Moreover, by substracting the ORD curve of Ⅵ from that of Ⅲ, the contribution of the two carbonyl groups at C-11 and C-15 were eliminated and the resultant curve showed a positive Cotton effect whose amplitude (a=ca. +92) was comparable to that of 14β,17β-acetyl. On the contrary, the substraction of the ORD curve of Ⅷ from that of Ⅳ gave a negative Cotton effect whose sign and amplitude (a=ca. −74) were characteristic for a 14β,17α-acetyl in steroids.

The position of a hydroxyl group in the D ring of γ-digiprogenin acetate was presumed to be C-17 from the fact that it did not undergo acetylation in the previous paper,[1] and this position was supported by the datum of NMR and resistibility of this acetate to the oxidation with chromium trioxide in the later studies.

Since the epimerization of 17-hydroxypregnan-20-one at the C-17 position have never been reported in the literature, the further detailed examination on the mechanism for the epimerization is now in progress.

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Received May 25, 1964

[Chem. Pharm. Bull. 12 (8) 981 ~ 984]

UDC 547.918 : 582.938

On the Structure of Tomentogenin

The isolation of sarcostin and tomentogenin from the stem of *Marsdenia tomentosa* Decne. (Asclepiadaceae) has been reported previously[1] and a tentative structure was proposed.[2]

In this communication, experiments leading to the structural determination of tomentogenin (I) and the correlation of utendin*1 are described. In the previous paper,[1] the molecular formula of "tomentogenin" was given as $C_{21}H_{34}O_5$, but careful examination by paper chromatography (formamide-$CHCl_3$)[3] showed very close two spots, in about 3:1 intensity ratio, which were hardly separable. Crude tomentogenin absorbed about 1/3 mole of hydrogen by catalytic hydrogenation to give a compound which showed a single spot on the paper chromatogram, as the spot was identical with the major spot of crude tomentogenin, it seems probable that the crude tomentogenin is a mixture of tomentogenin (I) and dehydrotomentogenin (I′).

Tomentogenin (I), m.p. 265~268°, $C_{21}H_{36}O_5$ (*Anal.* Calcd.: C, 68.44; H. 9.85. Found: C, 68.15; H, 9.99); IR ν_{max}^{Nujol} cm^{-1}: 3400, 3150, $[\alpha]_D^{16}$ +36° (c=0.95, MeOH) seems to have

*1 Professor T. Reichstein suggested the possible identity of tomentogenin with utendin (Helv. Chim. Acta, **42**, 1014, 1959, IUPAC Symposium, 1964, Kyoto) and sent a sample (march 9, 1964). The two compounds were compared by thin-layer chromatography and paper chromatography. Utendin and dehydrotomentogenin are very similar. $[\alpha]_D$ of these compounds in MeOH are; utendin +9.6°, tomentogenin dehydrotomentogenin mixture (about 3:1) +23°, and tomentogenin +36°. Professor Reichstein sent us again tri-O-acetyl-5α-dihydroutendin (may 19, 1964), the identity of this compound and tomentogenin triacetate (Ⅱ) was established by mixed melting point and paper chromatography.

1) H. Mitsuhashi, I. Takemori, Y.Shimizu, T. Nomura, E. Yamada: This Bulletin, **10**, 804 (1962).
2) A part of this work was reported at the 83rd Annual Meeting of the Pharmaceutcal Society of Japan, Nov. 2, 1963, Tokyo.
3) H. Mitsuhashi, Y. Shimizu, E. Yamada, I. Takemori, T. Nomura: This Bulletin, **10**, 808 (1962).

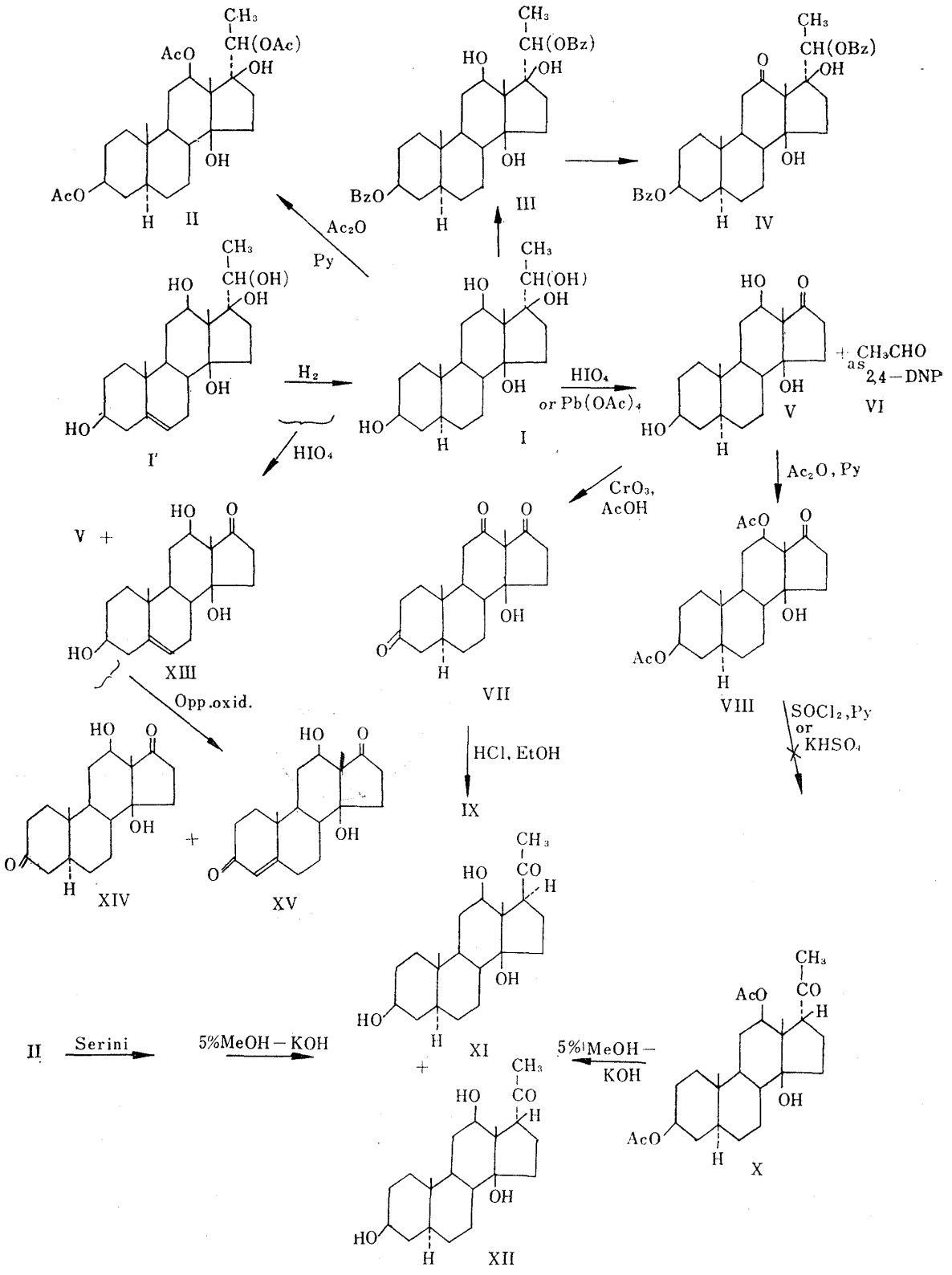

Chart 1.

no carbonyl group. Acetylation of I afforded a triacetate (II), m.p. 293°, and I formed a dibenzoate (III), m.p. 247~253°. By consuming one mole of lead tetraacetate or periodic acid, I afforded acetaldehyde (VI) and a compound (V) of m.p. 242~245°, $C_{19}H_{30}O_4$ (*Anal.* Calcd.: C, 70.77; H, 9.38. Found: C, 70.76; H, 8.97). IR ν_{max}^{Nujol} cm^{-1}: 3500, 1736 (5-

membered ring ketone), which does not reduce Tollen's reagent or tetrazolium chloride. The triacetate (II) does not react with lead tetraacetate. The optical rotatory dispersion of V showed a positive Cotton effect, a=4250° in dioxane. This result indicated that V is C/D *cis* 17-one steroid, by comparison of C/D *trans* steroid.[4,5]

TABLE I. Rotatory Dispersion

Compound	$a \times 10^{-2}$
Androstan-17-one	+148°
3β,14β-Dihydroxyandrostan-17-one-3-acetate	+ 45.6°
V	+ 42.5°
17 (20)-Secosarcostin (17-one)	+ 46.0°

The chromic acid oxidation of the dibenzoate (III) afforded a compound (IV), m.p. 219~223°, $C_{35}H_{42}O_7$ (*Anal.* Calcd. : C, 73.15; H, 7.37. Found : C, 73.15; H, 7.27). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1716 (6-membered ring ketone) which does not form an oxime.[6,7] This observation and the results of acylation on I suggest the presence of 11α-OH or 12β-OH and 14β-OH.[8]

Oxidation of V with chromic acid yielded a compound (VII), m. p. 227~232°, $C_{19}H_{26}O_4$ (*Anal.* Calcd. : C, 71.67; H, 8.23. Found: C, 72.02; H, 8.18. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 3500, 1756, 1715). The infrared absorption at 1756 cm^{-1} is assigned to a 5-membered ring ketone by comparison with 3α-hydroxyandrostane-11, 17-dione (1751, 1713 cm^{-1}), 3α-hydroxyethiocholane-11, 17-dione (1754, 1716 cm^{-1}), and androst-4-ene-3,11,17-trione (1751, 1719, 1674 cm^{-1}).[9] Acetylation of V afforded a diacetate (VIII), m.p. 197~200°, IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 3600.

To determine the location of the tertiary hydroxyl group, VIII was treated by the dehydration reaction applied for 14β-OH steroids, ($SOCl_2$-pyridine or $KHSO_4$), but did not show any good result.

Dehydration of VII with 15% hydrochloric acid-ethanol was attempted. After 92 hours, the reaction mixture showed ultraviolet maximum at 246 mμ. This compound (IX) could not be purified further but this absorption requires the presence of α,β-unsaturated ketone.*2 Combination of these results lead to the possible partial structure of I as 8β,11α-di-OH or 12β,14β-di-OH.

Tomentogenin triacetate (II) was submitted to the Serini reaction by refluxing in xylene with active zinc. This reaction product was compared with dihydrodiacetylramanone (X)[10] by thin-layer chromatography, but both compounds showed different spots. The reaction mixture was hydrolyzed by refluxing in 5% methanolic potassium hydroxide for 5 hr. Dihydrodiacetylramanone (X) was treated in the same manner. Both reaction mixtures were examined using paper chromatography. The chromatogram developed by chloroform-formamide system showed exactly the same spots. (XI and XII).[3,10]

This result evidently shows hydroxyl groups of I and dihydroramanone take the same position and the configuration of the side chain of I is established as C-17-α-methylcarbinol.

The nature of the double bond in dehydrotomentogenin (I′) was characterized as follows: A mixture of I and I′ (about 3:1) was oxidized with periodic acid to afford V and XIII and this mixture was subjected to Oppenauer oxidation to give XIV and XV,

*2 Calcd. for $\Delta^{8(9)}$-11-one : 249 mμ.

4) K.A. Jaeggi, E.K. Weiss, T. Reichstein : Helv. Chim. Acta, **46**, 694 (1963).
5) F. Sondheimer, S. Bummer, R. Mechoulam : J. Am. Chem. Soc., **82**, 3209 (1960).
6) E.P. Oliveto, *et al.* : *Ibid.*, **78**, 1736 (1956).
7) P. Bladon, *et al.* : J. Chem. Soc., **1953**, 2921.
8) A. Katz,T Reichstein : Pharm. Acta Helv., **19**, 231 (1944).
9) R. Jones, P. Humphries, K. Dobriner : J. Am. Chem. Soc., **71**, 241 (1949).
10) H.Mitsuhashi, T. Nomura : Steroids, **3**, 271 (1964).

and XV seems to be 4-en-3-one compound from its ultraviolet spectrum. The nuclear magnetic resonance spectra were also measured and given in Table II.

TABLE II.

Compound	Solvent	Signal (τ)			
		18-CH_3	19-CH_3	21-CH_3	
I	pyridine	9.25	8.45	8.57	
I+I′	〃	9.20	8.34	8.48	5.60 (d, C-6 H) 4.25 (s, broad)
V+XIII	〃	9.15	8.40		5.97 (q, C-6 H) 4.25 (s)

These data also support the presence of Δ^5 in I′. Since sarcostin has been isolated from the same plant, biogenetic analogy would favor Δ^5-structure. Above evidences suggest the probable structure of I for tomentogenin (5α-dihydroutendin) and I′ for dehydrotomentogenin (utendin). Prof. Reichstein established the structure of utendin mainly on the basis of structural relation to digoxigenin.*1

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Received June 3, 1964

[Chem. Pharm. Bull. 12 (8) 984 ~ 987]

UDC 547.914.2.07 : 542.943

Selective Oxidation of the C_1- or C_{12}-Methyl Group in Antipodal Deoxypodocarpic Acid Type Compounds*1~*3

Selective oxidation of the C_1- or C_{12}-methyl group of the antipodal deoxypodocarpic acid type compounds, which was derived from abietic acid (I), would be a stimulating problem, for these oxidized compounds could be regarded as potential intermediates for syntheses of many kinds of natural diterpenoids. Now we like to report the syntheses of these oxidized compounds shown as XIX and XX.

The ester (III)[1], derived from abietic acid (I), was readily hydrogenated including hydrogenolysis (Pd-C, EtOAc, H_2SO_4) to 10β-acetoxy ester (V), NMR (τ)*4 : 8.73 (C_1-CH_3),

*1 This communication will be published in detail as Diterpenoids V. Part IV : Sci. Papers Inst. Phys. Chem. Res., 58, 15 (1964).

*2 This work was presented at the International Symposium on the Chemistry of Natural Products held at Kyoto, Japan, on April 16, 1964. (Symposium Abstracts, p. 41-2)

*3 All analytical values were in good agreement with the molecular formula shown. All melting points (except m. m. p.) were measured on the Kofler block and were uncorrected. All NMR spectra were measured at 60 Mc. (Varian Model A-60) in $CDCl_3$ *vs.* Me_4Si as internal reference. (Authors thank to Dr. K. Takeda and Dr. K. Tori, Shionogi & Co., Ltd., Osaka, for the NMR measurements and also to Dr. Y. Kawazoe, National Cancer Center, Tokyo, for his discussion on them.

*4 All assignments of the chemical shifts for methyl group of these compounds in this communication will be discussed in detail in our future report.

1) A. Tahara, O. Hoshino, Y. Hamazaki : This Bulletin, **11**, 1328 (1963).