a tricyclic ketone (47). The synthesis of this key product has now been achieved. The manner of acid isomerization of serratene derivatives has been also clarified. Serratenediol monoacetate, a minor triterpenoid constituent of *Lycopodium serratum*, was also established as (3), based on ORD examination of various ketonic derivatives.

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The structure and stereochemistry of serratenediol (1), a neutral constituent of *Lycopodium serratum*,[1] seem to be well established in two preliminary communications,[2,3] which presented one of new representatives in triterpenoid chemistry. In the present paper we give a detailed account of the experiments that permits the derivation of the structure and stereochemistry of this unique triterpenoid.

Serratenediol is a pentacyclic triterpenoid-diol having one trisubstituted double bond, which was shown by the mild infrared band at 798 cm^{-1} and the nuclear magnetic resonance peak at 4.69τ corresponding to one olefinic proton. Mass spectra of serratenediol diacetate (2) and the corresponding hydrocarbon, serratene (4) (see below), confirmed their formulae as $C_{34}H_{54}O_4$ and $C_{30}H_{50}$, respectively. The nuclear magnetic resonance spectrum of the diacetate (2) showed the C-methyl peaks at 9.31,[*4] 9.16 and 9.11τ. The intensity ratio of 1:5:1 corresponding to seven C-methyl groups suggests that serratenediol lacks, though the compound is C_{30} triterpenoid, one C-methyl group in contrast to the usual C_{30} triterpenoid which always contains eight C-methyl groups or their oxidative equivalent. The both hydroxyl groups in serratenediol are secondary one; the diol was converted into the dione (4) which gave a bis-hydrazone but had a single infrared absorption at 1709 cm^{-1} and no aldehyde peak in the nuclear magnetic resonance spectrum. Hydride reduction of serratenedione (4) or more satisfactorily reduction with sodium in propanol reformed serratenediol indicating that the both hydroxyl groups of serratenediol are at unhindered positions and have equatorial orientations. Wolff-Kishner reduction of serratenedione furnished the unsaturated

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[*3] Studies on the Constituents of Domestic Lycopodium Genus Plants; Part Ⅲ. Part Ⅱ, Yakugaku Zasshi, 84, 1108 (1964).

[*4] The value presented in the communication[2] as 9.21 is a misprint, which must be revised to this value.

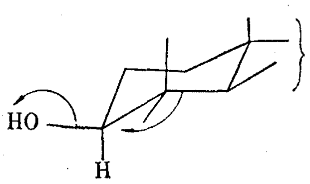
[*5] We express our thanks to Dr. K. Takeda, Takeda Chemical Industries, Ltd., for providing the sample of taraxerene (shikimiene).

1) Y. Inubushi, Y. Tsuda, H. Ishii, M. Hosokawa, T. Sano: Yakugaku Zasshi, 82, 1339 (1962); Y. Inubushi, Y. Tsuda, H. Ishii, T. Sano, M. Hosokawa, T. Harayama: *Ibid.*, 84, 1108 (1964).
2) Y. Inubushi, T. Sano, Y. Tsuda: Tetrahedron Letters, No. 21, 1303 (1964).
3) Y. Tsuda, T. Sano, K. Kawaguchi, Y. Inubushi: Tetrahedron Letters, No. 20, 1279 (1964).

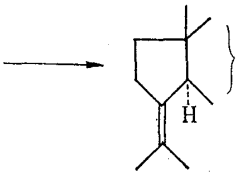
hydrocarbon, serratene (5), m.p. 237~239°, $[\alpha]_D$ −19°, which was apparently different from taraxerene[*5] (m.p. 238~240°, $[\alpha]_D$ +3°).[4] The nuclear magnetic resonance spectrum of serratene exhibited C-methyl peaks at 9.34, 9.19 and 9.15τ in ratio of 1:2:4 and one olefinic proton signal at 4.68τ. Serratene, like taraxerene, can be hydrogenated over Adams catalyst to an almost equi-amount mixture of two stereoisomeric hydrocarbons[*6] (43:57 as shown by VPC), resolved only by wasteful fractional crystallizations into α- and β-serratane (9 and 10), which differ in the configuration at C_{14}; the homogenities and the formulae of the both α- (m.p. 198~200°) and β-isomer (m.p. 184~187°) being confirmed by vapor phase chromatography and the mass spectra.

Serratenediol diacetate (2) was similarly hydrogenated into serratanediol diacetate (6). Although the product showed a sharp melting point, the thin-layer chromatography indicated that this is a mixture of two isomers (the preparative separation being failed), as being confirmed by oxidation of serratanediol (7) and Wolff-Kishner reduction of the resulting dione (8) to yield a mixture of α- and β-serratane (vapor phase chromatography). Since none of serratene, isoserratene (acid isomerization product of serratene, see below), α- and β-serratane was identical with any hydrocarbon derived from the known triterpenoids and since serratenediol possesses seven (not eight) C-methyl groups, we have concluded that serratenediol is a new representative in triterpenoids.

The informations on the structure of terminal rings of serratenediol and the confirmation of the number of C-methyl groups were now obtained by phosphorus pentachloride reaction on serratenediol (1) and serratanediol (7). For usual triterpenoid with the partial structure (A) the reaction is known to cause retropinacol rearrangement affording ring contracted isopropylidene derivative (B).[5] Application of the reaction on serratenediol yielded a hydrocarbon (11), $C_{30}H_{46}$. In its nuclear magnetic resonance spectrum four vinyl methyls at 8.42 (6H) and 8.29τ (6H) which newly appeared, indicated the formation of two isopropylidene groups, and in higher field there were remained three methyl peaks at 9.46, 9.40 and 9.11τ each corresponding to exactly one methyl group. The olefinic proton signal at 4.66τ showed that the double bond had not been affected by the reaction. Serratanediol (7) similarly gave the corresponding bis-isopropylidene derivative (14), $C_{30}H_{48}$, which includes four vinyl methyls at 8.42 and 8.29τ and three other methyls at 9.40, 9.25 and 9.05τ. This (14) was rapidly isomerized by mild acid treatment into the bis-isopropyl derivative (15) which appeared again seven methyl group signals above 8.9τ in its nuclear magnetic resonance spectrum. Lehn[6] reported that isopropylidene derivative of the stereostructure (B) exhibits a C_{10} methyl signal at a shielded position about 9.4τ in its nuclear magnetic resonance spectrum. Two methyl signals in our isopropylidene derivative (9.46 and 9.40 for (11), 9.40 and 9.25 for (14)) seem to fall in this category, thus suggesting the presence of methyl groups at A/B and at D/E ring juncture, respectively. Osmolation of (14) and lead tetraacetate cleavage of the resulting product gave two moles of acetone (as its 2,4-dinitrophenyl hydrazone) and the expected hexanor-diketone (16), the latter being isolated after chromatography of the



A



B

[*6] This ratio largely depends on the hydrogenation condition employed, and the value (1:20) presented in the communication[2] actually is that for the crop obtained as crude β-serratane.

4) C. J. W. Brooks: J. Chem. Soc., **1955**, 1675.

5) D. H. R. Barton: "Chemistry of Carbon Compounds," Vol. II, Part B, 726 (1953). Elsvier Publishing Company, London.

6) J. M. Lehn: Bull. soc. chim. France, **1962**, 1832.

non-volatile portion of the product. This diketone must have *cis*-hydrindanone configuration since the initial *trans*-fused product is known to be easily epimerized during chromatography,⁽⁷⁾ and the single infrared absorption for both ketone groups at 1736 cm^{-1} due to cyclopentanone accounts well for that of the *cis*-fused structure rather than the *trans*-hydrindanone (1748~1751 cm^{-1}).⁽⁸⁾ Hence we can conclude that the both terminal rings of serratenediol have the partial structure (A) and that the compound includes one remaining quaternary methyl group at ring juncture of B/C or C/D.

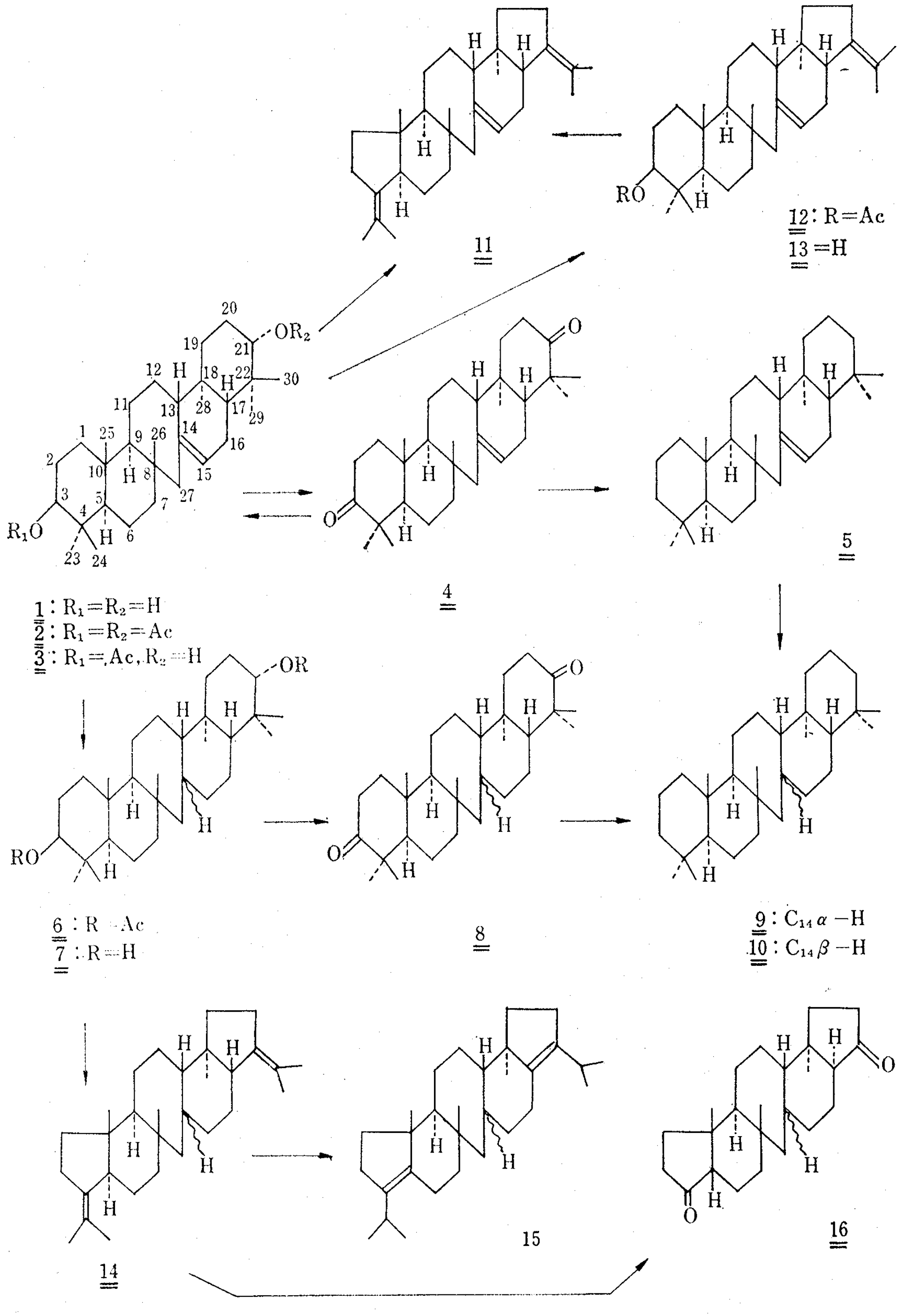


Chart 1.

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[7] J. F. Biellmann, D. Kučan, M. Rajic, P. Witz, G. Ourisson: Bull. soc. chim. France, **1962**, 330.

[8] G. V. Baddeley, T. G. Halsall, E. R. H. Johnes: J. Chem. Soc., **1960**, 1715.

This chemical feature was again supported by the examination of serratenediol monoacetate (3) which was isolated from the same plant as a minor component.[1] This gave the monoisopropylidene derivative (12), being confirmed by its nuclear magnetic resonance spectrum (two vinyl methyls at 8.42 and 8.32τ). Saponification and application of the phosphorus pentachloride reaction on the resulting mono-ol (13) afforded the bis-isopropylidene derivative being identical with (11).

The trisubstituted double bond in serratenediol must be neither in terminal rings nor at $C_{5,6}$, $C_{16,17}$, since neither serratenedione (4) nor bis-isopropylidene derivative (11) showed a conjugation in the ultraviolet spectra, but it can be isomerized by acid into a tetrasubstituted one. Serratenediol diacetate (2), serratenedione (4), and serratene (5) when heated with hydrochloric acid-acetic acid isomerized into a new series of compounds; isoserratenediol diacetate (17), isoserratenedione (19), and isoserratene (20), respectively.

This isomerization, however, is in equilibration, since the product after purification was always contaminated by the starting material except the case of isoserratenedione (19) which can be obtained in pure form by fractional crystallizations of the isomerization product; pure isoserratenediol (18) and isoserratene (20) being therefore prepared from the iso-dione (19). Pure isoserratene (20) when heated with hydrochloric acid-acetic acid at 100° for 16 hours reformed *ca.* 20% of serratene (5) as being shown by vapor phase chromatography of the crude product. That the double bond in iso-compounds had migrated into the tetrasubstituted position was shown by disappearance of the olefinic proton signals in their nuclear magnetic resonance spectra. Similar double bond migration was also observed during the oxidation by sodium dichromate in hot acetic acid. Serratenediol diacetate (2) and isoserratenediol diacetate (17) gave the same conjuated ketone (38) (λ_{max} 256 mμ) whose double bond is tetrasubstituted. Serratene (5) and isoserratene (20) similarly gave the same conjugated ketone (37) (λ_{max} 258 mμ) which on hydrogenation reformed isoserratene (20), and α- and β-serratane (9 and 10); the formation of the latters might exclude the possibility of skeletal change during the course of isomerization. Such an acid equilibration of double bond and the fixation of the double bond into tetrasubstituted position during the course of oxidation are quite similar to the double bond migration from Δ^7 to Δ^8 in lanostenol derivatives,[9] and the ultraviolet absorption of the enones (37 and 38) (λ_{max} 256~258 mμ) is also in good agreement with that of Δ^8-7-oxolanostenol (29) (λ_{max} 255 mμ)[10]; these evidences suggest that the situation of the double bond in serratenediol is similar to that of Δ^7-lanostene. The second evidence for the position of double bond was provided by the preparation of a conjugated hetero-annular diene (28). Oxidation of serratenediol diacetate with selenium dioxide in acetic acid afforded a diene (28) which showed a broad nuclear magntic resonance peak at 4.57τ corresponding to two olefinic protons and intense ultraviolet absorption maxima at 233, 241 and 248 mμ (log ε, 4.11, 4.16 and 4.04), the latter being typical for 7:9(11)-diene chromophore in triterenoid field (cf. fernadiene[11] (30): λ_{max} 233, 241 and 248 mμ; arboradiene[12] (31): λ_{max} 236, 243 and 257 mμ).

Conclusively, the feature of serratene-isoserratene isomerization and at the same time the gross structure of serratenediol were evidenced from the optical rotatory dispersion studies of the various ketonic derivatives. Oxidation of serratenediol

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9) *a*) R.E. Marker, E.L. Wittle, L.W. Mixon: J. Am. Chem. Soc., **59**, 1368 (1937). *b*) R.B. Woodward, A.A. Patchett, K.H.R. Barton, D.A.J. Ives, R.B. Kelly: J. Am. Chem. Soc., **76**, 2852 (1954).
10) L. Ruzicka, Ed. Rey, A.C. Muhr: Helv. Chim. Acta, **27**, 472 (1944).
11) H. Ageta, K. Iwata, S. Natori: Tetrahedron Letters, **1963**, 1447.
12) H. Vorbrüggen, S. Pakrashi, C. Kjerassi: Ann., **668**, 57 (1963).

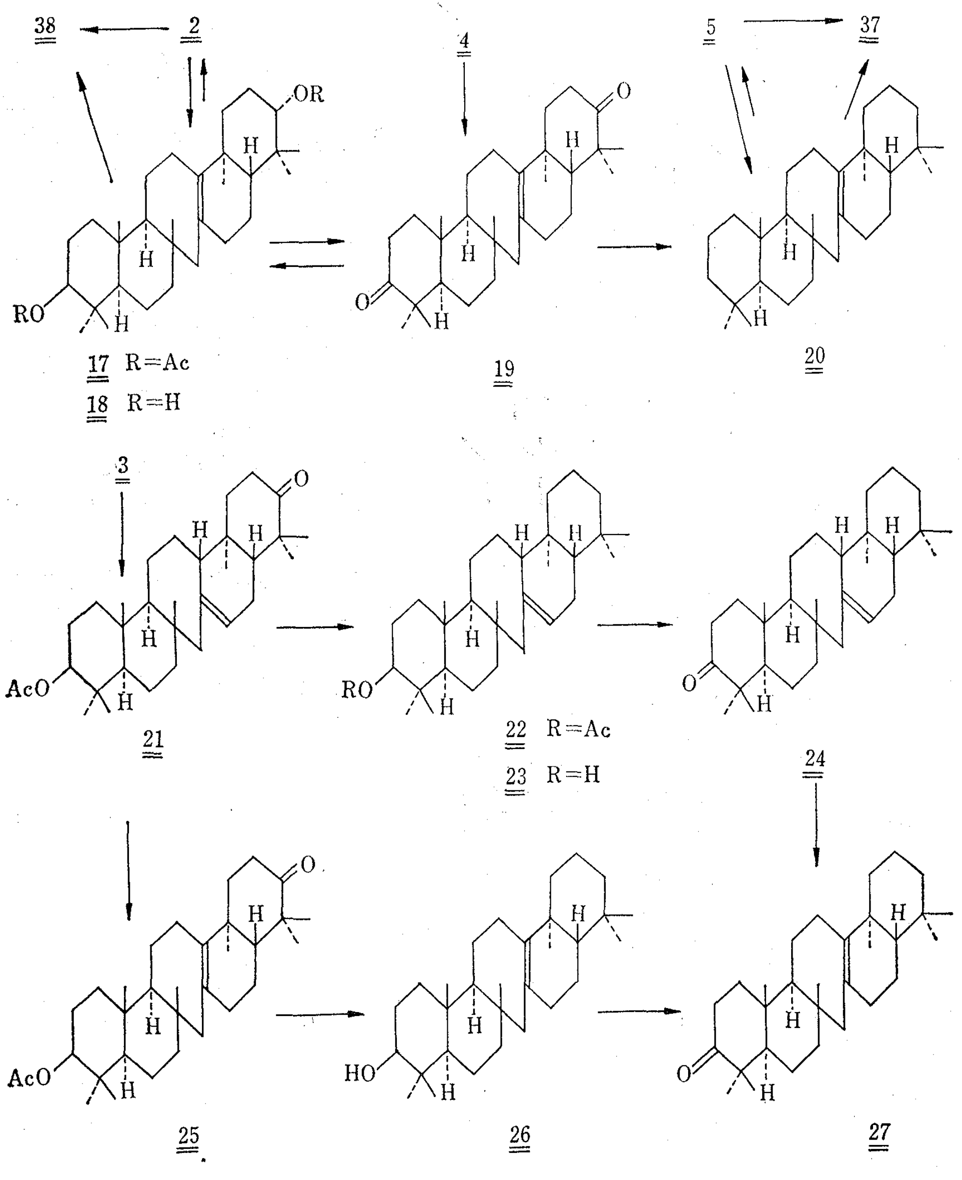

Chart 2.

mono-acetate (3) gave a keto-acetate (21), which by Wolff-Kishner reduction was converted into serraten-3β-ol (23). Oxidation of this afforded a mono-ketone, serraten-3-one(24). The ketonic functions of (21) and (24) must be at the opposite terminal rings as understood from the course of reactions. Serraten-21-on-3β-ol acetate (21) and serraten-3-one (24) was able to isomerize by acid into isoserraten-21-on-3β-ol acetate (25) and isoserraten-3-one (27), respectively. The optical rotatory dispersion curves of serraten-3-one (24) and isoserraten-3-one (27) gave the positive Cotton effect being observed usually for 3-keto-triterpenoid with C_8-β methyl group,[13] whereas that of serraten-21-on-3β-ol acetate (21) showed the negative Cotton effect which changed into the positive one by isomerization into iso-compound (25). This change of the Cotton effect is characteristic of the migration of the double bond from Δ^7 to Δ^8, as illustrated in Δ^7-lanosten-3-one to Δ^8-lanosten-3-one[13] or bauerenone to isobauerenone.[14] Therefore serratenediol monoacetate must include the partial structures (C) and (D).

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13) C. Djerassi, O. Halpern, V. Halpern, B. Riniker: J. Am. Chem. Soc., **80**, 4001 (1958).

14) F. N. Lahey, M. V. Leeding: Proceeding Chem. Soc., **1958**, 342; C. Djerassi: "Optical Rotatory Dispersion," p. 97 (1960), McGraw-Hill, New York.

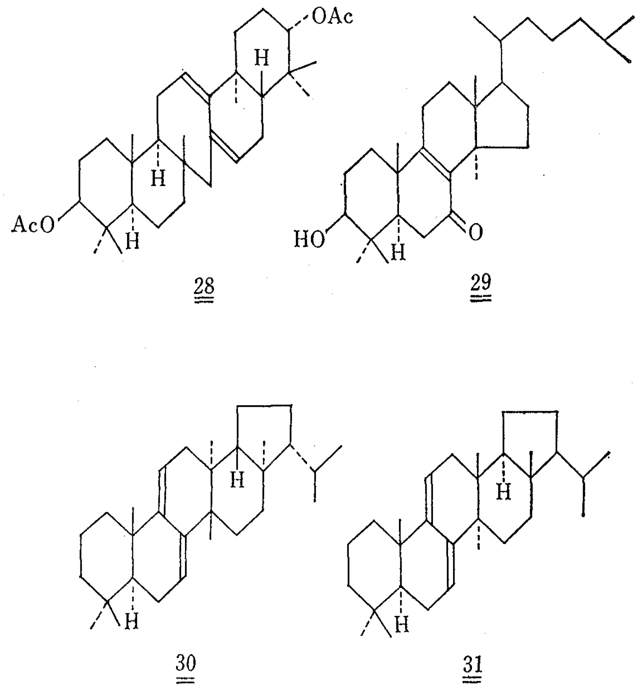

Chart 3.

In accordance with this conclusion, the weak negative Cotton effect of serratenedione (4) changed into the strong positive one in isoserratenedione (19), whose both ketonic functions had to change to give positive Cotton effects. By combining two partial structures (C and D), we can advance the structures of serratenediol to (1) and its monoacetate to (3).

Mass spectrometry gave also the good support for the structure (1). If our assignment is correct, serratene (5) and its derivatives must show the peak due to the retro-Diels-Alder decomposition similar to that of taraxerene.[15] Mass spectra of serratene (5), serraten-3-one (24), and serraten-3β-ol acetate (22) clearly showed the expected peaks (ion a) at m/e 286, 300 and 344, respectively. The peaks (ion b) at m/e 271 for (5), 285 for (24), and 329 for (22) are also responsible to the same decomposition, since they could be formed by the loss of methyl group from ion a. In the last compound (22) further loss of acetic acid from ion a and b were observed by peaks at m/e 284 and 269.

The direct chemical evidence on ring B,C and D was obtained by the oxidative studies of serratan-15-one which, after several fruitless attempts, has been prepared from serratene (5). Hydroboration of serratene (5) followed by the oxidation with alkaline hydrogen peroxide gave an alcohol (32) which was smoothly oxidized by chromic acid into the corresponding ketone, β-serratan-15-one (34), showing the infrared band at 1692 cm^{-1}. This is the less stable isomer concerning on the stereochemistry at C_{14} and isomerized by base into the more stable isomer, α-serratan-15-one (35), showing the infrared band at 1703 cm^{-1}. Wolff-Kishner reduction of both α- and β-serratan-15-one (36 and 37) afforded α-serratane (9) as the major product, indicating that no skeletal change had taken place during the above transfomations. (We now

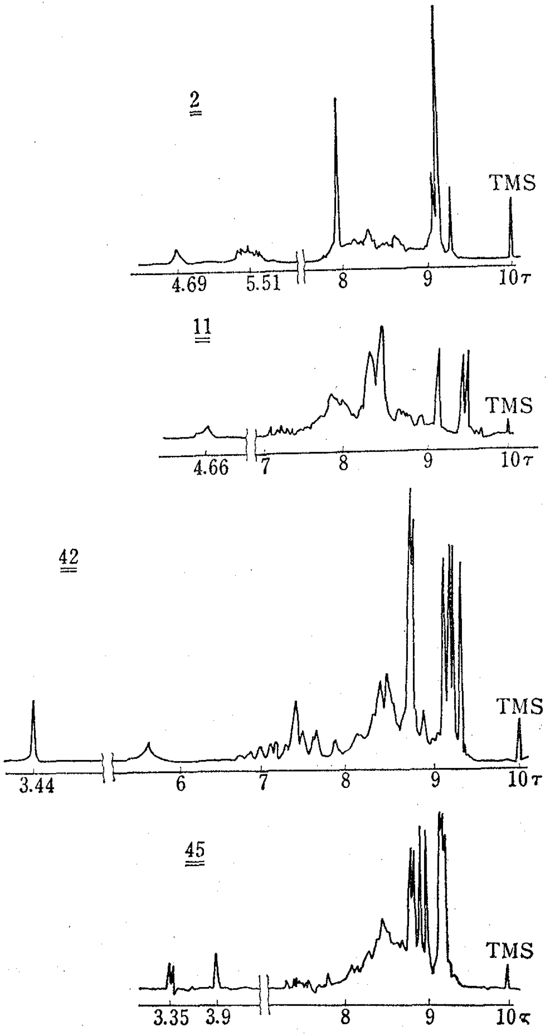

Fig. 1. NMR Spectra of Serratene Derivatives

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[15] H. Budzickewicz, J.M. Wilson, C. Djerassi: J. Am. Chem. Soc., 85, 3688 (1963).

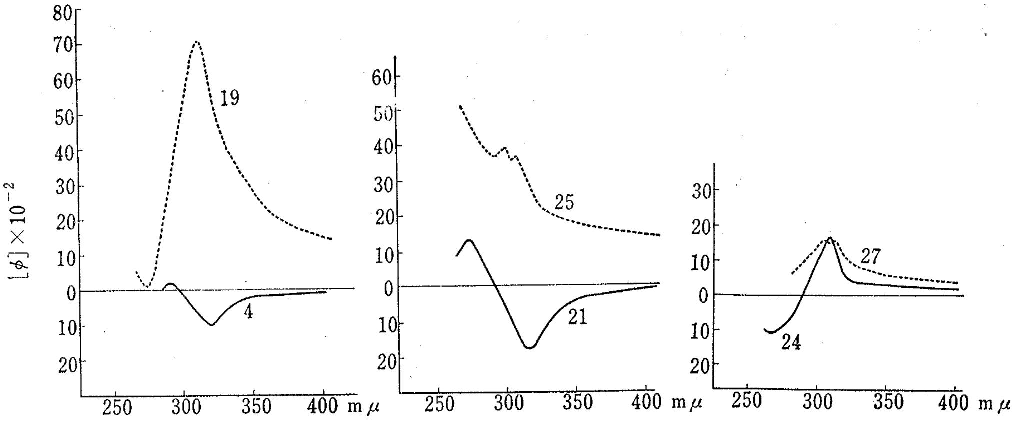
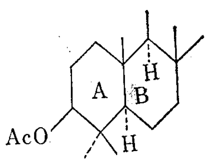
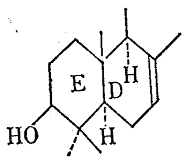


Fig. 2. Optical Rotatory Dispersions of the Ketones

tentatively assign the 14α-H to the stereochemistry of α-series compounds which have more stable C/D *trans*-fused structure and the 14β-H to that of β-series compounds which have C/D *cis*-fused structure, respectively. This point will be fully discussed in a separate paper.)



C



D

Oxidation of β-serratan-15-one (34) by fuming nitric acid gave a seco-dicarboxylic acid, which was isolated as its dimethyl ester (36). The result confirmed the partial structure -CO-CH$_2$- in (34).

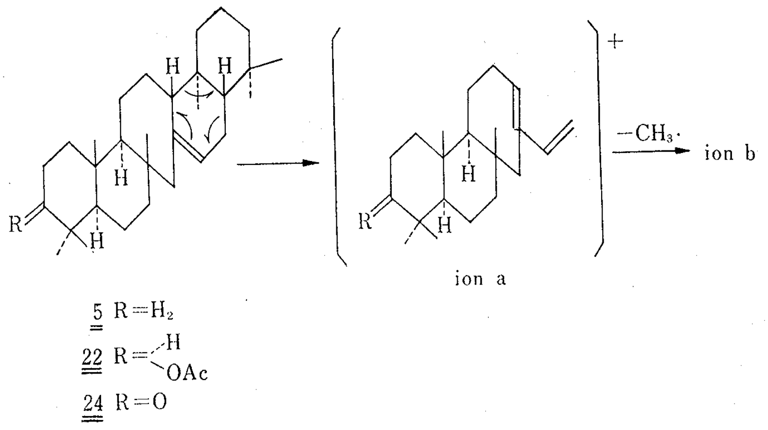


Chart 4.

Bromination of β-serratan-15-one (34) gave a labile bromoketone, which was smoothly dehydrobrominated to a conjugated ketone (37). In the nuclear magnetic resonance spectrum it showed no olefinic proton signal and the same enone was obtained from serratene (5) or more satisfactorily from *iso*-serratene (20) by dichromate-acetic acid oxidation (see above). These facts led us to assign unambiguously its structure as (37). Selenium dioxide oxidation of (37) in acetic acid afforded the expected dienone (39) as an only isolable product. This showed an olefinic proton signal at 3.74τ as a sharp singlet. Its ultraviolet and infrared spectra (see Experimental) all are consistent with the structure (39). On the other hand, direct selenium dioxide oxidation of β-serratan-15-one (34) gave, together with isoserraten-15-one (37) and serratadienone (39), a new dienone (45) though the yield was poor (3%). Elementary analysis showed that it is isomeric with (39), but its ultraviolet absorption was more bathochromic (266 mμ). Its infrared spectrum exhibited two strong bands at 1650 and 1597 cm^{-1}. The nuclear magnetic resonance spectrum in the olefinic proton region showed a sharp singlet at 3.89τ and a clean doublet (J=2.5 c.p.s.) at 3.34τ, each corresponding to one proton. The coupling pattern of the latter is well explainable by the structure (45), since in this structure the C_{14-27} double bond and C_{13}-H are arranged almost rectangularly, so that the π-electron and C_{13}-hydrogen must gain the maximum overlapping and the

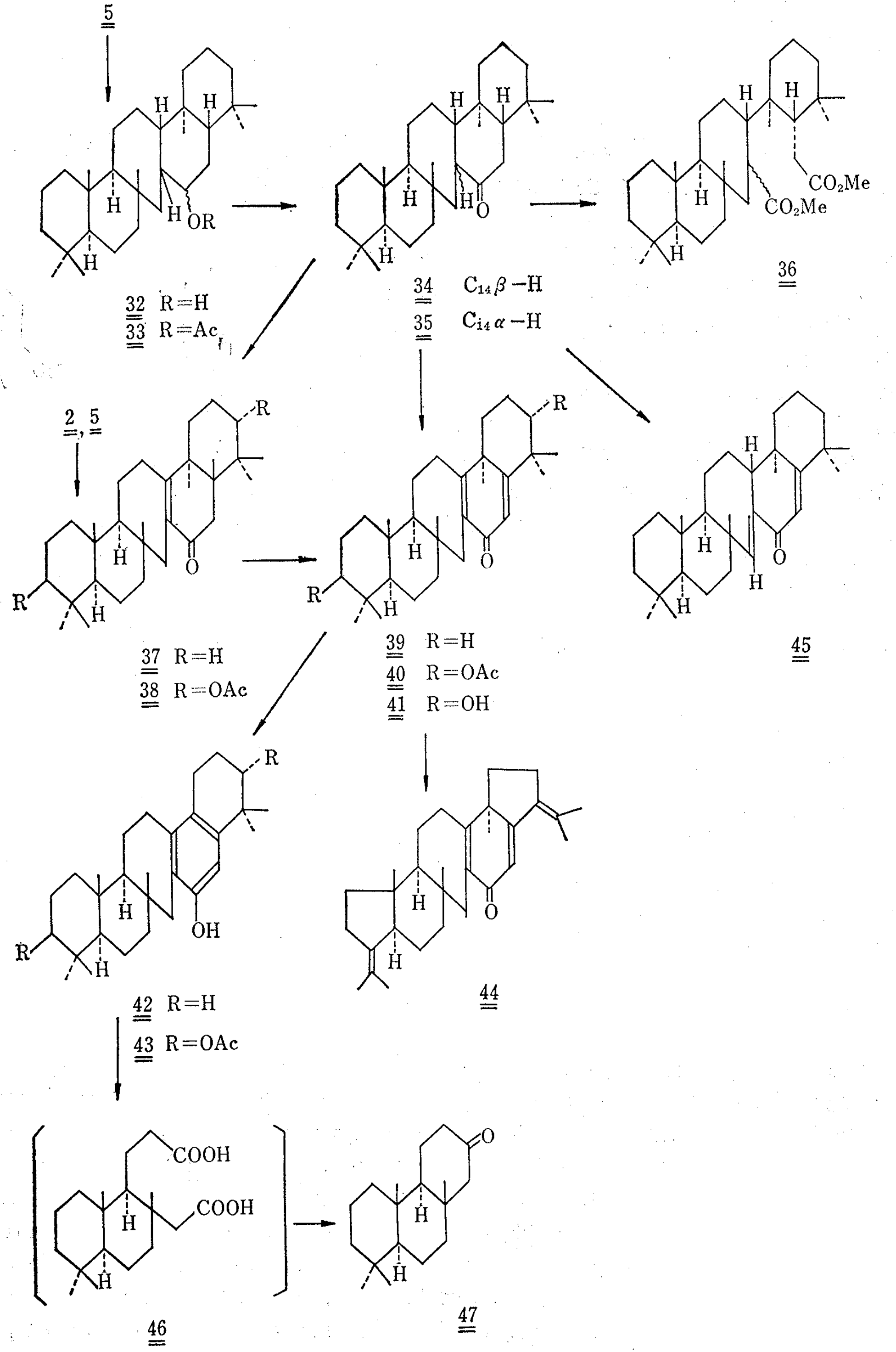


Chart 5.

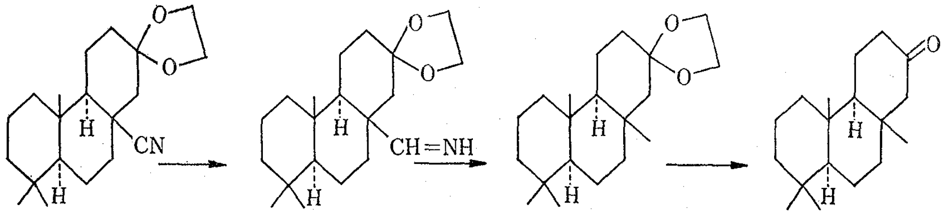
coupling constant between C_{13}-H and C_{27}-H must show the value 2~3 c.p.s.[16] The structure (45) of this dienone hence gives the fiirst evidence for the presence of methylene group (C_{27}) adjacent to C_{14}.

On heating with zinc dust in acetic acid, the dienone (39) was aromatized, with loss of one methyl group, to give the expected nor-phenol (42), whose formation was confirmed by its six C-methyl peaks in the nuclear magnetic resonance spectrum and the aromatic ultraviolet absorptions (λ_{max} 285 and 291 mμ). Since the formation of the nor-phenol from the dienone of type (39) is well known in steroid and lanosterol chemistry,[17] this aromatization established chemically the presence of C-methyl group at D/E juncture and confirmed the structure of ring D to be six-membered. Isoserraten-15-onediol diacetate (38) similarly gave the dienone (40), and the nor-phenol (43). Alkaline hydrolysis of (40) and the phosphorus pentachloride reaction on the resulting diol (41) gave the bis-isopropylidene derivative (44), in which one of the newly formed double bond is conjugated with the dienone system, as expected, being shown by the bathochromic shift of its ultraviolet absorption (λ_{max} 276 and 320 mμ).

For further degradations, we have ozonized the nor-phenol (42) and subsequently oxidized the ozonide by hydrogen peroxide-formic acid. The obtained acidic fraction was heated with acetic anhydride and then pyrolysed at 200°. There was yielded a ketone in about 5% yield from (42). This ketone showed in its optical rotatory dispersion the positive Cotton effect peak at 314 mμ, α +1700, and the infrared carbonyl absorption at 1716 cm^{-1}, indicating the presence of a cyclohexanone rather than a cyclopentanone. In its nuclear magnetic resonance spectrum two C-methyl peaks were observed at 9.15 (6H) and 9.12τ (6H). The ketone therefore must be represented by the tricyclic structure (47) which provides the direct proof that ring C of serratenediol is seven-membered, since it had to be formed by the cyclization of the intermediate dicarboxylic acid (46).

The synthesis of its racemate (51) has now been achieved by starting from the *dl*-cyanoketal (48), which was kindly provided by Dr. W. Nagata.*7 Short reduction of the *dl*-cyanoketal (48) with lithium aluminum hydride in ether afforded the imine (49), which on Wolff-Kishner reduction gave the ketal (50). Hydrolysis of this by acid gave the *dl*-ketone (51). The infrared spectrum in carbon tetrachloride of this was superimposable with that of the tricyclic ketone (47), thus proving their identities.

We now briefly comment on the sterochemistry of the tricyclic ketone (47). The several analogous compounds (52, 53, 54, 55 and 56) of the established absolute configuration have been known in the diterpenoid chemistry. The sign and the



48 49 50 51

Chart 6.

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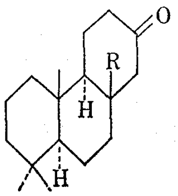
*7 We express our cordial gratitude for this to Dr. W. Nagata, Shionogi Research Laboratory.

16) N. S. Bhacca, D. H. Williams: "Applications of NMR spectroscopy in Organic Chemistry," 108 (1964). Holden-Day, Inc., San Francisco.

17) K. Tsuda, E. Ohki, S. Nozoe, N. Ikekawa: J. Org. Chem., **26**, 2614 (1961).

TABLE I.



R	a[a]		ref.
CH_2COOMe	+32	(52)	18)
H	+48	(53)	18)
CH_3	+55	(47)	
CN	+65	(54)	18)
OH	+76	(55)	18)
COOMe	+80	(56)	18)

a) $a=[[\phi]peak-[\phi]trough]\times 10^{-2}$

amplitude of their Cotton effects in optical rotatory dispersion are listed in Table I. The excellent agreement of the value (a +55) of our tricyclic ketone (47) with those of the above compounds provides another confirmation of the absolute stereochemistry of the tricyclic ketone and hence of serratenediol.

Experimental

Unless otherwise stated, melting points were determined on a Kofler hot stage and are uncorrected, ultraviolet absorption spectra were determined in 95% EtOH solutions, infrared spectra were taken on Nujol mulls, and nuclear magnetic resonance spectra were measured on an A-60 spectrometer in $CDCl_3$ solutions with tetramethylsilane as an internal standard. Mass spectra (MS) were measured on Hitachi RMU-6C and/or 6D single focused spectrometer at 70 eV and fragmentations above m/e 100 were presented with relative intensities in parenthesis. Optical rotatory dispersions are for dioxane solutions and $[\alpha]_D$ are for $CHCl_3$ solutions. Acid washed alumina was used for column chromatography, and for thin-layer chromatography silica gel G as absorbent and $CHCl_3$-MeOH as developing solvent. Vapor phase chromatography (VPC) was carried over 1.5% SE-30 on chromosorb W column and retention time (RRT) was presented relative to cholestane. Organic extracts had been washed with H_2O and dried over $MgSO_4$ before evaporation. Identities were confirmed by the infrared spectra and thin-layer chromatography comparisons.

Serratenediol (1)——Serratenediol crystallizes in two forms depending on the solvent for crystallization employed. The semi-hydrate[1] forms needles from $CHCl_3$-MeOH, m.p. 300°. *Anal.* Calcd. for $C_{30}H_{50}O_2\cdot\frac{1}{2}H_2O$: C, 79.76; H, 11.38. Found: C, 79.81; H, 11.24. The anhydrous form had m.p. 282~284°, $[\alpha]_D$ −22°(c=0.7), (needles from benzene-EtOH). IR (KBr) cm^{-1}: 3330, 1034; NMR (τ): $\gg$C-CH_3, 9.31 (3H), 9.20 (3H), 9.17 (3H), 9.14 (6H), 9.02 (6H); >CH-O$\underline{H}$, 8.57 (2H); >C$\underline{H}$-OH, 6.80 (2H); >C=C$\underline{H}$-, 4.69 (1H, multiplet). *Anal.* Calcd. for $C_{30}H_{50}O_2$: C, 80.80; H, 11.38. Found: C, 80.96; H, 11.28.

Serratenediol Diacetate (2)[1]——The diacetate crystallizes in colorless prisms from $CHCl_3$-MeOH, m.p. 336~338°(open capillary), $[\alpha]_D$ +19.5 (c=0.77). NMR (τ): $\gg$C-CH_3, 9.31 (3H), 9.16 (15H), 9.11 (3H); -$OCOCH_3$, 7.97 (6H); >C$\underline{H}$OAc, 5.51 (2H, multiplet); >C=C$\underline{H}$-, 4.69 (1H, multiplet). MS: M^+ 526 (3), 511 (1.5), 484 (17.5), 466 (22), 451 (7.5), 425 (9.5), 406 (5), 391 (8.6), 355 (6.8), 344 (4.7), 285 (5), 276 (7.2), 269 (8.8), 262 (26.3), 255 (7.2), 249 (18.3), 239 (12), 237 (10.5), 220 (18), 217 (18), 203 (41.5), 189 (100), 187 (42.2).

Serratenedione (4)——Serratenediol (1) (200 mg.) in pyridine (2 ml.) and chromium trioxide-pyridine complex (200 mg. of CrO_3 and 5 ml. of pyridine) were mixed and the mixture was kept overnight at room temperature, then poured into H_2O and extracted with $CHCl_3$. The extract was evaporated to dryness to give the residue which was passed in $CHCl_3$ through a column of SiO_2 to give (4) (170 mg.) as colorless prisms from $CHCl_3$-MeOH, m.p. 208~210°, $[\alpha]_D$ −3.7°(c=2.7). IR cm^{-1}: 1709 (cyclohexanone). NMR (τ): $\gg$C-CH_3, 9.11 (3H), 9.08 (6H), 8.96 (6H), 8.92 (6H); >C=C$\underline{H}$-, 4.59 (1H, multiplet). ORD: $[\phi]_{327}^{trough}$ −1050°, $[\phi]_{290}^{peak}$ +219°(c=0.56). *Anal.* Calcd. for $C_{30}H_{46}O_2$: C, 82.13; H, 10.57. Found: C, 81.84; H, 10.57.

The diketone (4) was recovered unchanged on treatment with 5% NaOH-MeOH under reflux for 2 hr.

The bis-hydrazone crystallizes in needles, m.p. 277~279°(decomp.). IR cm^{-1}: 3344, 3226 (NH), 1703 (C=N). *Anal.* Calcd. for $C_{30}H_{50}N_4$: N, 12.01. Found: N, 11.94.

Reduction of Serratenedione (4)——a) To a boiling solution of serratenedione (4) (90 mg.) in *n*-PrOH (25 ml.) was added 2 g. of Na in several portions, and the heating was continued for further 2 hr. Working up as usual, serratenediol (1), m.p. and mixed m.p. 298~300°, was isolated. Acetylation of this gave serratenediol diacetate (2), m.p. and mixed m.p. 335~337°(open capillary).

b) Serratenedione (4) (30 mg.) and excess of $NaBH_4$ in MeOH (5 ml.) were stirred for 2 hr. at room temperature. After acetylation of the product, serratenediol diacetate (2), m.p. 335~337°(open capillary), was isolated.

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18) C. Djerassi, W. Klyne: J. Chem. Soc., **1962**, 4929.

Serratene (5)——Serratenedione (4) (200 mg.) and anhydrous hydrazine (0.6 ml.) in diethyleneglycol (6 ml.) containing Na (0.5 g.) were heated at 180° for 4 hr., then the temperature was raised to 210° and the mixture kept for 4 hr. The mixture was poured into H_2O, extracted with ether and the extract was evaporated to dryness. The residue in *n*-hexane was chromatographed to give (5) (170 mg.) as colorless prisms from $CHCl_3$–MeOH, m.p. 237～239°, $[\alpha]_D$ $-19°$(c=3.52). RRT: 2.48. NMR (τ): $\geqslant$C–CH_3, 9.34 (3H), 9.16 (15H), 9.11 (3H); ⟩C=C$\underline{H}$–, 4.68 (1H, multiplet). MS: M^+ 410 (40), 395 (6.5), 286 (14), 271 (7.5), 257 (6.5), 245 (3.5), 231 (6.5), 229 (6.5), 217 (10.5), 218 (20.5), 216 (10), 206 (15), 205 (29), 204 (76), 203 (11.5), 192 (35.4), 191 (100), 190 (26), 189 (25), 187 (47). *Anal.* Calcd. for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 87.46; H, 12.12.

Hydrogenation of Serratene (5)——Serratene (5) (65 mg.) in *n*-hexane (10 ml.) and AcOH (10 ml.) was hydrogenated over PtO_2 (100 mg.) until the solution was saturated to tetranitromethane. The catalyst was removed by filtration and the filtrate was evaporated to dryness. The product in VPC showed two peaks in ratio of 57:43 at RRT 2.60 and 2.15. The residue was crystallized several times from Me_2CO to afford α-serratane (14α-Serratane) (9) (4 mg.) as prisms, m.p. 198～200°. RRT: 2.15. MS: M^+ 412. *Anal.* Calcd. for $C_{30}H_{52}$: C, 87.30; H, 12.70. Found: C, 87.60; H, 12.89. The combined mother liquor from α-serratane was again dissolved in Me_2CO and slowly evaporated at room temperature, until two crystalline forms, needles and prisms, appeared in the solution. The needles which are more soluble in Me_2CO were collected by mechanically and crystallized several times from Me_2CO to give β-serratane (14β-Serratane) (10) (20 mg.) as needles, m.p. 184～187°. RRT: 2.60. MS: M^+ 412. *Anal.* Calcd for $C_{30}H_{52}$: C, 87.30; H, 12.70. Found: C, 87.58; H, 12.65.

Hydrogenation of Serratenediol Diacetate (2)——Serratenediol diacetate (2) (1.2 g.) in cyclohexane (20 ml.) and AcOH (20 ml.) were similarly hydrogenated over PtO_2 (500 mg.). The catalyst was then removed by filtration, the filtrate was evaporated to dryness *in vacuo* and the residue in benzene was chromatographed to give a mixture of 14α- and 14β-serratanediol diacetate (6) (1.1 g.), which after crystallization from benzene formed colorless needles, m.p. 300°, $[\alpha]_D$ $+21.0°$(c=2.1). *Anal.* Calcd. for $C_{34}H_{56}O_4$: C, 77.22; H, 10.67. Found: C, 76.96; H, 10.44. The compound showed two spots in TLC.

Hydrolysis of crude serratanediol diacetate (6) (1.0 g.) in dioxane (25. ml.) and MeOH (10 ml.) with KOH (1 g.) for 1 hr. under reflux gave serratanediol (7) as colorless needles, m.p. 264～265°. *Anal.* Calcd. for $C_{30}H_{50}O_2 \cdot H_2O$: C, 77.86; H, 11.76. Found: C, 77.96; H, 11.53.

Conversion of Serratanediols (7) into Serratanes (9 and 10)——Serratanediols (7) (350 mg.) and CrO_3 (0.5 g.) in pyridine (6 ml.) were stirred overnight at room temperature. The mixture was poured into H_2O, extracted with $CHCl_3$, and the extract was evaporated to dryness. Chromatography of the oily residue in $CHCl_3$ over SiO_2 and several crystallizations of the eluate from MeOH gave serratanedione (8) (0.3 g.) as needles m.p. 152～155°, $[\alpha]_D$ $+9.9°$(c=2.62). IR cm^{-1}: 1707 (cyclohexanone). *Anal.* Calcd. for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98. Found: C, 81.57; H, 10.68.

The above serratanedione (100 mg.) and anhydrous hydrazine (1 ml.) in diethyleneglycol (12 ml.) containing sodium (0.6 g.) were treated as described above. Crystallization of the hydrocarbon product from Me_2CO gave β-serratane (10) as needles, m.p. and mixed m.p. 184～187°. The mother liquor from β-serratane showed in VPC a small peak at RRT 2.15 corresponding to α-serratane (9) together with a major peak of β-serratane (10) at RRT: 2.60.

Reaction of Phosphorus Pentachloride on Serratenediol (1)——To a stirred solution of serratenediol (1) (495 mg.) in dry benzene (200 ml.) was added PCl_5 (1 g.) portionwise at room temperature. The stirring was continued for 1 hr. under dry nitrogen and protection from moisture. The mixture was poured into 5% K_2CO_3 and the separated benzene layer was washed with 5% K_2CO_3 solution, and evaporated to dryness to give a pale yellow crystalline solid (420 mg.). Crystallization of this from $CHCl_3$–MeOH gave the bis-isopropylidene derivative (11) as colorless needles, m.p. 221～223°, $[\alpha]_D$ $-108°$(c=0.89). NMR (τ): $\geqslant$C–CH_3, 9.46 (3H), 9.40 (3H), 9.11 (3H); ⟩C=C–CH_3; 8.42 (6H, broad s.), 8.29 (6H, broad s.); ⟩C=C$\underline{H}$–, 4.66 (1H, multiplet). *Anal.* Calcd. for $C_{30}H_{46}$: C, 88.60; H, 11.40. Found: C, 88.81; H, 11.45.

Reaction of Phosphorus Pentachloride on Serratanediol (7)——A solution of serratanediol (7) (196 mg.) in dry benzene (50 ml.) was treated with PCl_5 (420 mg.), and the mixture was worked up as above. Chromatography of the crystalline product in *n*-hexane gave the bis-isopropylidene derivative (14) as prisms from $CHCl_3$–MeOH, m.p. 182～186°, $[\alpha]_D$ $-66.7°$(c=1.34). NMR (τ): $\geqslant$C–CH_3, 9.40 (3H), 9.25 (3H), 9.11 (3H); ⟩C=C–CH_3, 8.42 (6H, broad s.), 8.29 (6H, broad s.). *Anal.* Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 88.39; H, 11.79. The VPC showed that this compound is not completely homogeneous.

Reaction of Phosphorus Pentachloride on Serratenediol Monoacetate (3)——Serratenediol monoacetate (3)[1] (390 mg.) in dry benzene (250 ml.) was treated with PCl_5 (235 mg.) as above. Chromatography of the product in benzene afforded the isopropylidene derivative (12) (193 mg.) as plates from *n*-hexane, m.p. 263～266°. NMR (τ): $\geqslant$C–CH_3, 9.46 (3H), 9.15 (12H); $OCOCH_3$, 7.95 (3H); ⟩C$\underline{H}$OAc, 5.55 (1H, multiplet); ⟩C=C$\underline{H}$–, 4.68 (1H, multiplet). *Anal.* Calcd. for $C_{32}H_{50}O_2$: C, 82.34; H, 10.80. Found: C, 82.34; H, 11.06.

Alkaline hydrolysis of (12) and the reaction of PCl_5 on the product gave the bis-isopropylidene derivative (11), m.p. and mixed m.p. 221～223°.

Acid Isomerization of the Bis-isopropylidene Derivative (14)——The bis-isopropylidene derivative (14) (98 mg.) in 3% HCl–EtOH was heated under reflux for 30 min. The cooled mixture was neutralized with

$NaHCO_3$, evaporated to dryness, and the residue was extracted with ether. The product from the ethereal extract was crystallized from Me_2CO to give the bis-isopropyl derivative(15) as needles, m.p. 119~121°. NMR (τ): $\geqslant$C–CH_3, 9.20 (3H), 9.13 (3H), 9.09 (3H), 9.05 (6H), 9.02 (3H), 8.96 (3H). *Anal.* Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 87.95; H, 11.65.

Hydroxylation and Lead Tetraacetate Cleavage of the Bis-isopropylidene Derivative (14)——The bis-isopropylidene derivative (14) (260 mg.) and OsO_4 (220 mg.) in dioxane (10 ml.) were kept in the dark for 14 days. Hydrogen sulfide was bubbled into the mixture, and the black precipitate was filtered and repeatedly washed with ether. Evaporation of the combined filtrate left a gum (285 mg.) which failed to crystallize. The gum (245 mg.) and lead tetracetate (300 mg.) in AcOH (10 ml.) were kept at 40° for 4 hr. The mixture was diluted with H_2O (60 ml.) and distilled into a solution of 2,4-dinitrophenylhydrazine (0.4 g.) in H_2O (2 ml.) and EtOH (10 ml.) containing conc. H_2SO_4 (2 ml.). The yellow precipitate (130 mg., 53% based on two isopropylidene groups) was collected by filtration crystallized from EtOH to give acetone 2,4-dinitrophenylhydrazone as needles, m.p. and mixed m.p. 125~126°.

The residual aqueous solution was extracted with $CHCl_3$ and the extract was evaporated to dryness to leave a gum (206 mg.) which was chromatographed in *n*-hexane. The benzene eluate (100 mg.) was distilled at 6×10^{-4} mm. and 150° to give hexanordiketone (16) (10 mg.) as colorless prisms from *n*-hexane-ether, m.p. 173~176°. IR cm^{-1}: 1735 (cyclopentanone). *Anal.* Calcd. for $C_{24}H_{36}O_2$: C, 80.85; H, 10.18. Found: C, 80.79; H, 10.05.

Isoserratenedione (19)——a) Serratenedione (14) (0.1 g.) in AcOH (20 ml.) and conc. HCl (1 ml.) were heated under reflux for 28~30 hr. The mixture was evaporated to dryness under reduced pressure and the residue (0.1 g.) was extracted with $CHCl_3$, washed with 5% K_2CO_3, and chromatographed over SiO_2 to give (19) (70 mg.) as prisms from MeOH, m.p. 169~170°, $[\alpha]_D$ +160°(c=3.33). IR cm^{-1}: 1709 (cyclohexanone). NMR (τ): $\geqslant$C–CH_3, 9.14 (3H), 9.12 (3H), 9.06 (3H), 8.95 (6H), 8.92 (3H), 8.89 (3H); no vinylic proton. ORD: $[\phi]_{312}^{peak}$ +7100°, $[\phi]_{275}^{trough}$ +100° (c=0.437). *Anal.* Calcd. for $C_{30}H_{46}O_2$: C, 82.13; H, 10.57. Found: C, 82.13; H, 10.58.

b) To a solution of serratenedion (4) (0.2 g.) in AcOH (20 ml.) was added conc. H_2SO_4 (1.5 ml.) in AcOH (2 ml.) under cooling at 0° and the mixture kept for 14 hr. at room temperature. The mixture was poured into H_2O, extracted with $CHCl_3$, and the extract was washed with 5% NaOH, and evaporated to give a solid which after chromatography afforded (19), m.p. and mixed m.p. 169~170°.

Isoserratenediol (18)——Isoserratenedione (19) (50 mg.) and $NaBH_4$ (200 mg.) in MeOH were stirred for 4 hr. at room temperature. After the addition of a few drops of AcOH and H_2O the precipitate was collected by filtration and crystallized from $CHCl_3$–MeOH to give (18) as needles, m.p. 267~269°. *Anal.* Calcd. for $C_{30}H_{50}O_2 \cdot H_2O$: C, 78.20; H, 11.38. Found: C, 78.15; H, 11.26. Acetylation of this with Ac_2O and pyridine gave isoserratenediol diacetate (17), as prisms, m.p. 294~296°(open capillary), $[\alpha]_D$ +83.8°(c=1.6). NMR (τ): $\geqslant$C–CH_3, 9.16 (18H), 9.11 (3H); $OCOCH_3$, 7.97 (3H), 7.94 (3H): $\rangle\underline{CH}$–OAc, 5.50 (2H, multiplet). *Anal.* Calcd. for $C_{34}H_{54}O_4$: C, 77.52; H, 10.33. Found: C, 77.32; H, 10.25.

Isoserratene (20)——Isoserratenedione (19) (200 mg.) and anhydrous hydrazine (2 ml.) in diethyleneglycol (16 ml.) containing Na (700 mg.) were heated in the same way as described above. After working up, there was isolated (20) (140 mg.) as needles from $CHCl_3$–MeOH, m.p. 174~178°, $[\alpha]_D$ +78.5(c=1.78). RRT: 2.01. *Anal.* Calcd. for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 87.71; H, 12.53.

Acid Isomerization of Serratenediol (1) and Serratene (5)——Serratenediol diacetate (2) (672 mg.) was isomerized by the method b). The product, after chromatography gave 200 mg. of isoserratenediol diacetate (17) m.p. and mixed m.p. 294~296°(open capillary). This was found to be contaminated by serratenediol diacetate, since its NMR spectrum showed accompanying weak peaks at 4.69 τ due to a vinylic proton and at 9.31 τ due to a C_{28}-methyl group of serratenediol diacetate.

2) Serratenediol (1) (200 mg.) was isomerized by the method a). The product, after chromatography, gave isoserratenediol diacetate (17) (20 mg.), identical with that of obtained above, m.p. and mixed m.p. 294~296°(open capillary). Saponification of this with 5% KOH–MeOH furnished isoserratenediol (18), m.p. and mixed m.p. 267~269°.

3) Serratene (5) (30 mg.) in AcOH (21 ml.) and benzene (2 ml.) was treated with conc. H_2SO_4 (3.5 ml.) for 18 hr. at room temperature. Crystallization of the product from $CHCl_3$–MeOH gave isoserratene (20) (10 mg.) as needles, m.p. 175~178°, identical with that obtained by Wolff-Kishner reduction of isoserratenedione (19). However, VPC showed that this is a mixture of isoserratene (84%) and serratene (16%).

4) The combined solution of serratene (5) (11 mg.) in $CHCl_3$ (1 ml.) and 15 v/v% HCl–AcOH (10 ml.) was heated at 100° for 16 hr. The hydrocarbon product (5.6 mg.) showed two peaks at RRT: 2.01 (isoserratene) and at 2.48 (serratene) with relative intensity (3:1).

5) Isoserratene (10 mg.) was treated in the same way to give a mixture of serratene (5) and isoserratene (20) in ratio of 4:1.

Serraten-21-on-3β-ol Acetate (21)——Serratenediol monoacetate (3) (300 mg.) in pyridine (5 ml.) was stirred with CrO_3–pyridine complex (400 mg. of CrO_3 and 9 ml. of pyridine) overnight at room temperature. Chromatography of the product afforded (21) (235 mg.) as prisms from $CHCl_3$–MeOH, m.p. 305~307°(open capillary). IR cm^{-1}: 1724, 1240 (OAc); 1709 (cyclohexanone). ORD: $[\phi]_{320}^{trough}$ −1835°, $[\phi]_{275}^{peak}$ +1326° (c=0.18). NMR (τ): $\geqslant$C–CH_3, 9.16 (12H), 9.07 (3H), 8.95 (3H), 8.91 (3H); $OCOCH_3$, 7.95 (3H); $\rangle C\underline{H}OAc$, 5.54 (1H, multiplet); $>$C=C$\underline{\text{H}}$–, 4.62 (1H, multiplet). *Anal.* Calcd. for $C_{32}H_{52}O_3$: C, 79.62; H, 10.44. Found: C, 79.39; H, 10.25.

Serraten-3β-ol Acetate (22)——Serraten-21-on-3β-ol acetate (21) (230 mg.) and anhydrous hydrazine (2 ml.) in diethyleneglycol (28 ml.) containing Na (1.4 g.) were heated as described already. The product was acetylated with Ac_2O (1.5 ml.) and pyridine (3 ml.) at room temperature for 24 hr. Chromatography of the resulting acetate in benzene gave (22) (181 mg.) as plates from $CHCl_3$–MeOH, m.p. 301～305°(open capillary). IR cm^{-1}: 1729, 1242 (OAc). NMR (τ) : $\geqslant$C–CH_3, 9.34 (3H), 9.16 (18H); –$OCOCH_3$, 7.95 (3H); $>$C$\underline{\text{H}}$OAc, 5.54 (1H, multiplet); $>$C=C$\underline{\text{H}}$–, 4.61 (1H, multiplet). MS : M^+ 468 (54), 453 (19.5), 408 (8), 344 (11.6), 285 (8.7), 284 (10.5), 276 (11), 269 (10.5), 257 (6.5), 249 (13), 245 (6.7), 231 (7), 229 (19), 217 (14), 205 (29), 204 (58), 203 (23), 201 (13), 191 (33), 190 (34), 189 (68), 187 (25), 109 (100). *Anal.* Calcd. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.58. Found : C, 82.18; H, 11.54.

Serraten-3-one (24)——Serraten-3β-ol acetate (22) (130 mg.) and KOH (0.5 g.) in dioxane (5 ml.) and MeOH (5 ml.) were heated under reflux for 2 hr. Water was added to the mixture, and the precipitate collected by filtration crystallized from $CHCl_3$–MeOH to give serraten-3β-ol (23) as prisms, m.p. 266～267°.

Serraten-3β-ol (23) (104 mg.) and CrO_3 (300 mg.) in pyridine (5 ml.) were kept overnight at room temperature. The product, being worked up as usual, was chromatographed in benzene to give (24) (82 mg.) as prisms from $CHCl_3$–MeOH, m.p. 204～206°. IR cm^{-1} : 1697 (cyclohexanone). ORD : $[\phi]_{310}^{\text{peak}}$ +1650°, $[\phi]_{265}^{\text{trough}}$ –1190°(c=0.438). NMR (τ) : $\geqslant$C–CH_3, 9.34 (3H), 9.16 (6H), 9.13 (6H), 8.97 (3H), 8.92 (3H); $>$C=C$\underline{\text{H}}$–, 4.68 (1H, multiplet). MS : M^+ 424 (53), 409 (100), 395 (16), 300 (38), 232 (47), 219 (30), 218 (24), 205 (87), 204 (51), 203 (41), 193 (47), 191 (55), 189 (45). *Anal.* Calcd. for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found : C, 84.90; H, 11.41.

Isoserraten-21-on-3β-ol Acetate (Serrat-13-en-21-on-3β-ol Acetate) (25)——Serraten-21-on-3β-ol acetate (21) (180 mg.) was isomerized by the method b). Crystallization of the product (150 mg.) from $CHCl_3$–MeOH gave (25) as prisms, m.p. 290～292°, $[\alpha]_D$ +60.5 (c=0.76), IR (KBr) cm^{-1} : 1712 (cyclohexanone), 1730, 1240 (OAc). ORD : $[\phi]_{300}^{\text{peak}}$ +3940°. *Anal.* Calcd. for $C_{32}H_{52}O_3$: C, 79.62; H, 10.44. Found : C, 79.48; H, 10.20.

Isoserraten-3β-ol (Serrat-13-en-3β-ol) (26)——Isoserraten-21-on-3β-ol acetate (25) (120 mg.) and anhydrous hydrazine (0.5 ml.) in diethyleneglycol (10 ml.) containing Na (0.5 g.) were heated and worked up as already described. Chromatography of the product in benzene and crystallization of the ether eluates from $CHCl_3$–MeOH afforded (26) as prisms, m.p. 185～187°, $[\alpha]_D$ +42.1°(c=0.76). *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found : C, 84.25; H, 11.64.

Isoserraten-3-one (Serrat-13-en-3-one) (27)——a) Isoserraten-3β-ol (26) (75 mg.) in benzene (8 ml.) and AcOH (15 ml.) was treated overnight with CrO_3 (20 mg.) in AcOH (1 ml.) at 20°. After addition of H_2O, the mixture was extracted with ether. The extract was washed with 5% K_2CO_3 and evaporated to dryness. Chromatography of the residue in benzene yielded (27) (50 mg.) as prisms from benzene–EtOH, m.p. 220～222°. IR (KBr) cm^{-1} : 1712 (cyclohexanone). ORD $[\phi]_{304\text{ and }312}^{\text{peak}}$ +1560°. MS : M^+ 424 (55), 409 (29), 300 (35), 232 (50), 219 (31), 218 (22), 217 (24), 205 (90), 204 (52), 203 (41), 193 (48), 191 (59), 177 (29), 175 (47). *Anal.* Calcd. for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found : C, 84.68; H, 11.31.

b) Serraten-3-one (24) (20 mg.) was isomerized by the method b). Chromatography of the product afforded (27), m.p. and mixed m.p. 219～221°.

Oxidation of Serratenediol Diacetate (2) with Selenium Dioxide——Serratenediol diacetate (2) (210 mg.) and SeO_2 (210 mg.) in AcOH (50 ml.) were heated at 70° for 1 hr. The solution was separated from a brownish red precipitate by filtration, and the residue was washed with AcOH. The combined filtrate was diluted with H_2O and extracted with ether, the extract was washed with 5% $NaHCO_3$, evaporated to dryness, and the residue in benzene–*n*-hexane (1:1) was chromatographed. Elution with the same solvent, followed by crystallization from $CHCl_3$–MeOH gave serratadienediol diacetate (28) (35 mg.) as needles, m.p. 292～293°. IR cm^{-1}; 1724, 1243 (OAc), 803 ($>$C=CH–). UV λ_{max} mμ (log ε) : 233 (4.11), 241 (4.16), 248 (4.04). NMR (τ): $\geqslant$C–CH_3, 9.08 (18H), 9.01 (3H); –$OCOCH_3$, 7.92 (6H); $>$C$\underline{\text{H}}$OAc, 5.50 (2H, multiplet); $>$C=C$\underline{\text{H}}$–, 4.57 (2H, multiplet).

Serratan-15ξ-ol (32)——To a stirred solution of BF_3-etherate (2.3 g.) and serratene (5) (1.36 g.) in abs. ether (60 ml.) was added $LiAlH_4$ (0.9 g.) in abs. ether (25 ml.) during 1 hr. at 0°. The stirring was continued at room temperature for further 3 hr., then the excess hydride decomposed by adding a saturated solution of Na_2SO_4, and the mixture filtrated. To the residue from the filtrate in tetrahydrofuran (60 ml.) was added a mixture of 30% H_2O_2 (45 ml.) and 10% NaOH (45 ml.) with stirring during 1 hr. at 0°. The mixture was extracted with ether and the ethereal extract was evaporated to give a residue (1.4 g.) which was acetylated with Ac_2O (5 ml.) and pyridine (10 ml.) by keeping overnight at room temperature. The product in *n*-hexane was chromatographed to give serratan-15ξ-ol acetate (33) (1.0 g.) as needles from Me_2CO, m.p. 175～177°, $[\alpha]_D$ –40°(c=2.5). *Anal.* Calcd. for $C_{32}H_{54}O_2$: C, 81.64; H, 11.56. Found : C, 81.55; H, 11.48.

Hydrolysis of serratan-15ξ-ol acetate (33) (1.2 g.) by KOH (4 g.) in boiling MeOH (25 ml.)-dioxane (15 ml.) for 1 hr. gave (32) (1.0 g.) as needles from *n*-hexane, m.p. 174～178°. *Anal.* Calcd. for $C_{30}H_{52}O$: C, 84.04; H, 12.23. Found : C, 83.74; H, 11.90.

β-Serratan-15-one (34)——A solution of serratan-15ξ-ol (32) (1.2 g.) in pyridine (10 ml.) was oxidized with CrO_3-pyridine complex (1 g. of CrO_3 and 5 ml. of pyridine) overnight at room temperature. Chromatography of the product in $CHCl_3$ over SiO_2 afforded (34) (1.0 g.) as colorless prisms from $CHCl_3$-MeOH, m.p. 202~204°, $[\alpha]_D$ $-60°$(c=2.55). IR cm^{-1}: 1692 (cyclohexanone). *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81 Found: C, 84.17; H, 11.79

α-Serratan-15-one (35)——β-Serratan-15-one (34) (76 mg.) and 2% MeOH-$NaOCH_3$ (10 ml.) in benzene (5 ml.) were stirred at room temperature for 3 hr. The mixture was poured into H_2O, extracted with $CHCl_3$, and the extract was evaporated to give a crystalline solid which showed two spots in a thin-layer chromatography. The separation of these two compounds were achieved by the preparative thin-layer chromatography (solvent: benzene-*n*-hexane (1:1)). Stripping of the upper zone and extraction with $CHCl_3$ afforded (35) (52 mg.) as needles from $CHCl_3$-MeOH, m.p. 196~198°. IR cm^{-1}: 1703 (cyclohexanone). *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.37; H, 11.90. The lower zone gave the starting material (10 mg.) m.p. and mixed m.p. 202~204°.

Wolff-Kishner Reduction of Serratan-15-ones——a) Serratan-15-one (34) (100 mg.) and anhydrous hydrazine (1 ml.) in diethyleneglycol (40 ml.) containing Na (4.0 g.) were treated as described already. The product, isolated with ether was chromatographed in *n*-hexane and the eluate was crystallized from Me_2CO to give α-serratane (9) (45 mg.) as prisms, m.p. and mixed m.p. 200~203°, RRT: 2.15. The mother liquor from α-serratane gave crystals of m.p. 180~195° whose VPC showed two peaks corresponding to those of α- and β-serratane.

b) α-Serratan-15-one (35) similarly gave α-serratane (9) m.p. and mixed m.p. 200~202° as a major product.

Isoserraten-15-one (Serrat-13-en-15-one) (37)——a) To a stirred solution of β-serratan-15-one (34) (71 mg.) in AcOH (5 ml.) containing one drop of HBr-AcOH was added 0.91 W/v% of Br_2 in AcOH. After absorption of 1 mol. of Br_2 during 10 min., H_2O was added to the mixture, and extracted with $CHCl_3$. The extract was washed with 2% NaOH, and evaporated *in vacuo*. Trituration of the residue with *n*-hexane gave a crystalline bromo-compound (75 mg.) which was labile and failed to obtain in pure form. The bromo-compound was then heated in pyridine (5 ml.) on a water-bath for 3 hr. After removal of pyridine *in vacuo*, the residue in benzene was chromatographed to give (37) (54 mg.) as leaflets from $CHCl_3$-MeOH. m.p. 247~249°, $[\alpha]_D$ $+19.3°$(c=1.17), UV λ_{max} mμ (log ε): 258 (4.00), IR cm^{-1}: 1645, 1613 (cyclohexenone). NMR (ε): ⋗C-CH_3, 9.35 (3H), 9.26 (3H), 9.15 (3H), 9.11 (6H), 8.97 (3H). *Anal.* Calcd. for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 84.96; H, 11.19.

b) Serratene (5) (1.0 g.) and $Na_2Cr_2O_7 \cdot 2H_2O$ (1 g.) in AcOH (400 ml.) were heated under reflux for 3 hr., and the mixture was allowed to stand overnight at room temperature. After decomposition of the excess reagent by addition of EtOH, AcOH was removed *in vacuo*, and the residue extracted with $CHCl_3$. The extract was washed with 5% Na_2CO_3, and evaporated to dryness. Chromatography of the residue and crystallization of the *n*-hexane and benzene eluates from $CHCl_3$-MeOH gave (37) (200 mg.), m.p. and mixed m.p. 247~249°.

c) Isoserratene (20) (498 mg.) and $Na_2Cr_2O_7 \cdot 2H_2O$ (500 mg.) in AcOH (150 ml.) were heated under reflux for 3 hr. Crystallization of the product from $CHCl_3$-MeOH gave (37) (400 mg.) as leaflets, m.p. and mixed m.p. 245~247°.

Hydrogenation of Isoserraten-15-one (37)——Isoserraten-15-one (37) (53 mg.) and PtO_2 (63 mg.) in AcOH (20 ml.) and *n*-hexane (10 ml.) were stirred in H_2 for 8 hr. at room temperature. Removal of the catalyst and solvent left a crystalline solid which was chromatographed in *n*-hexane. The resulting hydrocarbon mixture (m.p. 170~192°) showed in VPC three peaks (RRT, 2.01, 2.15 and 2.60, in ratio of 1, 1.2 and 2.9, corresponding to those of isoserratene (20), α-serratane (9), and β-serratane (10), respectively.

Oxidation of β-Serratan-15-one (34) with Fuming Nitric Acid——To a solution of β-serratan-15-one (34) (323 mg.) in AcOH (10 ml.) was added fuming HNO_3 (10 ml.) at 0°, and the mixture was kept two days in a refrigerator. After being warmed for further 1 hr. at 50°, the mixture was poured into H_2O, extracted with ether, and the ethereal layer was washed with 2% NaOH. Acidification and ether extraction of the alkaline washings gave, on evaporation, an oil (155 mg.), which was methylated in ether with excess of CH_2N_2. The product isolated was chromatographed in benzene to give the dimethyl ester of the seco-acid (36) (20 mg.) as prisms from $CHCl_3$-MeOH, m.p. 146~148°, $[\alpha]_D$ $-27.1°$(c=0.59). IR cm^{-1}: 1732 (ester). *Anal.* Calcd. for $C_{32}H_{54}O_4$: C, 76.44; H, 10.83. Found: C, 76.36; H, 10.69.

Oxidation of Isoserraten-15-one (37) with Selenium Dioxide——Isoserraten-15-one (37) (100 mg.) and SeO_2 (100 mg.) in AcOH (50 ml.) were refluxed for 3 hr. The cooled mixture was filtered and the filtrate was evaporated to dryness to leave a pale yellow crystalline solid. Chromatography of this in benzene gave serratadienone-a (serrata-13,16-dien-15-one) (39) (85 mg.) as colorless prisms from MeOH, m.p. 226~228°, $[\alpha]_D$ $-39°$(c=1.4), IR cm^{-1}: 1647, 1623, 1603 (dienone), UV λ_{max} mμ (log ε): 250 (4.13), shoulder 282 (3.67). NMR (τ): ⋗C-CH_3, 9.33 (3H), 9.26 (3H), 9.20 (3H), 9.12 (3H), 8.77 (3H), 8.73 (6H); $>$C=C$\underline{H}$-, 3.74 (1H, singlet). *Anal.* Calcd. for $C_{30}H_{46}O$: C, 85.24; H, 10.97. Found: C, 84.98; H, 10.79.

Oxidation of β-Serratan-15-one (34) with Selenium Dioxide——β-Serratan-15-one (34) (984 mg.) and SeO_2 (513 mg.) in AcOH (150 mg.) were refluxed for 1 hr. The solution was separated from the precipitate and the residue thoroughly was washed with AcOH. The combined filtrate was evaporated *in vacuo* to dryness, and the residue redissolved in benzene, and again filtered. The benzene filtrate was passed through a short column of Al_2O_3 and the eluate in benzene was chromatographed on SiO_2, (40 g.) to give the following products; i) elution with benzene (100 ml.) gave isoserraten-15-one (37) (158 mg.), m.p. and mixed m.p. 247~249°. ii) Further elution with benzene (100 ml.) gave a mixture (100 mg.) which was separated by the preparative thin-layer chromatography (solvent : benzene) into serratadienone-a (39) and serratadienon-b (serrata-14(27),16-dien-15-one) (45) (31 mg.) as prisms from $CHCl_3$-MeOH, m.p. 189~191°, $[\alpha]_D$ −181° (c=0.73). IR cm^{-1} : 1650, 1597 (dienone). UV λ_{max} mμ (logε) : 266 (4.11). NMR (τ) : $\geqslant$C–CH_3, 9.20 (3H), 9.16 (3H), 9.14 (3H), 8.97 (3H), 8.90 (3H), 8.83 (3H), 8.79 (3H); $>$C=C$\underline{H}$–, 3.89 (1H, s.), 3.35 (1H, d., J=2.5 c.p.s.). *Anal.* Calcd. for $C_{30}H_{46}O$: C, 85.24; H, 10.97. Found : C, 85.44; H, 10.90. iii) Further elution with benzene (200 ml.) gave serratadienone-a (39) (350 mg.), m.p. and mixed m.p. 226~228°.

Treatment of Serratadienone-a (39) with Zinc Dust——Serratadienone-a (39) (400 mg.) and Zn dust (10 g.) in AcOH (100 ml.) were heated under reflux for 4 hr. The mixture was filtered, and the filtrate was diluted with H_2O, then extracted with ether. The ethereal layer was washed with 5% $NaHCO_3$, and evaporated to give a crystalline residue. Chromatography of the residue in benzene afforded the nor-phenol (43) (300 mg.) as needles from *n*-hexane, m.p. 238~239°, $[\alpha]_D$ −20.5 (c=1.17). UV λ_{max} mμ (logε) : 285 (3.45), 291 (3.49). NMR (τ) : $\geqslant$C–CH_3, 9.35 (3H), 9.25 (3H), 9.20 (3H), 9.13 (3H), 8.78 (3H), 8.75 (3H); –O–$\underline{H}$, 5.61 (1H, broad s.); ArH, 3.44 (1H, s.). *Anal.* Calcd. for $C_{29}H_{42}O$: C, 85.65; H, 10.41. Found: C, 85.42; H, 10.70.

Isoserraten-15-onediol Diacetate (Serrat-13-en-15-one-13β,21α-diol Diacetate (38)——a) Serratenediol diacetate (2) (2.23 g.) was refluxed in AcOH (390 ml.) containing $Na_2Cr_2O_7 \cdot 2H_2O$ (2.3 g.) for 3 hr. After decomposition of excess of $Na_2Cr_2O_7$ by MeOH, the product was isolated as usual and chromatographed in benzene to give (38) (675 mg.) as prisms from $CHCl_3$-MeOH, m.p. 312~314° (open capillary), $[\alpha]_D$ +35°(c=1.94). IR cm^{-1} : 1724, 1250 (OAc); 1650, 1616 (cyclohexenone). UV λ_{max} mμ (log ε) : 256 (3.97). NMR (τ) : $\geqslant$C–CH_3, 9.36 (3H), 9.22 (3H), 9.15 (6H), 9.11 (3H), 9.05 (3H), 8.95 (3H); $OCOCH_3$, 7.96 (3H), 7.92 (3H); $>$C$\underline{H}$OAc, 5.5 (2H, multiplet). *Anal.* Calcd. for $C_{34}H_{52}O_5$: C, 75.51; H, 9.69. Found : C, 75.53; H, 9.46.

b) Isoserratenediol diacetate (17) (510 mg.) was refluxed in AcOH (100 ml.) containing $Na_2Cr_2O_7 \cdot 2H_2O$ (500 mg.) for 4 hr. Chromatography of the product in benzene gave (38) (240 mg.) as prisms from $CHCl_3$-MeOH, m.p. and mixed m.p. 312~314°(open capillary).

Serrata-13,16-dien-15-one-3β,21α-diol Diacetate (40)——Isoserraten-15-onediol diacetate (38) (100 mg.) was refluxed in AcOH (15 ml.) containing SeO_2 (100 mg.) for 5 hr. Isolation of the product and chromatography in benzene gave (40) (85 mg.) as prisms from $CHCl_3$-MeOH, m.p. 295~297°, $[\alpha]_D$ +11.8°(c=1.36), IR cm^{-1}: 1724, 1237 (OAc); 1647, 1613, 1603 (dienone), UV λ_{max} mμ (log ε) : 248 (4.20), 281 (3.76). NMR (τ) : $\geqslant$C–CH_3, 9.34 (3H), 9.22 (3H), 9.15 (3H), 9.14 (3H), 8.79 (3H), 8.70 (6H); –$OCOCH_3$, 7.95 (3H), 7.91 (3H); $>$C$\underline{H}$OAc, 5.50 (2H, multiplet); $>$C=C$\underline{H}$–, 3.7 (1H, s.). *Anal.* Calcd. for $C_{34}H_{50}O_5$: C, 75.80; H, 9.36. Found : C, 76.07; H, 9.34.

Treatment of the Dienonediol Diacetate (40) with Zinc Dust——The dienone diacetate (40) (300 mg.) and Zn dust (15 g.) in AcOH (100 ml.) were heated under reflux for 4 hr. Crystallization of the product from $CHCl_3$-MeOH afforded the nor-phenol derivative (43) (201 mg.) as prisms from $CHCl_3$-MeOH, m.p. 280~282°, $[\alpha]_D$ +25°(c=1.05). IR cm^{-1} : 3500 (OH), 1735~1700 (OAc), 1610, 1570 (Ar). UV λ_{max} mμ (log ε) : 282 (3.24), 291 (3.25). NMR (τ) : $\geqslant$C–CH_3, 9.35 (3H), 9.22 (3H), 9.16 (3H), 9.13 (3H), 8.76 (6H); –$OCOCH_3$, 7.95 (6H); $>$C$\underline{H}$OAc, 5.51 (1H, multiplet); –O$\underline{H}$, 4.92 (1H, s.); ArH, 3.40 (1H, s.) *Anal.* Calcd. for $C_{33}H_{48}O_5$: C, 75.53; H, 9.22. Found : C, 75.37; H, 9.35.

Serrata-13,16-dien-15-one-3β,21α-diol (41)——The dienonediol diacetate (40) (200 mg.) was hydrolysed with 2.5% MeOH-KOH (20 ml.) under reflux for 2. hr. Crystallization of the product from $CHCl_3$-MeOH afforded (41) (180 mg.) as prisms, m.p. 296~298°, IR cm^{-1} : 3280 (OH), 1650, 1623, 1603 (dienone). *Anal.* Calcd. for $C_{30}H_{46}O_3 \cdot H_2O$: C, 76.22; H, 10.24. Found : C, 76.36; H, 10.48.

Reaction of Phosphorus Pentachloride on the Dienonediol (41)——To a stirred solution of the dienonediol (41) (259 mg.) in dry benzene (70 ml.) was added PCl_5 (397 mg.) portionwise at room temperature. After 2 hr's stirring, the mixture was poured into large excess of 5% K_2CO_3 and the separated benzene layer was washed with H_2O, then evaporated. Chromatography of the residue in *n*-hexane gave the bis-isopropylidene derivative (44) (85 mg.) as prisms from Me_2CO, m.p. 225~228°, $[\alpha]_D$ −209°(c=1.02), IR cm^{-1}: 1647, 1618, 1597 (trienone), UV λ_{max} mμ (log ε) : 276 (4.04), 320 (4.00). NMR (τ) : $\geqslant$C–CH_3, 9.48 (3H), 9.34 (3H), 8.88 (3H); $>$C=C–CH_3, 8.43 (3H), 8.26 (3H), 8.14 (6H); $>$C=C$\underline{H}$–, 3.78 (1H, s.). *Anal.* Calcd. for $C_{30}H_{42}O$: C, 86.06; H, 10.11. Found : C, 85.82; H, 9.90.

The Tricyclic Ketone (47)——To a solution of the nor-phenol (42) (305 mg.) in AcOEt (15 ml.) was bubbled O_2 stream containing O_3 for 7 hr. at room temperature. After being kept overnight, the mixture was concentrated to *ca.* 5 ml. and then heated with HCOOH (5 ml.) and 30% H_2O_2 (1 ml.) for 2 hr. on a steam bath. The mixture was then poured into H_2O, extracted with ether, and the extract was evaporated to leave an oil (307 mg.) which was heated under reflux with Ac_2O (10 ml.) for 3 hr. After removal of Ac_2O, the residue was heated at 200° for 3 hr., then distilled at 100~200° and 0.1 mm. to give a pale yellow oil (85 mg.). The oil after re-distillation at 120~140° and 0.1 mm. formed colorless crystals (40 mg.) which were recrystallized from MeOH to give the tricyclic ketone (47) (18 mg.) as needles, m.p. 156~158°, IR

(CCl_4) cm^{-1} : 1716 (cyclohexanone). ORD : $[\phi]_{314}^{peak}$ +4400°, $[\phi]_{277}^{trough}$ −1100° (c=0.467). NMR (τ) : $\geqslant$C–CH_3, 9.15 (6H), 9.12 (6H). *Anal.* Calcd. for $C_{18}H_{30}O$: C, 82.38; H, 11.30. Found : C, 82.61; H, 11.56.

The Synthesis of the *dl*-Tricyclic Ketone (51)——The *dl*-cyanoketal (48) (210 mg.) and $LiAlH_4$ (227 mg.) in abs. ether (60 ml.) was refluxed for 2 hr. After decomposition with H_2O the mixture was extracted with ether, and evaporated to afford the *dl*-imine (49) (214 mg.) as prisms from hexane, m.p. 183~187°, IR $(CHCl_3)$ cm^{-1} : 1622 (C=N). A mixture of the *dl*-imine (49) (210 mg.), 85% hydrazine hydrate (4 ml.) and hydrazine hydrochloride (735 mg.) in triethyleneglycol (23 ml.) were heated for 2 hr. at 140°. After cooling, KOH pellets (1.2 g.) were added and the mixture was again heated at 210° for 2.5 hr. The mixture was poured into ice-water, extracted with ether to give the *dl*-ketal (50) (190 mg.), prisms from *n*-hexane m.p. 135~140°, which showed no absorption between 1500~1800 cm^{-1} in the IR spectrum. The *dl*-ketal (50) (104 mg.) in Me_2CO (10 ml.) was treated with 2*N* HCl (1.5 ml.) under reflux for 35 min. Anhyd. NaOAc (500 mg.) was added to the cooled mixture, the solvent was evaporated to dryness *in vacuo* and the residue was taken up in ether. The ethereal extract gave, on evaporation, a crystalline residue (40 mg.), which was sublimed at 150° and 1 mm. to give the *dl*-ketone (51) (10 mg.), m.p. 153~155°, IR (CCl_4) cm^{-1} : 1716 (cyclohexanone). *Anal.* Calcd. for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found : C, 82.61; H, 11.56. The infrared spectrum of this in CCl_4 was indistinguishable from that of the tricyclic ketone (47) obtained above.

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