total sugar, 64% (calcd. for gitonin trihydrate: aglycone, 39.2%; total sugar, 62.6%). Molar ratio of glucose, galactose and xylose: 1.3:2.1:1.0. The aglycone was recrystallized from MeOH to give needles, m.p. 274~276°. Mixed melting point with gitogenin (m.p. 274~278°)[*8] showed no depression.

**Saponin (I-3)**——Fr. 81~104 was recrystallized from BuOH saturated with $H_2O$ to provide fine needles, m.p. 243~245° (decomp.), $[\alpha]_D^{20}$ $-71.4°$ (c=0.28, pyridine). *Anal.* Calcd. for $C_{50}H_{82}O_{24}\cdot 2H_2O$ (desglucodigitonin dihydrate): C, 54.4; H, 7.9. Found: C, 54.7; H, 8.1. Examination of the hydrolyzate by P.C.: aglycone, Rf 0.27; sugar, Rg 0.85, 1.00, 1.23. Yields of the hydrolysis products: aglycone, 40%; total sugar, 65% (calcd. for desglucodigitonin dihydrate: aglycone, 40.6%; total sugar, 62.6%). Molar ratio of glucose, galactose and xylose: 1.3:2.1:1.0. The aglycone was recrystallized from MeOH to give needles, m.p. 288~290° (digitogenin,[3a)] m.p. 288~291°).

**Saponin (II)**——Hydrolyzed and the aglycone was examined by thin-layer chromatography on silica gel G using AcOEt-hexane (2:1) as solvent: Rf 0.31 ++, 0.38 ±, 0.63 ± (Rf of reference compound: digitogenin, 0.31; gitogenin, 0.38; tigogenin, 0.78). The sapogenin of Rf 0.63 was regarded as digalogenin.[4a)] That of Rf 0.38 was detected only in trace but the presence of gitogenin pentaglycoside in saponin (II) seems to be suggested.

The authors thank Prof. T. Momose and Dr. Y. Mukai for the kind advices and helps in the micro determination of sugars, and Mr. M. Shido for elemental analysis. This work was supported in part by a Grant-in-Aid of Scientific Reserch from the Ministry of Education, to which the authors are also grateful.

## Summary

Two saponins (I) and (II) which are detected by conventional paper chromatography of the seed saponins of *Digitalis purpurea* L. (commercial "digitonin") were isolated by column chromatography on alumina and it was found that I is composed of three tetraglycosides, desglucotigonin, gitonin (m.p. 238~241° (decomp.), $[\alpha]_D^{20}$ $-60.0°$) and desglucodigitonin (m.p. 243~245° (decomp.), $[\alpha]_D^{20}$ $-71.4°$), while II is a mixture of two pentaglycosides, digalonin and digitonin.

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## **Toshio Nambara**: Chemistry of $3\beta$,12-Dihydroxy-$5\alpha$-androstan-17-ones

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In the extension of the previous works on the stereochemistry of C/D-*cis* steroids,[1~4)] the preparation of $3\beta$-hydroxy-$5\alpha$-androst-14-en-17-one possessing oxygen substituent at C-12 has become an essential prerequisite.

For this purpose the initial attempt was directed towards the Johnson's method[5)] employed for the synthesis of 14-isoestrone. The starting material, $3\beta$,$12\beta$-dihydroxy-$5\alpha$-androstan-17-one (IIa), was readily prepared by way of different route from that reported by Adams, *et al.*[6)] Conversion of $3\beta$, $12\beta$-dihydroxy-$5\alpha$-pregn-16-en-20-one 3-acetate (Ia) into its oxime (Ib), m.p. 267~270°, followed by Beckmann rearrangement

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1) T. Nambara, J. Fishman: J. Org. Chem., **26**, 4569 (1961).

2) *Idem*: *Ibid.*, **27**, 2131 (1962).

3) C. Djerassi, J. Fishman, T. Nambara: Experientia, **17**, 565 (1961).

4) T. Nambara, K. Hirai: This Bulletin, **12**, 836 (1964).

5) W.S. Johnson, W.E. Jones: J. Am. Chem. Soc., **79**, 2005 (1957).

6) W.T. Adams, D.N. Kirk, D.K. Patel, V. Petrow, I.A. Stuart-Webb: J. Chem. Soc., **1955**, 871.

and alkaline hydrolysis gave IIa in satisfactory yield. On treatment with isopropenyl acetate and catalytic amounts of sulfuric acid IIa afforded oily product, but infrared spectrum indicated that it consisted substantially of 3$\beta$,12$\beta$-dihydroxy-5$\alpha$-androstan-17-one diacetate (IIb) and transformation into enol acetate (IIIa) took place scarcely. In fact, when bromine was added to carbontetrachloride solution of the crude product until immediate decoloration was not observed any more, only small amounts of the corresponding 16$\xi$-bromo-17-ketone (IVa), m.p. 187~189°, was yielded. On the other hand, its 12-epimer, 3$\beta$,12$\alpha$-dihydroxy-5$\alpha$-androstan-17-one (Va), undergoing the same treatment as IIa, furnished 17-enol acetate (IIIb), m.p. 140~142°, almost quantitatively. It is noteworthy that the marked difference in reactivities may be due to the significant steric interaction between 12$\beta$-substituent and $\Delta^{16}$-17-acetoxy group. Upon quantitative consumption of bromine in the presence of potassium carbonate, IIIb was converted to 16$\xi$-bromo-17-ketone (IVb), but the difficulties were thereafter encountered in leading to 17-ethyleneketal derivative. Hence, the author changed the initial project and attempted to introduce a hydroxyl group directly at C-14 by chemical means.

In 1952, St. André, *et al.*[7~9] reported that chromium trioxide oxidation of dehydroisoandrosterone acetate 5,6-dibromide in acetic acid under the anhydrous conditions afforded 14$\alpha$-hydroxy derivative[*2] in 25% yield, whereas in the cases of isoandrosterone acetate and androstane-3$\beta$,17$\beta$-diol diacetate, oxidation by the same procedure provided two main products, which were identified as 5$\alpha$-hydroxy and 6-oxo derivatives. They concluded that when positions 5 and 6 of the steroid nucleus are unsubstituted, chromium trioxide first reacts with the molecule at these sites rather than position 14. Nevertheless, since only these informations were available in the literature, examination was made on the oxidation of 12$\alpha$-acetoxy derivative, in which the negative group at C-12 was expected to bring about somewhat enhanced reactivity to C-14. The starting material for this work, 3$\beta$,12$\alpha$-dihydroxy-5$\alpha$-androstan-17-one diacetate (Vc), m.p. 209~211°, was prepared from Va by heating with acetic anhydride and pyridine, while mild acetylation gave a mixture of Vc and 3$\beta$,12$\alpha$-diol 3-monoacetate (Vb), m.p. 192~193°. The monoacetate was further acetylated to give Vc, and was oxidized with Jones' reagent yielding 3$\beta$-hydroxy-5$\alpha$-androstane-12,17-dione acetate (VII). From 3$\beta$,17$\alpha$-dihydroxy-5$\alpha$-pregnane-12,20-dione 3-acetate (VI), Vb was also obtained by sodium borohydride reduction and subsequent sodium bismuthate oxidation. Following the procedure reported by St. André, *et al.* oxidation of Vc with chromium trioxide in glacial acetic acid and subsequent chromatographic separation on alumina afforded two main crystalline products. The result of elemental analysis suggested that one of these had empirical formula $C_{23}H_{34}O_6$ and therefore contained one additional oxygen atom. Infrared spectrum and chromatographic behavior of this compound were indicative of the presence of free hydroxyl group, which was resistant to usual acetylation with use of acetic anhydride and pyridine. In view of the analogous reactions mentioned above, orientation of hydroxyl group was supposed to be C-5 or C-14. This oxidation product (VIII), m.p. 213~215°, was submitted to dehydration by refluxing with fused potassium bisulfate in acetic anhydride to produce a compound (IXb), m.p. 227~228°, having a new, nonconjugated double bond. On catalytic hydrogenation of IXb over palladium-on-charcoal one mole of hydrogen was taken up and the resulting product proved to be idintical with Vc. It has been already established that Zimmermann reaction with 17-ketosteroids having 14-hydro-

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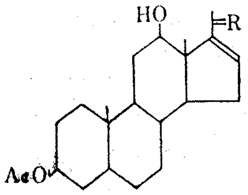
[*2] The configuration of the 14-hydroxyl group was not proved definitely by these authors, but later shown to be alpha by Eppstein, *et al.* (J. Am. Chem. Soc., **80**, 3382 (1958)).

7) A.F. St. André, H.B. MacPhillamy, J.A. Nelson, A.C. Shabica, C.R. Scholz: J. Am. Chem. Soc., **74**, 5506 (1952).

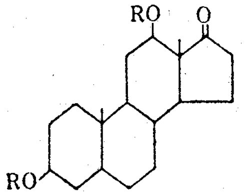
8) F. Sondheimer, S. Burstein, R. Mechoulam: *Ibid.*, **82**, 3209 (1960).

9) H.B. MacPhillamy, C.R. Scholz: *Ibid.*, **74**, 5512 (1952).

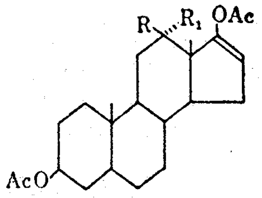
xyl group or $\Delta^{14}$-double bond resulted in no characteristic coloration.[10,11] In the present case, however, the hydroxylated compound as well as its dehydrated product showed the typical Zimmermann color according to the Callow's method.[12] Based upon these facts it seemed more likely that the position of hydroxyl group introduced would be assigned to C-5 rather than C-14. Elucidation of this point was accomplished by the following sequence. On treatment of IXb with acid or base the ultraviolet spectrum showed only end absorption and no significant change in comparison with that before addition of the isomerizing catalyst.[*3] But, the unsaturated 3,12,17-trioxo compound obtained from IXb by acid hydrolysis and subsequent chromic acid oxidation[13] had still no characteristic ultraviolet absorption, whereas upon addition of a few drops of sodium hydroxide solution, it exhibited immediately an ultraviolet absorption maximum at 240 mμ. These behaviors were indicative of isomerization of $\beta,\gamma$-unsaturated ketone to conjugated ketone



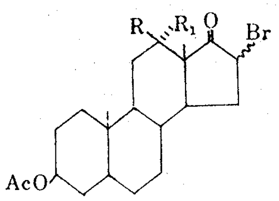
Ia : R=O
Ib : R=NOH



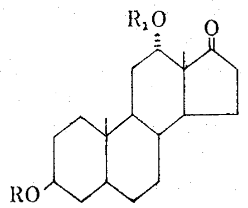
IIa : R=H
IIb : R=Ac



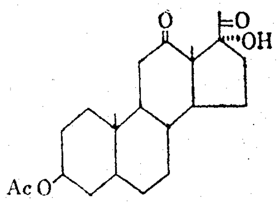
IIIa : R=AcO, R₁ =H
IIIb : R=H, R₁ =AcO



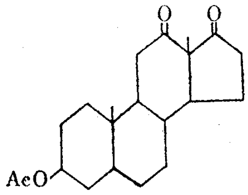
IVa : R=AcO, R₁ =H
IVb : R=H, R₁ =AcO



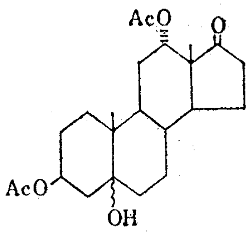
Va : R=R₁ =H
Vb : R=Ac, R₁ =H
Vc : R=R₁ =Ac



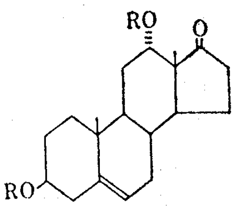
VI



VII



VIII



IXa : R=H
IXb : R=Ac

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[*3] It has already been reported by Sondheimer, *et al.*[8] that 3$\beta$-hydroxy-5$\alpha$-androst-14-en-17-one acetate could be readily isomerized to 3$\beta$-hydroxy-5$\alpha$,14$\beta$-androst-15-en-17-one ($\lambda_{max}$ 229 mμ) with boiling aqueous sulfuric acid-dioxane, or preferably with potassium hydroxide in refluxing aqueous *tert*-butanol.

10) A.B. Roy : Austral. J. exp. Biol., 40, 415 (1962).

11) T. Nambara, M. Katō : To be published.

12) N.H. Callow, R.K. Callow, C.W. Emmens : Biochem. J., 32, 1312 (1938).

13) C. Djerassi, R.R. Engel, A. Bowers : J. Org. Chem., 21, 1547 (1956).

and entirely same as those of androst-5-ene-3,17-dione.[13] Thus, it was concluded that tertiary hydroxyl group of the oxidation product (Ⅷ) should be put at C-5 and the introduced double bond of the dehydrated compound (Ⅸb) between C-5 and C-6.

The second oxidation product, m.p. 208～211°, also contained one additional oxygen atom as shown by the formula $C_{23}H_{32}O_6$, suggesting the presence of six-membered ring carbonyl comparing with the starting material. It has not been further investigated because of insufficient amounts available for elaboration. It should be noted that none of the major products were the result of oxidation at C-14.

Further studies on this problem are in progress in our laboratory.

## Experimental[*4]

**3β,12β-Dihydroxy-5α-pregn-16-en-20-one 3-Acetate Oxime (Ib)**——A solution of 3β,12β-dihydroxy-5α-pregn-16-en-20-one 3-acetate (Ia) (1.2 g.), $NH_2OH \cdot HCl$ (0.5 g.) and pyridine (2.5 ml.) in EtOH (10 ml.) was boiled under reflux for 1 hr., and cooled in refrigerator overnight. The separated crystalline product was filtered, washed with hot $H_2O$ and dried. Colorless prisms, m.p. 265～268° (decomp.). Yield, 780 mg. The analytical sample recrystallized from EtOH melted at 267～270° with decomposition. $[\alpha]_D^{26}$ +12.7°. *Anal.* Calcd. for $C_{23}H_{35}O_4N$ : C, 70.92; H, 9.06; N, 3.60. Found : C, 71.15; H, 8.90; N, 3.58.

**3β,12β-Dihydroxy-5α-androstan-17-one (IIa)**——To a solution of Ib (700 mg.) in pyridine (3 ml.) was added a solution of *p*-acetamidobenzenesulfonyl chloride (1 g.) in pyridine (5 ml.) dropwise over a period of 2 hr. under cooling in an ice-bath. The reaction mixture was poured into ice-water and the precipitated reddish-brown gummy substance was separated by decantation. The $CHCl_3$ solution of crude product was washed with $H_2O$ and dried. Upon evaporation of solvent, the crude product was boiled under reflux in 5% methanolic KOH solution (10 ml.) for 1 hr. Treatment in the usual manner gave a yellow oil, which was extracted with benzene and chromatographed on alumina (12.5 g.). Elution with $Et_2O$ and $Et_2O-Me_2CO$ (9:1) gave 102 mg. and 223 mg. of crystalline product respectively. Recrystallization from $Me_2CO$-petr. ether gave Ⅱa (254 mg.). m.p. 179～181°. Analytical sample melted at 181～182°. $[\alpha]_D^{26}$ +63.4° (Adams, *et al.*[6]) prepared the same compound by different method and reported m.p. 179～180°). *Anal.* Calcd. for $C_{19}H_{30}O_3$ : C, 74.47; H, 9.87. Found : C, 74.38; H, 9.92.

**16ξ-Bromo-3β,12β-dihydroxy-5α-androstan-17-one Diacetate (IVa)**——Ⅱa (130 mg.) was treated with isopropenyl acetate and conc. $H_2SO_4$ in the same manner as 12α-epimer, and colorless crude oily product (167 mg.) was obtained. The IR spectrum indicated that the product consisted substantially of 3β,12β-dihydroxy-5α-androstan-17-one diacetate. To a solution of the crude product (130 mg.) in $CCl_4$ was added $Br_2$ solution in $CCl_4$ dropwise in the presence of anhyd. $K_2CO_3$ under cooling in an ice-bath. The filtrate was washed with $NaHSO_3$ solution and $H_2O$, dried. After evaporation of solvent, the oily product obtained was dissolved in petr. ether and chromatographed on acid-washed alumina (5 g.). Elution with petr. ether-benzene (6:4 and 4:6) yielded 13 mg. and 25 mg. of Ⅳa respectively. Recrystallization from aq. MeOH gave colorless prisms, m.p. 183～187°. The analytical sample melted at 187～189°. $[\alpha]_D^{26}$ −26.2°. *Anal.* Calcd. for $C_{23}H_{33}O_5Br$ : C, 58.85; H, 7.09; Br, 17.02. Found : C, 58.77; H, 7.11; Br, 16.80.

**5α-Androst-16-en-3β,12α,17-triol Triacetate (IIIb)**——To a solution of 3β,12α-dihydroxy-5α-androstan-17-one (Va) (130 mg.) in isopropenyl acetate (5 ml.) was added several drops of catalyst solution (isopropenyl acetate (5 ml.) and conc. $H_2SO_4$ (0.1 ml.)) and approximately 2.5 ml. of the reagent was distilled over a period of 2 hr. An additional 2.5 ml. of isopropenyl acetate containing a few drops of catalyst solution was added and the reaction mixture was concentrated to one-half of its volume by slow distillation over another 2 hr. The solution was diluted with $Et_2O$, and washed with cold $NaHCO_3$ solution and $H_2O$, dried. After evaporation of solvent the residue was dissolved in petr. ether and filtered through alumina (1 g.). Upon concentration of the filtrate a crystalline product was obtained. Recrystallization from aq. MeOH gave Ⅲb (110 mg.), m.p. 136～138°, as colorless needles. The analytical sample melted at 140～142°. $[\alpha]_D^{31.5}$ +45.2°. *Anal.* Calcd. for $C_{25}H_{36}O_6$ : C, 69.42; H, 8.39. Found : C, 69.54; H, 8.44.

**16ξ-Bromo-3β,12α-dihydroxy-5α-androstan-17-one Diacetate (IVb)**——To a solution of Ⅲb (60 mg.) in $CCl_4$ (30 ml.) was added the calculated amounts of $Br_2$ solution in $CCl_4$ dropwise in the presence of anhyd. $K_2CO_3$ (0.3 g.) under cooling in an ice-bath. The reaction mixture was washed with $NaHSO_3$ solution and $H_2O$, dried. Upon evaporation of solvent, the oily residue was obtained. IR spectrum showed the absorptions of carbonyl at 1758, 1742 $cm^{-1}$ and none of α-methylene group adjacent to 17-ketone.

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[*4] All melting points are corrected and all rotations were measured in $CHCl_3$ solution. The NMR spectra were measured by a Varian A-60 Spectrometer at 60 Mc.p.s., in $CHCl_3$ with use of $(CH_3)_4Si$ as an internal standard.

**3β,12α-Dihydroxy-5α-androstan-17-one 3-Acetate (Vb)**——To a solution of 3β,17α-dihydroxy-5α-pregnane-12,20-dione 3-acetate (VI) (750 mg.) in MeOH (10 ml.) was added $NaBH_4$ (200 mg.) portionwise. The reaction mixture was allowed to stand at room temperature for 3 hr., and diluted with $H_2O$. The $CHCl_3$ extract was washed with $H_2O$, dried and concentrated to give the oily residue. To a solution of the crude product in 50% AcOH (80 ml.) was added $NaBiO_3$ (5 g.) and the reaction mixture was vigorously stirred at room temperature for 3 hr. The filtrate was concentrated almost to dryness and extracted with AcOEt. After washing with $H_2O$, the organic layer was concentrated and chromatographed on alumina (20 g.). Elution with benzene and benzene-$Et_2O$ (7:3) yielded 310 mg. of crude product, which was recrystallized from $Et_2O$-petr. ether to give Vb (200 mg.), m.p. 190~193°. The analytical sample melted at 192~193°. $[\alpha]_D^{31.5}$ +121°. *Anal.* Calcd. for $C_{21}H_{32}O_4$ : C, 72.38; H, 9.26. Found : C, 72.55; H, 9.20.

**3β-Hydroxy-5α-androstane-12,17-dione 3-Acetate (VII)**——To a solution of Vb (420 mg.) in $Me_2CO$ (15 ml.) was added 8*N* chromic acid[14] (2 ml.) dropwise under cooling in cold $H_2O$. After allowing it to stand at room temperature for 30 min., the reaction mixture was diluted with $H_2O$ and extracted with $Et_2O$. After evaporation of solvent, the residue obtained was recrystallized from $Me_2CO$-petr. ether to give VII (380 mg.) as colorless leaflets, m.p. 167~169°. (Adams, *et al.*[15] prepared the same compound by different method and reported m.p. 165~166°).

**3β,12α-Dihydroxy-5α-androstan-17-one Diacetate (Vc)**——A solution of Va (750 mg.) dissolved in pyridine (8 ml.) and $Ac_2O$ (4 ml.) was heated on the water-bath for 2 hr. Upon usual work-up, Vc was obtained in quantitative yield. Recrystallization from $Me_2CO$-petr. ether gave colorless prisms, m.p. 209~211°, $[\alpha]_D^{14.2}$ +169°. (reported[16] : m.p. 197~199°, $[\alpha]_D^{25}$ +137°). *Anal.* Calcd. for $C_{23}H_{34}O_5$ : C, 70.74; H, 8.78. Found : C, 70.94; H, 8.85. NMR : τ 9.15, 9.11 (18-, 19-$CH_3$).

**Oxidation of Vc with Chromium Trioxide**——To a solution of Vc (700 mg.) in glacial AcOH (25 ml.) was added the pulverized $CrO_3$ (4 g.) over a period of 10 min. The reaction mixture was stirred vigorously maintaining the temperature at 16~18° for 1 hr. The solution was then decanted away from the excess solid $CrO_3$ and after cooling in an ice-bath, 30% $NaHSO_3$ solution was added until excess $CrO_3$ was reduced. An equal volume of $H_2O$ was added and the mixture was extracted with $CHCl_3$ three times. The organic layer was washed with $NaHCO_3$ solution and $H_2O$. After evaporation of solvent the oily residue obtained was chromatographed on alumina (20 g.). Elution with petr. ether-benzene (5:5) yielded the starting material (Vc) (220 mg.). Elution with benzene gave 114 mg. of the crystalline product, whose IR spectrum indicated the presence of six-membered ring carbonyl group. Recrystallization from aq. MeOH gave colorless needles, m.p. 208~211°, $[\alpha]_D^{31.5}$ +103.9°. *Anal.* Calcd. for $C_{23}H_{32}O_6$ : C, 68.29; H, 7.97. Found : C, 68.38; H, 8.03. Elution with benzene increasing $Et_2O$ yielded 144 mg. of the second crystalline product, which contained a free hydroxyl group. Recrystallization from $Me_2CO$-petr. ether gave 3β,5ξ,12α-trihydroxyandrostan-17-one 3,12-diacetate (VIII) as colorless needles, m.p. 208~211°. The analytical sample melted at 213~215°. $[\alpha]_D^{31.5}$ +129°. *Anal.* Calcd. for $C_{23}H_{34}O_6$ : C, 67.95; H, 8.43. Found : C, 68. 16; H, 8. 48. NMR : τ 9.11 (18-$CH_3$), 8.98 (19-$CH_3$). Acetylation of VIII with $Ac_2O$ and pyridine resulted in the complete recovery of unchanged starting material.

**3β,12α-Dihydroxyandrost-5-en-17-one Diacetate (IXb)**——A solution of VIII (40 mg.) in $Ac_2O$ (1 ml.) containing freshly fused $KHSO_4$ (100 mg.) was refluxed for 1 hr. The reaction mixture was diluted with $Et_2O$ and washed with $NaHCO_3$ solution and $H_2O$. After evaporation of solvent, 29 mg. of the semisolid residue obtained was chromatographed on acid-washed alumina (2.5 g.). Elution with benzene yielded IXb (25 mg.). Recrystallization from aq. MeOH gave colorless needles, m.p. 223~224°. Analytical sample melted at 227~228°. $[\alpha]_D^{30.5}$ +73.2°. *Anal.* Calcd. for $C_{23}H_{32}O_5$ : C, 71.10; H, 8.30. Found : C, 71.25; H, 8.69.

**Catalytic Hydrogenation of IXb**——A solution of IXb (30 mg.) in EtOH (20 ml.) was shaken with 10% Pd/C (15 mg.) under the current of $H_2$ for 2 hr. The filtrate and washing EtOH were combined and concentrated to give the crystalline product. Recrystallization from $Me_2CO$ gave 25 mg. of colorless prisms, m.p. 195°. Mixed melting point and IR spectra comparison proved it to be identical with Vc.

**Conversion of IXb into Androst-5-ene-3,12,17-trione**——A solution of IXb (50 mg.) dissolved in 5% methanolic $H_2SO_4$ (5 ml.) was refluxed for 12 hr. The reaction mixture was diluted with AcOEt, washed with $NaHCO_3$ solution and $H_2O$. After evaporation of solvent, the residue obtained was chromatographed on acid-washed alumina (2 g.). Elution with $CHCl_3$-MeOH (8:2) afforded 30 mg. of colorless crystalline product. Recrystallization from $Me_2CO$-petr. ether gave 3β, 12α-dihydroxyandrost-5-en-17-one (IXa) as colorless needles, m.p. 191~193°. *Anal.* Calcd. for $C_{19}H_{28}O_3$ : C, 74.96; H, 9.27. Found : C, 74.51; H, 10.42. To a cold (12~13°) solution of IXa (25 mg.) dissolved in $Me_2CO$ (3 ml.) was added Jones' reagent (0.05 ml.) with stirring. After 4 min., the reaction mixture was diluted with $H_2O$ and extracted with $Et_2O$. The $Et_2O$ extract was dried and concentrated to give 12 mg. of colorless semisolid product. Upon addition

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14) K. Bowden, I.M. Heilbron, E.R.H. Jones, B.C.I. Weedon : J. Chem. Soc., **1946**, 39.
15) W.J. Adams, D.N. Kirk, D.K. Patel, V. Petrow, I.A. Stuart-Webb : *Ibid.*, **1954**, 2298.
16) *Idem* : *Ibid.*, **1954**, 2209.

of two drops of $N$ NaOH to the ethanolic solution (25 ml.) of this crude product (ca. 2 mg.), a high-intensity absorption in the UV ($\lambda_{max}$ 240 m$\mu$) appeared immediately.

The author expresses his deep gratitudes to Dr. T. F. Gallagher, Dr. J. Fishman of Montefiore Hospital in New York for their support and encouragement throughout the course of this work. He wishes to thank Mrs. Beatrice S. Gallagher for the infrared spectra measurement and their interpretation. He is also indebted to Professor Z. Tamura of University of Tokyo for his interest.

## Summary

The chromium trioxide oxidation of 3$\beta$,12$\alpha$-dihydroxy-5$\alpha$-androstan-17-one diacetate in glacial acetic acid has been examined and one of the main products isolated has proved to be 3$\beta$,5$\xi$,12$\alpha$-trihydroxyandrostan-17-one 3,12-diacetate. The preparation of enol acetates derived from epimeric 3$\beta$,12-dihydroxy-5$\alpha$-androstan-17-ones is also described.

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