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OXIDATION OF STEROIDAL KETONES[1]—IV

REINVESTIGATION OF SELENIUM DIOXIDE–HYDROGEN PEROXIDE OXIDATION OF RING A SATURATED 3-KETONES[2,3]

E. CASPI,[4a] Y. SHIMIZU[4b] and (in part) S. N. BALASUBRAHMANYAM[4c]

Worcester Foundation for Experimental Biology, Shrewsbury, Massachusetts, U.S.A.

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Abstract—Oxidation of steroidal 3-ketones in the 5α and 5β series leads to ring A contracted acids and to products of bond scission on either side of the carbonyl. No directional influence by the ring A/B junction on the course of reaction previously indicated[3] was detected. The published results[3] are appropriately amended.

AN APPARENT influence of the ring A/B junction on the direction of selenium dioxide–hydrogen peroxide oxidation[5] of saturated 3-keto steroids was indicated in a previous communication.[3] The results then reported were based mainly on fractional crystallization and thin-layer chromatography of the rather difficult-to-separate mixtures of reaction products. Recently, improved procedures were developed for thin-layer chromatographic separation of derivatives of these closely related compounds.[6] Using the new methods, the previous results were reinvestigated and amended. No directional influence of ring A/B junction on the course of reaction was observed.[3]

Treatment of a solution of 17β-acetoxy-5α-androstan-3-one (Ia) in t-butanol with hydrogen peroxide in the presence of catalytic amounts of selenium dioxide[5,2,3] gave a large sodium carbonate "insoluble" fraction (A) and a smaller base soluble (B) residue. From the "neutral" fraction (A) a relatively small amount of the lactone VIIa was crystallized. Attempts to resolve the "neutral" mother liquor either by fractional crystallization or thin-layer chromatography failed. Consequently, the mixture was saponified and the acids were esterified with diazomethane. The mixture of esters was then easily resolved by t.l.c. into four products, which were saponified to free acids. The acids were identified as IIa, IIIa, IVa, and Va and are listed in order of increasing mobility of the corresponding methyl esters.

The 2,3-seco-hydroxy acid IIa, m.p. 257–262° (change of crystalline structure at

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[2] Paper II, E. Caspi and S. N. Balasubrahmanyam, *Experientia* **19**, 396 (1963), Paper III, E. Caspi and S. N. Balasubrahmanyam, *J. Org. Chem.* **28**, 3383 (1963).

[3] E. Caspi and S. N. Balasubrahmanyam, *Tetrahedron Letters* 745 (1963).

[4a] Recipient of U.S. Public Health Research Career Program Award CA-K3-16, 614;

[b] Post-Doctoral Fellow on leave from Hokkaido University, Japan;

[c] Post-Doctoral Fellow, 1962-1963. Present address: Indian Institute of Science, Bangalore, India.

[5] G. Payne and C. W. Smith, *J. Org. Chem.* **22**, 1680 (1957).

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200–220°), on oxidation with chromium trioxide in acetic acid followed by reduction with sodium borohydride in aqueous sodium hydroxide gave IVa. The diacid IVa was identical to an authentic sample prepared by two other routes. Oxidation of Ia with chromic acid in acetic acid,[7] followed by removal of the acetate moiety at C-17 gave[7,8] IVa, m.p. 273° (reported[7] 285° and[8] 273°). Alternatively, IVa was prepared by oxidation of the 2-hydroxymethylene derivative[9] IXa with the potassium permanganate–periodic acid reagent.[10] The hydroxy acid IIa on boiling with acetic anhydride gave lactone VIIIa.

The 3,4-seco-hydroxy acid IIIa showed a double m.p. 155° and 224–232°, and its structure was proven as follows. Treatment of a chloroform solution of Ia with an excess of perbenzoic acid[6] gave lactone VIIa (40% yield), m.p. 238–242°, different from lactone VIIIa. Saponification of VIIa gave the acid IIIa. Saponification of the mother liquor from the perbenzoic acid oxidation of Ia gave acids IIa and IIIa. The overall ratio of VIIa and VIIIa in the perbenzoic acid oxidation was about 7:3.

The third product IVa was identical to the dicarboxylic acid described above.

The last compound obtained, the A-nor acid Va, m.p. 263–268°, was only partially identified. On treatment with diborane[11] it gave a diol VIa. When the acidic residue "B" was processed as fraction (A), the same products were isolated. In order to evaluate the overall ratio of products formed, the oxidation of Ia was repeated and the recovered products were saponified. The isolated acids were chromatographically separated (as their esters), and the relative yields of the products were approximately found to be IIa:IIIa:IVa:Va as 1:1·3:0·3:1·2.

When 17β-acetoxy-5β-androstan-3-one (Ib) was oxidized and processed as described for Ia, a crystalline neutral fraction (C) and an acidic residue (D) were obtained. Again attempts to resolve the neutral fraction (C) by thin-layer chromatography or fractional crystallization were not successful. Consequently, the residue was saponified, and the acids were esterified and resolved by thin-layer chromatography. The two zones observed were eluted and saponified. The less mobile fraction proved to be a mixture which on fractional crystallization from ethyl acetate gave IIb. Diborane reduction of IIb gave triol X, which was identical to an authentic sample. The authentic sample was prepared by ozonolysis of the 2-hydroxymethylene derivatives[12] IXb to yield the dicarboxylic acid IVb. The latter, IVb, was reduced with diborane to X.

The mother liquor of IIb consisted mainly of the 3,4-seco acid IIIb, m.p. 184–188°, and was reduced by diborane to the triol XI. Alternatively, the triol XI was synthesized by diborane reduction of authentic dicarboxylic acid XII, m.p. 268–272°, prepared by chromic acid oxidation[13] of Ib.

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[8] C. Djerassi and C. R. Scholz, *J. Amer. Chem. Soc.* **69**, 2406 (1947).
[9] H. J. Ringold, E. Batres, O. Halpern and E. Necochea, *J. Amer. Chem. Soc.* **81**, 427 (1959).
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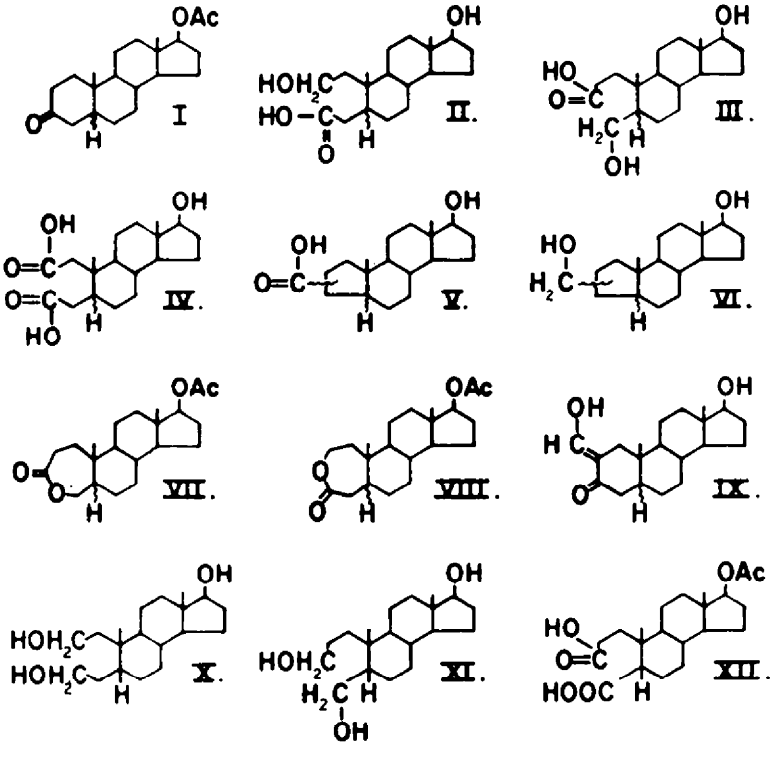
[11] G. R. Pettit and T. R. Kasturi, *J. Org. Chem.* **26**, 4557 (1961).
[12] R. O. Clinton, R. L. Clarke, F. W. Stonnes, A. J. Manson, K. F. Jennings and D. K. Phillips, *J. Org. Chem.* **27**, 2800 (1962).
[13] L. Ruzicka, V. Prelog and P. Meister, *Helv. Chim. Acta* **28**, 1651 (1945); R. Langer, *Z. Phys. Chem.* **216**, 189 (1933).

Finally, the product obtained from the second chromatographic zone was acid Vb, which resisted crystallization, and was partially identified through triol VIb, m.p. 174–180°.

The same three products were isolated from the acidic fraction (D). The approximate overall ratio of products IIb: IIIb: Vb was about 1:2:2. The acids IIIb and IIb on refluxing with acetic anhydride gave lactones VIIb, m.p. 201–204°, and VIIIb, 217–224°, respectively. The lactones, when chromatographed on t.l.c. systems using silica gel HF_{254} with either chloroform, chloroform–ethyl acetate (3:1), or benzene–ethyl acetate (3:1), showed the same mobility. A mixture of the two could not be resolved.

The reason for the isolation of acids IVa, Va and Vb from the base insoluble "neutral" fraction is not apparent at present. Three possible explanations can be tentatively forwarded: a. low solubility of the appropriate anions in water; b. solvation effects in the system ethyl acetate, t-butanol, and water resulting in increased solubility of the anions in the organic phase; c. the acids exist in some esterified form.



a = 5αH
b = 5βH

EXPERIMENTAL

IR spectra were taken on solids incorporated in KBr blotters on a Perkin Elmer Model 237-Infracord spectrometer. NMR spectra were taken on a Varian 4300 spectrometer in the indicated solvents, and the results are expressed in τ units. Analyses by Ilse Beetz, Kronach, W. Germany.

The m.ps were determined on a micro hot stage and are corrected.

Oxidation of 17β-*acetoxy*-5α-*androstan*-3-*one* (Ia)

a. A mixture of Ia (650 mg), t-butanol (30 ml), hydrogen peroxide (50%; 1·5 ml) and selenium dioxide (50 mg) was refluxed 7 hr. Ethyl acetate was then added, and the mixture washed with water, a dil. solution of $FeCl_2$ in HCl, and again with water. The ethyl acetate solution was then partitioned with a 1 N Na_2CO_3 aq. to yield a base soluble residue (B; 120 mg) and a base insoluble residue (A; 500 mg). The "neutral" base insoluble residue (A) after repeated recrystallization from ethyl acetate gave VIIa (52 mg). The combined mother liquors were dissolved in methanol (15 ml), 1 N NaOH (15 ml) was added, and the mixture was refluxed 2 hr in an atm. of N_2. The recovered crystalline acids were treated with excess ethereal diazomethane, and the esters chromatographed on four 20 × 20 cm t.l.c. plates. The plates were prepared with silica gel HF_{254} and were developed with chloroform–ethyl acetate (3:1). Four zones were detected and subsequently eluted with ethyl acetate. The residue of each zone was refluxed with methanolic NaOH aq. to yield acids II, IIIa, IVa, and Va after conventional work-up. The acidic fraction (B) was first saponified, then esterified with diazomethane and similarly chromatographed. Following elution and saponification, the same products IIa, IIIa, IVa and Va were obtained.

b. A solution of Ia (650 mg) was oxidized and the products were recovered as above. The total recovered residue was dissolved in methanol (15 ml), 1 N NaOH (15 ml) was added, and the mixture was boiled 1 hr in an atm. of N_2. After the usual work-up, a base soluble fraction (609 mg) was obtained and was treated with diazomethane. A portion of the ester (290 mg) was chromatographed on three t.l.c. 20 × 20 cm plates to yield after processing IIa (70 mg), IIIa (89 mg), IVa (24 mg), and Va (82 mg).

17β-*Acetoxy*-A-*homo*-3a-*oxa*-5α-*androstan*-3-*one* (VIIa)

a. The above-described neutral fraction (A) was crystallized several times from ethyl acetate to yield VIIa (52 mg), m.p. 238–242°.

b. To a solution of Ia (500 mg) in chloroform (10 ml) a chloroform solution (30 ml) of perbenzoic acid (2·2 equiv.) was added, and the mixture was stored for one week in a refrigerator. Ethyl acetate was then added, and the mixture was washed (consecutively with $Na_2S_2O_3$ aq., $NaHCO_3$ aq., and water, then dried over Na_2SO_4). On concentration, a solid was obtained from which, after several crystallizations, VIIa was isolated (220 mg), m.p. 238–240°.

A sample was recrystallized from ethyl acetate to a m.p. 240–242°; ν_{max}^{KBr} 1720, 1710 (shoulder), 1235 cm^{-1}. (Found: C, 72·24; H, 9·08. Calc. for $C_{21}H_{32}O_4$: C, 72·38; H, 9·26%).

2,17β-*Dihydroxy*-2,3-*seco*-5α-*androstane*-3-*carboxylic acid* (IIa)

a. The acid, m.p. 257–260°, was isolated from the residues "A" and "B".

b. On oxidation of Ia with perbenzoic acid, after the isolation of VIIa, there remained a crystalline mother liquor. This solid was dissolved in methanol and saponified with NaOH aq. A portion of the recovered acids (32 mg) was treated with diazomethane and chromatographed on t.l.c. Two products were obtained from which, after saponification, the acids IIa, (13·0 mg) and IIIa (14·0 mg) were isolated.

A sample was crystallized from methanol–ethyl acetate (needles) to a m.p. 257–262° (change of crystalline structure ab. 200–220°); ν_{max}^{KBr} 3450 (broad), 2600 (broad), 1720 (shoulder), 1705 cm^{-1}. (Found: C, 70·50; H, 9·79. Calc. for $C_{19}H_{32}O_4$: C, 70·33; H, 9·94%).

4,17β-*Dihydroxy*-3,4-*seco*-5α-*androstane*-3-*carboxylic acid* (IIIa)

a. The acid IIIa was isolated from the above described fractions "A" and "B" and from the mother liquors of the perbenzoic acid oxidation of Ia.

b. A mixture of lactone VIIa (90 mg), methanol (15 ml), and 1 N NaOH (15 ml) was refluxed 1 hr in an atm. of N_2. The acid IIIa was recovered in the conventional manner.

Crystallization from aqueous methanol gave needles, double m.p. 155° and 224–232° (loss of water at ab. 100°); ν_{max}^{KBr} 3350 (broad), 2600 (broad), 1700 cm^{-1}. (Found: C, 69·88; H, 9·78. Calc. for $C_{19}H_{32}O_4$: C, 70·33; H, 9·94%).

17β-*Hydroxy*-2,3-*seco*-5α-*androstane*-2,3-*dicarboxylic acid* (IVa)

a. The hydroxy acid IIa (10 mg) was treated for 2 hr with a mixture of CrO_3 (20 mg) in acetic acid (1 ml) at ambient temp. Excess chromic acid was decomposed with methanol, and the steroid was recovered with ethyl acetate. The washed residue left after solvent removal was dissolved in

0·25 N NaOH (2 ml), $NaBH_4$ (10 mg) was added, and the mixture was left 5 hr at ambient temp. After acidification with a dil. HCl aq., IVa (5 mg) was recovered with ethyl acetate, m.p. 268–272°.

b. The acid IVa was isolated from residues "A" and "B."

c. A mixture of Ia (200 mg), acetic acid (12 ml), and CrO_3 (500 mg) was kept at 60° for 2·5 hr with occasional stirring. The reaction was terminated with methanol, and after dilution with water the product was extracted into ethyl acetate. The ethyl acetate solution was washed with water, then with a sat. $NaHCO_3$ aq. From the alkaline solution the 17β-acetoxy-2,3-seco-5α-androstane-2,3-dicarboxylic acid was recovered in the conventional manner (120 mg). The product crystallized from aqueous methanol as prisms, m.p. 223–225°. (Found: C, 66·09; H, 8·87. Calc. for $C_{21}H_{32}O_6$: C, 66·30; H, 8·48%).

The 17β-acetoxy-2,3-dicarboxylic acid (5 mg) was dissolved in 1 N NaOH (1 ml), and the mixture was kept at 60° for 1·5 hr. After the usual work-up, IVa, m.p. 273°, was obtained.

d. A mixture of Ia (340 mg), benzene (15 ml), ethyl formate (3 ml), and sodium hydride (400 mg; 50% oil dispersion) was stirred for 16 hr with exclusion of moisture. Water (50 ml) was added, and the stirring continued for 1 hr. The phases were separated and the aqueous layer was extracted twice with methylene chloride–benzene (1:3). To the alkaline aqueous phase containing the sodium salt of the hydroxymethylene product IXa, a solution of $KMnO_4$ (100 mg) and $NaIO_4$ (2 g) in water (100 ml) was added. The mixture was agitated for 2 hr at room temp.

The oxidants were destroyed with SO_2, and the solution rendered acidic with HCl aq. The products were extracted with ethyl acetate. Removal of the solvent after washing of the combined extracts left light yellow crystals. Traces of elemental S were eliminated by redissolving the material in a dil. $NaHCO_3$ aq., filtering through Celite, and recovering of the organic acid.

The samples from experiments a-d gave identical IR spectra and did not depress their m.ps mutually.

A sample was recrystallized twice from ethyl acetate–methanol; m.p. 278–280°; ν_{max}^{KBr} 3320 (broad), 2650 (broad), 1700 cm^{-1}. (Found: C, 67·70; H, 8·83. Calc. for $C_{19}H_{30}O_5$: C, 67·43; H, 8·94%).

Esterification with diazomethane gave the dimethyl ester.

τ (in $CDCl_3$): 4·98, 6·38 (6H), 9·17, 9·27

*17β-Hydroxy-*A*-nor-5α-androstan-ξ-carboxylic acid* (Va)

The acid was isolated from fractions "A" and "B" and was recrystallized from methanol–ethyl acetate to give needles; m.p. 263–268°; ν_{max}^{KBr} 3325 (broad), 2600 (broad), 1700, 1250 cm^{-1}. (Found: C, 74·44; H, 9·75. Calc for $C_{19}H_{30}O_3$: C, 74·47; H, 9·87%).

*17β-Hydroxy-ξ-hydroxymethyl-*A*-nor-5α-androstane* (VIa)

Diborane generated by adding boron trifluoride etherate to a suspenson of $NaBH_4$ in diglyme was swept with a slow stream of dry N_2 into a solution of Va (10 mg) in dry dioxane (5 ml). After the solution was stored for 16 hr, methanol and water were added. The product was extracted in ethyl acetate and the organic phase was washed with Na_2CO_3 aq., water, then dried and concentrated to a residue. The product, when chromatographed on t.l.c. using chloroform–ethyl acetate (3:1) for development, showed a single spot.

The diol VIa was crystallized from wet ether, m.p. 148–155°; ν_{max}^{KBr} no carbonyl absorption. (Found: C, 77·71; H, 11·06. Calc. for $C_{19}H_{32}O_3$: C, 78·03; H, 11·03%).

*17β-Acetoxy-*A*-homo-2α-oxa-5α-androstan-3-one* (VIIIa)

A solution of IIa (10 mg) in acetic anhydride (1 ml) was heated on a steam bath for 2·5 hr. The mixture was poured on ice, and the crystalline solid was collected by filtration. Recrystallization from methanol gave solvated needles; m.p. 218–223°; ν_{max}^{KBr} 1720, 1245 cm^{-1}. (Found: C, 71·93; H, 8·86. Calc. for $C_{21}H_{32}O_4$: C, 72·38; H, 9·26%).

Oxidation of 17β-acetoxy-5β-androstan-3-one (Ib)

The ketone Ib (650 mg) was oxidized as described for Ia. The products were recovered with a mixture of methylene chloride–ether (1:3) to yield by partitioning with 1 N Na_2CO_3 a base soluble fraction (D) (329 mg) and a base insoluble residue (C; 360 mg).

Attempts to resolve the crystalline neutral residue either by fractional crystallization or in several t.l.c. systems described in the introductory part of the paper failed. Consequently, the neutral residue was saponified, esterified with diazomethane, and chromatographed on t.l.c. using chloroform–ethyl acetate (3:1) for development. The two zones detected were eluted and saponified. The zone of greater mobility consisted of Vb, which resisted crystallization. The less mobile zone on fractional crystallization from ethyl acetate gave IIb. The mother liquor consisted mainly of IIIb.

The acidic fraction was also saponified and esterified with diazomethane. The esters were resolved by t.l.c. into two zones from which Vb, IIb, and IIIb were obtained after saponification.

From 280 mg of the saponified and diazomethane-treated acidic residue (D) after t.l.c. chromatography, IIb (22 mg), IIIb (56 mg), and Vb (95 mg) were obtained.

From 220 mg of the saponified and diazomethane-treated neutral residue, after t.l.c. chromatography, IIb (40 mg), IIIb (110 mg), and Vb (24 mg) were isolated.

2,17β-*Dihydroxy*-2,3-*seco*-5β-*androstane*-3-*carboxylic acid* (IIb)

The acid was crystallized from methanol–ethyl acetate to yield needles; double m.p. 203° and 257–262°; ν_{max}^{KBr} 3275 (broad), 2750 (broad), 2600 (broad), 1680 cm^{-1}.
(Found: C, 69·73; H, 9·94. Calc for $C_{19}H_{32}O_4$: C, 70·33; H, 9·94%).

4,17β-*Dihydroxy*-3,4-*seco*-5β-*androstane*-3-*carboxylic acid* (IIIb)

The compound was crystallized from ethyl acetate, needles, m.p. 184–188°; ν_{max}^{KBr} 3375 (broad), 2650 (broad), 1695 cm^{-1}. (Found: C, 70·75; H, 10·07. Calc. for $C_{19}H_{32}O_4$: C, 70·33; H, 9·94%).

17β-*Hydroxy*-2,3-*seco*-5β-*androstane*-2,3-*dicarboxylic acid* (IVb)

To a suspension of sodium hydride (288 mg; 50% oil dispersion) in dry benzene (10 ml) was added anhydrous methanol (0·38 ml); and the mixture was briefly refluxed. The solution was cooled, and 17β-hydroxy-5β-androstan-3-one (950 mg) and dry ethyl formate (0·9 ml) were added.[18] The mixture was stirred under N_2 with exclusion of moisture for 24 hr.

After addition of water (150 ml), the phases were separated and the aqueous solution was extracted twice with ether. The organic extracts were washed once with 0·5 N NaOH (50 ml). The alkaline solutions were combined and saturated with CO_2 to yield the crystalline hydroxymethylene ketone X. The product was collected by filtration, air dried (520 mg; m.p. 153–156°), and used without further purification for the preparation of IVb.

A solution of the hydroxymethylene ketone IXb (500 mg) in methylene chloride was treated with a stream of ozonized oxygen at −70°. When the band at 294 mμ disappeared, the reaction was terminated. Water (100 ml) was added and the mixture was agitated for 5 hr at room temp. The methylene chloride was removed under red. press. The aqueous phase was then extracted with ethyl acetate, and the steroids were partitioned with Na_2CO_3 into acidic and neutral fractions. From the acidified sodium carbonate solution, the diacid IVb was recovered in the conventional manner.

Recrystallization from ethyl acetate gave an analytical sample; m.p. 228–230°; ν_{max}^{KBr} 3350 (broad), 3170 (broad), 2600 (broad), 1710, 1245, 1045 cm^{-1} τ (in CD_3OD) 6·38, 6·50, 8·74, 9·26. (Found: C, 67·28; H, 9·16. Calc. for $C_{19}H_{30}O_5$: C, 67·43; H, 8·94%).

17β-*Acetoxy*-3,4-*seco*-5β-*androstane*-3,4-*dicarboxylic acid* (XII)

A mixture of Ib (200 mg), acetic acid (10 ml), CrO_3 (300 mg), and water (1 ml) was stored at 60° for 3 hr. The reaction was terminated with methanol, ethyl acetate was added, and the solution was washed with water. After partitioning with a $NaHCO_3$ aq., the acid (130 mg) was recovered as usual.

The acid was crystallized from ethyl acetate to yield fine needles; m.p. 268–272°; ν_{max}^{KBr} 330: (broad), 2600 (broad), 1725, 1685, 1240 cm^{-1}. (Found: C, 66·12; H, 8·49. Calc. for $C_{21}H_{32}O_6$: C, 66·30; H, 8·48%).

2,3,17β-*Trihydroxy*-2,3-*seco*-5β-*androstane* (X)

a. Diborane generated by adding boron trifluoride etherate (10 ml) to a suspension of $NaBH_4$ (6 g) in diethylene glycol dimethyl ether (diglyme; 15 ml) was swept with a slow stream of dry N_2 into a solution of the diacid IVb (100 mg) in anhydrous tetrahydrofuran (10 ml). The gelatineous reaction mixture was stoppered and kept for 16 hr in a refrigerator. The excess diborane was destroyed with methanol, and the solvents removed *in vacuo*. The residue was treated with 1 N NaOH

(50 ml) and extracted with ethyl acetate–methylene chloride (3:1). The organic extract was washed, dried, and concentrated to yield X (72 mg).

b. A sample of IIb (15 mg) in dry tetrahydrofuran (2·5 ml) was reduced with diborane as above to yield X.

Recrystallization from methanol–ethyl acetate gave a sample showing a double m.p. 170–171° and 179°; ν_{max}^{KBr} 3300 (strong), 1050, 1020 cm^{-1}; τ (in CD_3COCD_3) 6·58 (8H), 8·98, 9·28. (Found: C, 73·08; H, 11·15. Calc. for $C_{19}H_{34}O_3$: C, 73·50; H, 11·04%).

The glycol was chromatographed using an FM Model 720 Gas Chromatographic instrument equipped with 0·25″ × 4′ column packed with 20% SE-30 silicon rubber on acid-washed Chromosorb P 60–80 mesh. The retention time at 249° with a He flow rate of 40 ml/min was 12 min.

3,4,17β-*Trihydroxy*-3,4-*seco*-5β-*androstane* (XI)

a. A sample of XII (50 mg) in dry tetrahydrofuran (5 ml) was reduced with diborane and processed as described for X to yield XI.

b. The dihydroxy acid IIIb (22 mg) in dry tetrahydrofuran (2·5 ml) gave XI after reduction with diborane.

The triol XI crystallized from methanol—ethyl acetate as needles; m.p. 188–195°; ν_{max}^{KBr} 3300, 1070, 1050, 1020 cm^{-1}. (Found: C, 72·99; H, 10·78. Calc. for $C_{19}H_{34}O_3$: C, 73·50; H, 11·04%).

17β-*Acetoxy*-A-*homo*-3a-*oxa*-5β-*androstan*-3-*one* (VIIb)

A solution of IIIb (20 mg) in acetic anhydride (1 ml) was refluxed for 2 hr. The mixture was poured on ice, and the solid collected by filtration.

Crystallization from methanol gave needles; m.p. 201–204°; ν_{max}^{KBr} 1725, 1240 cm^{-1}. (Found: C, 72·20; H, 8·94. Calc for $C_{21}H_{32}O_4$: C, 72·38; H, 9·26%).

17β-*Acetoxy*-A-*homo*-2a-*oxa*-5β-*androstan*-3-*one* (VIIIb)

A sample of IIb (15 mg) was treated with acetic anhydride (1 ml) as above to yield VIIIb. The product crystallized from methanol as plates; m.p. 217–224°; ν_{max}^{KBr} 1725 cm^{-1}. (Found: C, 72·90; H, 9·55. Calc. for $C_{21}H_{32}O_4$: C, 72·38; H, 9·26%).

17β-*Hydroxy*-ξ-*hydroxymethyl*-A-*nor*-5β-*androstane* (VIb)

A solution of Vb (90 mg) in tetrahydrofuran (30 ml) was reduced with diborane as described for VIa. The recovered product was crystallized several times from benzene, needles; m.p. 174–180°; ν_{max}^{KBr} no carbonyl absorption. (Found: C, 78·05; H, 10·88. Calc. for $C_{19}H_{32}O_2$: C, 78·03; H, 11·03%).