UDC 547.92.07

25. Kyosuke Tsuda, Eiji Ohki, Junnosuke Suzuki,[*1] and Hiroshi Shimizu[*2]: Steroid Studies. XXVII.[*3] A New Aromatization Reaction of the Homoannular Diene System. (1). On the Structure of the Phenolic Compound derived from 3β-Acetoxylanosta-5,8-dien-7-one.

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In an earlier report[1] of this series, synthesis of 4,4-dimethylcholecalciferol, one of vitamin D-type compounds derived from a compound having a skeleton corresponding to 14-demethyllanosterol (one of the metabolites of cholesterol biogenesis) was described. The present paper describes some new observations obtained during the synthesis of 4,4,14-trimethylcholecalciferol possessing methyl groups in the positions corresponding to those in lanosterol.

It was generally observed that the 8—9 double bond of steroid resists reduction and it was shown in the previous report[2] that the presence of *gem*-dimethyl group in 4-position in steroids interferes considerably in reduction of the 5—6 double bond. Based on these considerations, 3β-acetoxylanosta-5,8-dien-7-one[3,4][*4] (I), m.p. 184∼186°, $[\alpha]_D$ $-12°$, was prepared in a good yield from 3β-acetoxylanosta-5,8,11-trien-7-one[5] (II), m.p. 195∼196°, $[\alpha]_D$ $+68°$, by partial hydrogenation over 1% palladized charcoal in dioxane solution.

The infrared spectrum of (I) exhibited typical absorptions of a cross-conjugated dienone system at 1645, 1615, and 1592 cm^{-1}, and its physical constants were identical with those described in the published literature.[4] Oxidation of (I) with selenium dioxide and chromium trioxide gave the starting material (II) and a known 3β-acetoxylanosta-5,8-diene-7,11-dione,[6] m.p. 120∼123°, $[\alpha]_D$ $+80°$. Saponification of (I) with alkali afforded a free alcohol, 3β-hydroxylanosta-5,8-dien-7-one (III), m.p. 174∼175°, $[\alpha]_D$ $+23°$, which was converted to 3-oxo derivative, lanosta-5,8-diene-3,7-dione, m.p. 114∼116°, $[\alpha]_D$ $+143°$, by oxidation with chromium trioxide in pyridine solution.

The compounds having a dienone system in the molecule, such as santonin or the 1,4-dien-3-one steroids, easily undergo isomerisation to various interesting compounds, by the action of acid[7] or the irradiation of ultraviolet rays.[8] There has been little investigation[9,10] on the nature of the dienone system in the B-ring of steroids, in comparison with those in the terminal ring.[7] It therefore seemed of interest to examine the chemical and photochemical behavior of (I).

By short-period treatment with acetic anhydride containing a few drops of sulfuric acid,[9] (I) was converted to its enol acetate, 3,7-diacetoxy-5,7,9(11)-triene (IV), m.p. 139∼140°,

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[*3] Part XXVI. S. Akagi : This Bulletin (1961), in press.

[*4] Recently Barton and his collaborators synthesized (I) directly from 3β-acetoxylanost-8-en-7-one by an ingenious method. Cf. ref. (4).

1) E. Ohki : This Bulletin, 8, 47 (1960).
2) *Idem* : *Ibid.*, 8, 229 (1960).
3) D. H. R. Barton, B. R. Thomas : J. Chem. Soc., **1953**, 1842.
4) D. H. R. Barton, J. F. McGhie, M. Rosenberger : *Ibid.*, **1960**, in press. (I) was obtained in a small amount as a by-product in oxidation of γ-lanosteryl acetate with perbenzoic acid.
5) M. J. Birchenough, J. F. McGhie : *Ibid.*, **1950**, 1249; J. F. Cavalla, J. F. McGhie : *Ibid.*, **1951**, 744.
6) J. F. McGhie, M. K. Pradhan, J. F. Cavalla : *Ibid.*, **1952**, 3176.
7) L. F. Fieser, M. Fieser : "Steroids," 327 (1959). Reinhold Publishing Corp., New York.
8) D. H. R. Barton : Helv. Chim. Acta, **42**, 2604 (1959).
9) K. Tsuda, K. Arima, R. Hayatsu : J. Am. Chem. Soc., **76**, 2933 (1959).
10) P. Bladon : J. Chem. Soc., **1955**, 2176.

$[\alpha]_D$ −44°, λ_{max} 316 mμ, from which (III) was regenerated by saponification with alkali. Treatment of (I) with sulfuric acid–acetic anhydride (1:9) afforded an oily mixture of phenolic diacetates, from which a crystalline diacetate (V), $C_{34}H_{52}O_4$, m.p. 141∼142°, $[\alpha]_D$ 0°, λ_{max} 267 mμ, was obtained in a small amount by wasteful chromatographic purification. Saponification of (V) with alkali afforded a free alcohol, although it could not be entirely purified to a crystalline form. Its ultraviolet spectrum, λ_{max} 284 mμ, corresponding to the phenolic chromophore, did not shift to a longer wave-length region in an alkaline alcoholic solution. The structure of (V) could not be determined due to lack of the sample. The trienone compound (II) was inert to treatment with sulfuric acid–acetic anhyride mixture at room temperature. Moreover, (I) was not affected on allowing to stand with 50% sulfuric acid or conc. hydrochloric acid,[11] and only saponification of the acetyl group in the 3-position took place to form (III).

Barton and Thomas[3] obtained a phenolic compound of m.p. 212∼214°, $[\alpha]_D$ +51°, λ_{max} 287 mμ, by the treatment of (I) with zinc in boiling acetic acid, but its structure was not elucidated. The same phenolic compound (VI), m.p. 214∼216°, $[\alpha]_D$ +54°, λ_{max} 287 mμ, was obtained from (I) by the method of Barton and Thomas. Treatment of (VI) with acetic anhydride in pyridine afforded a diacetate (VII), m.p. 126∼128°, $[\alpha]_D$ +78°, λ_{max} 267 mμ. (VI) had been considered[10] to have a chemical structure of anthrasteroid-type compound (VIII). (VII) is not identical with (V) obtained by the conditions of the usual dienone-phenol rearrangement,[9] but the structure of (V) has not been elucidated. Ultraviolet spectrum of (VI) shows considerable change in an alkaline solution, while the free alcohol of (V) does not show much change as described above.

Saponification of (VI) with alkali gave no crystalline alcohol. Treatment of (VI) with dimethyl sulfate in boiling acetone solution afforded a methyl-ether monoacetate, m.p. 110∼112°, $[\alpha]_D$ +29.7°, λ_{max} 278∼283 mμ. It was converted to the 3-oxo-methyl ether by saponification with alkali and subsequent oxidation with chromium trioxide in pyridine. This ether was also not obtained in a crystalline form, but showed the absorption corresponding to a six-membered ketone at 1715 cm^{-1} in the infrared region and was characterized as its oxime derivative, m.p. 181∼183°, $[\alpha]_D$ +29°. From these considerations, it was found that the acetyl group in the 3-position was not affected during the reaction and only the dienone system in the B-ring underwent aromatization to the phenolic system.

Though bimolecular compounds like santonone and isosantonone have been obtained[12] by treatment of santonin with zinc, both (VI) and (VII) are monomolecular compounds from the result of molecular weight determinations. Infrared spectra of (VI) and its derivatives showed weak absorption at 865∼860 cm^{-1} corresponding to a pentasubstituted benzenoid hydrogen and the proton magnetic resonance spectrum[*5] of (VI) exhibited no signal in the region corresponding to a benzenoid methyl group, but one (0.71 p.p.m.) corresponding to aromatic hydrogen, as indicated in Fig. 1. These spectral data were quite contradictory with the anthrasteroid-type formula (VIII) suggested by Bladon[10] in 1955. Dehydrogenation of (VI) with selenium at 320∼340° for 40 hours afforded a mixture of aromatic hydrocarbons in a low yield. Spectral study of each fraction obtained by chromatographic separation of the mixture showed that the dehydrogenation product did not contain any anthracene derivative but phenanthrene and chrysene derivatives, as described in the experimental section. It was also found by gas chromatography[*6] with silica gel column that a considerable amount of methane is detected from the gas evolved by treatment of (I) with zinc in acetic acid.

[*5] Varian Model 4300 C, 56.4 Mc, NMR spectrometer was used.

[*6] C. E. C. Type 26∼201 gas chromatograph was used (column : silica gel 1.2 m., carrier gas : He 35 cc./min., temp. : 28°).

11) J. Simonsen, D. H. R. Barton : "Terpenes," Vol. **III**, 257, 263 (1952). Cambridge University Press.

12) *Idem* : *Ibid.*, Vol. **III**, 2733 (1952).

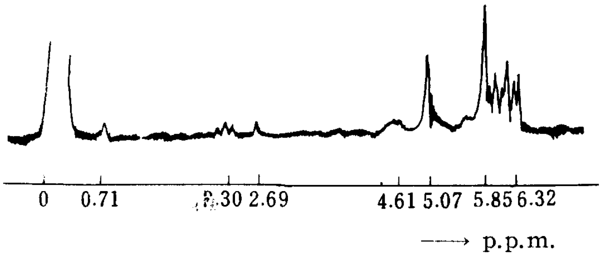


Fig. 1. Proton Magnetic Spectrum of (VI) ($CHCl_3$ as internal standard)

Consequently, it was concluded that (VI) would not have a structure of the anthrasteroid type (VIII) as suggested by Bladon,[10)] but would have one of neoergosterol type[13)] as shown in Chart 1 and methyl group in the 19-position of (I) would be eliminated in this reaction.[*7] The fission of a carbon-carbon bond easily effected under such moderate conditions is a new

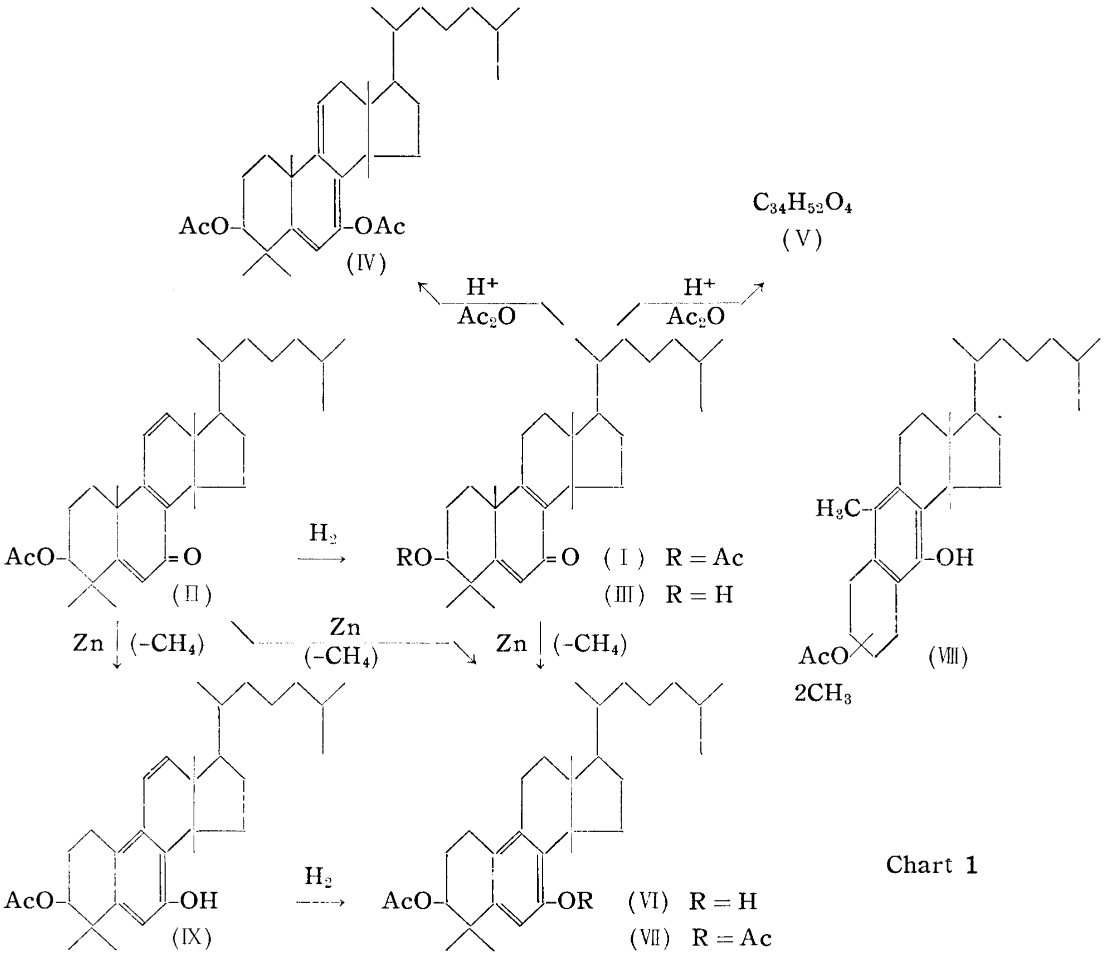
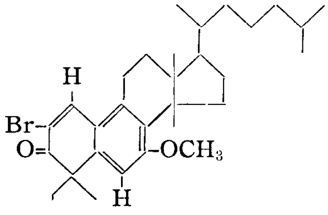


Chart 1

[*7] Proton magnetic resonance spectrum of (IX) (*v. i.*) shows the signal corresponding to vinyl proton (2.25 p.p.m.) but none in the region corresponding to the methyl group on the ethylenic linkage. Furthermore, the compound (i), derived from (VI), has a signal of vinyl proton (0.65 p.p.m.) and aromatic proton (0.57 p.p.m.) but no signal of methyl group on the ethylenic linkage. Therefore, there is no possibility that methyl group at C-10 migrated to the C-1 or C-11 position in this aromatization reaction.



(i)

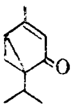
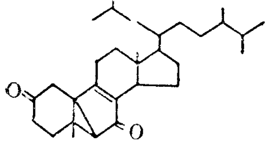
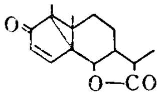
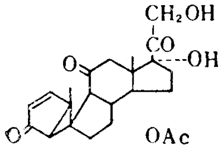
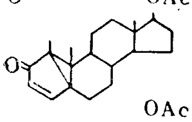
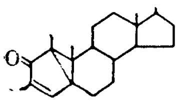
13) L. F. Fieser, M. Fieser : "Steroids," 106 (1959). Reinhold Publishing Corp., New York.

fragmentation reaction.[8] The general scope of this reaction is currently being examined in this laboratory.

Moreover, treatment of the trienone compound (II) with zinc in boiling acetic acid afforded (VI) by saturation of the double bond in the 11—12 position with hydrogen. It was also shown that, by treating with zinc in boiling ethylene glycol or amyl alcohol instead of acetic acid, (I) was converted to (VI), and (II) to an unsaturated phenolic compound (IX), m.p. 186~188°, $[\alpha]_D$ +99.8°, λ_{max} 280, 315 mμ, without the double bond in the 11—12 position being affected. (IX) was hydrogenated quantitatively into (VI) over 10% palladized charcoal.

Based on the many published reports8) that the homoannular dienone system is generally

Table I.

Umbellulone	UV mμ (ε)	IR (cm^{-1})	Ref.
	220 (5,900), 265 (3,290)	1701, 1616 (film) 1695, 1616 ($CHCl_3$)	a
	225 (5,200), 283 (3,100)	1673, 1617 (Nujol)	b
	239 (5,800)	1703, 1663 (Nujol) 1703, 1670 (CCl_4)	c
	218 (5,900), 265 (2,300)	1690, 1575 (Nujol)	d
	244 (4,200)	1692, 1577 ($CHCl_3$)	e
	244 (4,300)	1695, 1635 ($CHCl_3$)	e
Compound (X)	231 (5,800), 279 (3,200)	1685, 1610 (Nujol) 1660, 1606 ($CHCl_3$)	

a) R. H. Eastman: J. Am. Chem. Soc., **76**, 4115 (1954).
b) D. H. R. Barton, A. S. Kende: J. Chem. Soc., **1958**, 688.
c) D. H. R. Barton, P. de Mayo, M. Shafiq: *Ibid.*, **1958**, 140.
d) D. H. R. Barton, W. C. Taylor: *Ibid.*, **1958**, 2500.
e) K. Weinberg, E. C. Utzinger, D. Arigoni, O. Jeger: Helv. Chim. Acta, **43**, 236 (1960).

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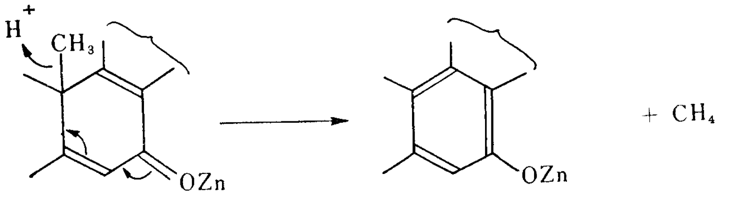
[8] It would be difficult to assume the mechanism of this reaction from these data, but reductive elimination of 19-methyl group by zinc would be possible if zinc and proton are placed in conjugation with an unsaturated ketonic group in accordance with the following mechanism:



According to subsequent investigations, this reaction is considered to suffer the effect of stereochemical environments of the dienone system. This point will be treated in the next paper of this series in the near future.

sensitive to light, photolysis of (I) was examined. By ultraviolet irradiation in boiling ethanol (I) easily underwent isomerisation about four times faster than santonin did in the same conditions. In the reaction process, infrared spectra of the reaction products showed that the absorption band of the cross-conjugated dienone system diminished rapidly and a new absorption band corresponding to an unsaturated ketonic group appeared at 1663 cm^{-1}, which also diminished after a long-period irradiation. When the new band became most strong, irradiation was stopped and the reaction product was treated. The amorphous solid residue so obtained was fractionally recrystallized to give a photochemical transformation product (X), $C_{32}H_{50}O_3$, m.p. 144.5~145°, $[\alpha]_D$ +189°. Spectral studies of (X) and its derivatives showed, as given in Table I, that they would have an umbellulone-type group in their molecule. The proton magnetic resonance spectrum*5 of (X) showed no signal in the region corresponding to a vinylic proton.14) Therefore, it was considered that there is no hydrogen atom on the carbon of the double bond of the umbellulone system. The double bond of (X) was inert to catalytic hydrogenation over either palladized charcoal or platinum, and was not oxidized with osmium tetroxide. Treatment of (X) with lithium in liquid ammonia gave no simple crystalline compound. Saponification of (X) with alkali under moderate conditions gave the free alcohol (XI), m.p. 162°, $[\alpha]_D$ +193°. Oxidation of (XI) with chromium trioxide in pyridine afforded 3-oxo compound (XII), m.p. 201~203°, $[\alpha]$ +162°, whose infrared spectrum exhibited an absorption at 1703 cm^{-1} corresponding to a six- or higher-membered ketone group. From these considerations, it is suggested that this photochemical transformation product (X) has an umbellulone-type structure in the B-ring such as shown in Chart 2.

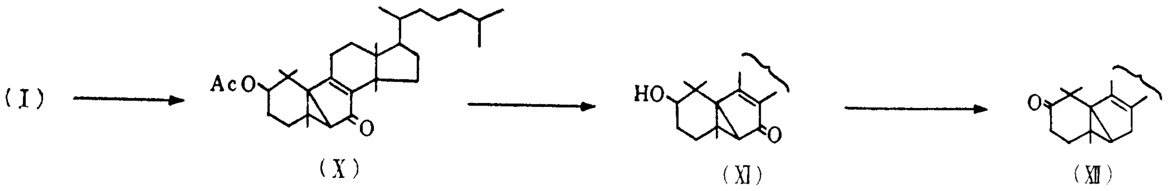


Chart 2.

While this photochemical study was in progress, Barton and his group presented a paper15) on the structure of the same compound (X) and their structure is in agreement with the structure suggested above. According to private communication from him and his manuscript,4) which was sent to one of the authors (K. T.) before publication, the structure of (X) was completely elucidated, structurally and configurationally, by two degradation processes.

It was found that the trienone compound (II) was changed very slowly by irradiation of ultraviolet rays and yielded a reaction product whose infrared spectrum showed a new band at 1673 cm^{-1} (Nujol), but crystalline compound could not be separated from it. Ultraviolet irradiation of the enol-acetate (IV) gave a resinous product which showed new characteristic absorption at 264 mμ in the ultraviolet region, but from which no crystalline compound was obtained.

Experimental

All m.p.s are uncorrected. Rotations were determined in $CHCl_3$ and ultraviolet spectra in MeOH. Analytical samples were dried for 15 hr. at room temperature in high vacuum.

3β-Acetoxylanosta-5,8-dien-7-one and Its Derivatives—A solution of 0.42 g. of 3β-acetoxylanosta-5,8,11-trien-7-one (II), m.p. 195~196°, $[\alpha]_D^{15}$ +68° (c=1.1), dissolved in 40 cc. of dioxane was shaken with 0.2 g. of 1% Pd-C at room temperature. After absorption of about 20 cc. of H_2, the hydrogenation was stopped. After removal of the catalyst and evaporation of the solvent, the solid residue

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14) K. Weinberg, E. C. Utzinger, D. Arigoni, O. Jeger : Helv. Chim. Acta, **43**, 236 (1960).
15) D. H. R. Barton : Abstr. of Papers, A. C. S. Meeting, Cleveland, U. S. A., April 5~14, 1960. 550.

which showed no trienone absorption in the ultraviolet region, was recrystallized from MeOH to afford 3β-acetoxylanosta-5,8-dien-7-one (I) as plates, m.p. 184∼186°, $[\alpha]_D^{12}$ $-12°$ (c=0.8). Yield, 0.36 g. UV : λ_{max} 248 mμ (log ε 4.0). IR ν_{max}^{Nujol} cm^{-1} : 1740, 1245 (AcO), 1644, 1616, 1590 (dienone). *Anal.* Calcd. for $C_{32}H_{50}O_3$: C, 79.62; H, 10.44. Found : C, 79.63; H, 10.44.

Oxidation of (I) with SeO_2 in AcOH, as in the previous work,[3] resulted in recovery of the starting material (II) and oxidation of (I) with CrO_3 in AcOH in the usual manner gave a crystalline mass, which was recrystallized from MeOH to 3β-acetoxylanosta-5,8-diene-7,11-dione, m.p. 120∼123°. UV : λ_{max} 268 mμ (log ε 4.07). The m.p. and infrared spectrum of the product were identical with those of an authentic sample.[6]

The free alcohol of (I), 3β-hydroxylanosta-5,8-dien-7-one (III), was obtained by saponification of (I) with 2% KOH-MeOH and recrystallization from hydr. MeOH to needles, m.p. 174∼175°, $[\alpha]_D^{28}$ $+23°$ (c=0.6). IR ν_{max}^{Nujol} cm^{-1} : 3410, 3210∼3160 (OH), 1645, 1620, 1600 (dienone). *Anal.* Calcd. for $C_{30}H_{48}O_2 \cdot \frac{1}{4}H_2O$: C, 80.98; H, 10.91. Found : C, 80.69; H, 10.84.

To a stirred solution of 30 cc. of pyridine containing 0.3 g. of CrO_3, 0.2 g. of (III) dissolved in 20 cc. of pyridine was added at 0° and the mixture was allowed to stand at room temperature for 2 days. After dilution with Et_2O and filtration of the precipitate, the filtrate was diluted with H_2O and extracted with Et_2O. The extract was washed with dil. HCl, dil. $NaHCO_3$, and, H_2O, dried over anhyd. Na_2SO_4, and evaporated *in vacuo* to leave a residue which crystallized from MeOH to prisms, m.p. 114∼116°, $[\alpha]_D^{30}$ $+143°$ (c=3.6). Yield, 0.1 g. IR ν_{max}^{Nujol} cm^{-1} : 1715 (CO), 1669, 1639, 1616 (dienone). *Anal.* Calcd. for $C_{30}H_{46}O_2$: C, 82.13; H, 10.57. Found : C, 81.75; H, 10.13.

3β,7-Diacetoxylanosta-5,7,9(11)-triene (IV)—One drop of conc. H_2SO_4 was added to a stirred suspension of 1 g. of (I) in 30 cc. of Ac_2O at room temperature. After the suspended crystals dissolved, the mixture was allowed to stand for 5 min. The solution was poured in cold H_2O and the crystalline precipitate, obtained after Ac_2O solution was decomposed completely, was collected and recrystallized from MeOH to plates (IV), m.p. 139∼140°, $[\alpha]_D^{20}$ $-44°$ (c=0.7). Yield, 0.4 g. UV : λ_{max} 316 mμ (log ε 3.9). IR ν_{max}^{Nujol} cm^{-1} : 1752, 1740, 1241, 1208 (AcO). *Anal.* Calcd. for $C_{34}H_{52}O_4$: C, 77.82; H, 9.99. Found: C, 77.67; H, 10.06.

Saponification of (IV) with 2% KOH-MeOH in the usual manner afforded 3β-hydroxylanosta-5,8-dien-7-one (III), m.p. 170∼172°. The mother liquor of recrystallization of (IV) showed ultraviolet absorption corresponding to that of the mixture of phenolic acetates (V) which will be described below.

Acid-catalysed Rearrangement of (I)—To a stirred suspension of 1 g. of (I) in 30 cc. of Ac_2O, 0.2 cc. of conc. H_2SO_4 was dropped gradually at 0°. After the suspended crystals dissolved, the mixture was allowed to stand for 2 hr. The reaction mixture was poured in cold H_2O. and after the Ac_2O solution was decomposed, extracted with Et_2O. The extract was washed with H_2O, dil. $NaHCO_3$, and H_2O, dried over anhyd. Na_2SO_4, and evaporated to leave an amorphous residue. The residue was purified through column chromatography over 20 g. of silica gel and a crystalline residue obtained by elution with petr. ether-benzene (1:2) was recrystallized from MeOH to needles, m.p. 141∼142°, $[\alpha]_D^{26}$ $\pm 0°$ (c=1.0). Yield, 35 mg. UV : λ_{max} 267 mμ (log ε 3.0). IR ν_{max}^{Nujol} cm^{-1} : 1740, 1240, 1210 (acetate). *Anal.* Calcd. for $C_{34}H_{52}O_4$: C, 77.82; H, 9.90. Found : C, 77.52; H, 10.10.

3β-Acetoxy-19-norlanosta-5,7,9-trien-7-ol (VI) and Its Derivatives—i) A solution of 0.5 g. of (I) dissolved in 100 cc. of AcOH, containing 10 g. of Zn, was boiled for 2 hr. After cool Zn was filtered off and washed with Et_2O. The filtrate was diluted with H_2O and extracted with Et_2O. The extract was washed with H_2O, dil. $NaHCO_3$, and H_2O, dried over anhyd. Na_2SO_4, and evaporated to leave a solid residue which was recrystallized from AcOEt or MeOH-Et_2O to needles (VI), m.p. 214∼216°, $[\alpha]_D^{20}$ $+54°$ (c=1.2). Yield, 0.39 g. UV : λ_{max} 287 mμ (log ε 3.43). IR ν_{max}^{Nujol} cm^{-1} : 3430 (OH), 1700, 1270 (AcO), 1630, 1589 (arom.), 865 (aromatic C-H). *Anal.* Calcd. for $C_{31}H_{48}O_3$: C, 79.43; H, 10.32; mol. wt., 482. Found : C, 79.62; H, 10.44; mol. wt., 426.

Acetylation of (VI) with Ac_2O-pyridine in the usual manner afforded a diacetate (VII), which was recrystallized to needles, m.p. 126∼128°, $[\alpha]_D^{20}$ $+78°$ (c=0.6). UV : λ_{max} 267 mμ (log ε 2.7). IR ν_{max}^{Nujol} cm^{-1} : 1765, 1745, 1246, 1205 (AcO), 1604, 1585 (arom.), 860 (aromatic C-H). *Anal.* Calcd. for $C_{33}H_{50}O_4$: C, 77.60; H, 9.98; mol. wt., 510. Found : C, 77.82; H, 9.99; mol. wt., 463.

A stirred solution of 0.35 g. of (VI) in 70 cc. of dehyd. Me_2CO, containing 5 g. of K_2CO_3 and 5 cc. of Me_2SO_4 was boiled for 16 hr. After cool, the reaction mixture was diluted with cold H_2O, neutrallized with dil. $NaHCO_3$, and extracted with Et_2O. The extract was washed with H_2O and dried over anhyd. Na_2SO_4. After removal of the solvent, the solid residue was recrystallized from Et_2O-MeOH to afford 3β-acetoxy-7-methoxy-19-norlanosta-5,7,9-triene as prisms, m.p. 110∼112°, $[\alpha]_D^{20}$ $+29.7°$ (c=4.3). UV : λ_{max} 278∼283 mμ (log ε 3.55). IR ν_{max}^{Nujol} cm^{-1} : 1728, 1240 (AcO), 1588, 1562 (arom.), 850 (aromatic C-H). *Anal.* Calcd. for $C_{32}H_{50}O_3$: C, 79.62; H, 10.44. Found : C, 79.91; H, 10.40.

Saponification of 32 g. of the methyl ether-acetate, described above, with 2% KOH-MeOH in the usual manner afforded an amorphous hydroxy-methyl ether. It was dissolved in 5 cc. of pyridine and added to a solution of 4 g. of CrO_3 in 15 cc. of pyridine at 0° and the reaction mixture was allowed to stand for 2 days. After dilution with Et_2O and filtration of the precipitate, the filtrate was diluted with H_2O and extracted with Et_2O. The extract was washed with dil. HCl, dil. $NaHCO_3$, and H_2O, dried over anhyd. Na_2SO_4, and evaporated *in vacuo* to leave an amorphous residue which was purified through chromatography over 15 g. of alumina.

An amorphous residue (0.18 g.) obtained by elution with petr. ether-benzene (9:1) exhibited the absorption at 1712 cm^{-1} in the infrared region and was converted in the usual manner with $NH_2OH \cdot HCl$-AcONa in EtOH to an oxime, which was recrystallized from MeOH to prisms, m.p. 181~183°, $[\alpha]^{30}_{D}$ +29.4° (c=0.6). UV : λ_{max} 277~284 mμ (log ε 3.5). *Anal.* Calcd. for $C_{30}H_{47}O_2N$: C, 79.42; H, 10.44; N, 3.09. Found : C, 79.13; H, 10.30; N, 3.27.

ii) Treatment of 0.52 g. of (II) with Zn in AcOH in the manner described above afforded 0.28 g. of (VI).

iii) A stirred solution of 0.53 g. of (I) in 70 cc. of ethylene glycol, containing 12 g. of Zn, was boiled for 3 hr. After cooling and filtration of Zn, the filtrate was diluted with H_2O and extracted with Et_2O. The extract was washed with dil. HCl and H_2O, and dried over anhyd. Na_2SO_4. The solvent was evaporated and the solid residue was recrystallized from Et_2O-MeOH to 0.22 g. of (VI).

Dehydrogenation of (VI) with Selenium—A mixture of 3.6 g. of (VI) and 6 g. of Se metal was placed in a tube replaced with N_2 atmosphere, with a capillary terminal. The tube was heated at 320~340° for 40 hr. in N_2 atmosphere. After cool, the reaction mixture was powdered and extracted with benzene. The extract was washed with dil. $NaHCO_3$ and H_2O, and dried over anhyd. Na_2SO_4, and evaporated to leave an oily residue (210 mg.) which was purified through chromatography over 6 g. of alumina.

Fract. No.	Solvent (30 cc.)	Eluate (mg.)
1	petr. ether	104
2	〃	23
3	〃	8
4	〃	3
5	〃	7
6	〃	2
7	petr. ether-benzene (20:1)	2
8	〃	5
9	〃	6
10	〃	3
11	benzene	10

Spectral studies of each fraction in the ultraviolet region showed that the dehydrogenation product did not contain any anthracene derivative. No. 2 fraction could not be purified to a simple crystalline compound or a crystalline trinitrobenzene derivative, though its ultraviolet spectrum exhibited the phenanthrene-type absorption. The crystalline residue eluted from fraction Nos. 4 to 6 was recrystallized twice from EtOH to prisms, m.p. 190~205° (5 mg.), which could not be purified further due to lack of the sample. *Anal.* Found : C, 92.11; H, 7.43; mol. wt. 294. Its ultraviolet spectrum exhibited the absorption corresponding to a chrysene homolog as shown in Fig. 2. It was also similar to one that Ruzicka and his group[16] had obtained by dehydrogenation of lanosterol with Se.

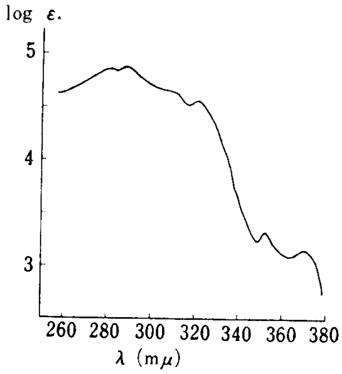

Fig. 2. Ultraviolet Absorption Spectrum of Dehydrogenation Product (in MeOH)

3β-Acetoxy-19-norlanosta-5,7,9-trien-7-ol (IX) and Its Acetate—Treatment of 0.52 g. of (II) with Zn in ethylene glycol in the manner described above provided a crystalline mass which was recrystallized from MeOH-Et_2O to (IX) as prisms, m.p. 186~188°, $[\alpha]^{22}_{D}$ +99.8° (c=0.8). *Anal.* Calcd. for

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16) L. Ruzicka, Ed. Rey, A.C. Muhr : Helv. Chim. Acta, **32**, 472 (1944).

$C_{31}H_{46}O_3$: C, 79.78; H, 9.94. Found : C, 79.46; H, 9.96. UV λ_{max} mμ (log ε) : 218 (4.4), 280 (3.9), 315 (3.4). IR ν_{max}^{Nujol} cm^{-1} : 3430 (OH), 1700, 1270 (AcO), 1615, 1579 (arom.).

A solution of 0.1 g. of (IX) dissolved in 30 cc. of EtOH was catalytically reduced over 10% Pd-C. After removal of the catalyst, the solvent was diluted with H_2O and the solid residue obtained was recrystallized from MeOH to 86 mg. of (VI). Acetylation of (IX) with Ac_2O in pyridine afforded a diacetate of (IX) which was recrystallized from MeOH to needles, m.p. 96~97°, $[\alpha]_D^{22}$ +52° (c=0.6). UV λ_{max} mμ (log ε) : 224 (4.42), 278 (4.0). *Anal.* Calcd. for $C_{33}H_{48}O_4$: C, 77.91; H, 9.51. Found : C, 78.03; H, 9.38.

Photolysis of (I)—A solution of 8.2 g. of (I) dissolved in 820 cc. of EtOH was irradiated for 4 hr. with a Hg lamp in N_2 atomosphere. The solution was concentrated to 1/10 the original volume and allowed to stand to regenerate 20% of (I) which was filtered off. The filtrate was evaporated to leave a solid residue which was fractionally recrystallized from EtOH to umbellulone 3-acetate (X) as plates, m.p. 144.5~145°, $[\alpha]_D^{18}$ +189° (c=0.8). Yield, 1.48 g. (18%). UV λ_{max} mμ (ε) : 231 (5,800), 279 (3,200). IR ν_{max}^{Nujol} cm^{-1} : 1743, 1250 (AcO), 1684, 1614 (umbellulone). *Anal.* Calcd. for $C_{32}H_{50}O_3$: C, 79.62; H, 10.44. Found : C, 79.71; H, 10.41.

To a solution of 200 mg. of (X) dissolved in 20 cc. of MeOH, 10 cc. of 10% K_2CO_3 solution was added and the mixture was boiled for 1 hr. After cooling and dilution with H_2O, the crystalline mass so obtained was recrystallized from hydr. MeOH to afford the free alcohol (XI) of (X) as needles, m.p. 162°, $[\alpha]_D^{30}$ +193° (c=1.0). UV λ_{max} mμ (ε) : 234 (5,400), 279 (3,000). IR ν_{max}^{Nujol} cm^{-1} : 3480 (OH), 1656, 1608 (umbellulone). *Anal.* Calcd. for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98. Found : C, 81.72; H, 10.92. Acetylation of (XI) with Ac_2O in pyridine in the usual manner provided (X).

To a stirred solution of 125 mg. of CrO_3 in 6 cc. of pyridine, 125 mg. of (XI) dissolved in 2 cc. of pyridine was added at 0° and the mixture was allowed to stand at room temperature for 36 hr. After dilution with Et_2O and filtration of the precipitate, the filtrate was diluted with H_2O and extracted with Et_2O. The extract was washed with dil. HCl, dil. $NaHCO_3$, and H_2O, dried over anhyd. Na_2SO_4, and evaporated *in vacuo* to leave a crystalline mass which was recrystallized from MeOH to the 3-oxo derivative (XII) as needles, m.p. 201~203°, $[\alpha]_D^{30}$ +163° (c=0.8). Yield, 120 mg. UV λ_{max} mμ (ε) : 223 (6,400), 277 (3,100). IR ν_{max}^{Nujol} cm^{-1} : 1703 (CO), 1678, 1619 (umbellulone). *Anal.* Calcd. for $C_{30}H_{46}O_2$: C, 82.13; H, 10.57. Found : C, 81.90; H, 10.55.

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Summary

It was observed that the methyl group in the 19-position of 3β-acetoxylanosta-5,8-dien-7-one (I) would be easily eliminated as methane and the B-ring was aromatized by treatment with zinc. The other chemical and photochemical behaviors of (I) were examined.

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