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The Bromination of 13α-Androstan-15-one[1]

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In order to examine the behaviors toward bromination 3β-acetoxy-5α,13α-androstan-15-one (X) was prepared from the 17-keto steroid (I) according to the method worked out by Djerassi, *et al.* with the C/D-*trans* steroid (see Chart 1). On treatment with bromine in acetic acid in the presence of hydrogen bromide, bromination occurred exclusively at C-16 yielding a mixture of 16β-bromo and 16,16-dibromo derivatives (XI and XII), which could be separated readily by preparative thin-layer chromatography.

The bromination of steroid ketones is of particular interest with respect to the mechanistic and stereochemical significance. In our previous studies on the 13α-steroid the keto groups in C-16 and C-17 positions have been explored from this point of view.[3] The 15-keto steroid, however, has not yet been investigated because of the comparative unavailability. Therefore it seemed to be attractive to us to examine the behaviors of 13α-androstan-15-one toward bromination. The desired compound, 3β-acetoxy-5α,13α-androstan-15-one, was prepared starting from the 17-ketone according to the method worked out by Djerassi, *et al.* with the usual C/D-*trans* steroid.[4]

First, 13α-isoandrosterone (I), derivable from isoandrosterone by the photochemical reaction,[5] was converted into the ethylene ketal to protect the 17-oxo group. Ketalization was effected by refluxing with ethylene glycol in the presence of pyridine hydrochloride as catalyst for a prolonged period to give the 17, 17-ethylenedioxy derivative (II) in 53% yield. The somewhat less reactivity of this ketone may probably be due to the characteristic feature of C/D-ring fusion where both sides of the molecule are sterically hindered.[3,6] Subsequent treatment with phenyltrimethylammonium perbromide[7] resulted in formation of the 16ξ-bromo derivative (III) in fairly good yield. When refluxed with potassium *tert*-butoxide in xylene, III underwent dehydrobromination with ease yielding the Δ^{15}-unsaturated compound (IV). Removal of the protecting group without influencing the double bond was achieved by treatment with *p*-toluenesulfonic acid in aqueous acetone to furnish the Δ^{15}-17-ketone (Va) having the expected ultraviolet absorption maximum at 233 mμ. However, this synthetic route appeared to be of disadvantage with respect to the overall yield and therefore an alternative method without protecting the 17-oxo group was undertaken.

1) This paper constitutes Part LI of the series entitled "Analytical Chemical Studies on Steroids"; Part L: T. Nambara, Y.H. Bae, and M. Nokubo, *J. Chromatog.*, **60**, 418 (1971).
2) Location: *Aobayama, Sendai.*
3) *a*) T. Nambara, H. Hosoda, and S. Goya, *Chem. Pharm. Bull.* (Tokyo), **16**, 1266 (1968); *b*) T. Nambara, H. Hosoda, and M. Usui, *ibid.*, **17**, 375 (1969); *c*) *Idem, ibid.*, **17**, 947 (1969); *d*) *Idem, ibid.*, **17**, 1687 (1969); *e*) T. Nambara, M. Usui, and H. Hosoda, *ibid.*, **17**, 1611 (1969); *f*) T. Nambara, T. Kudo, H. Hosoda, K. Motojima, and S. Goya, *ibid.*, **17**, 2366 (1969).
4) C. Djerassi, G. von Mutzenbecher, J. Fajkoš, D.H. Williams, and H. Budzikiewicz, *J. Am. Chem. Soc.*, **87**, 817 (1965); C. Djerassi and G. von Mutzenbecher, *Proc. Chem. Soc.*, **1963**, 377.
5) J.R. Billeter and K. Miescher, *Helv. Chim. Acta*, **34**, 2053 (1951); J.P.L. Bots, *Rec. Trav. Chim.*, **77**, 1010 (1958); T. Nambara, T. Kudo, H. Hosoda, and S. Goya, *J. Chromatog.*, **31**, 210 (1967).
6) L.J. Chinn, *J. Org. Chem.*, **30**, 4165 (1965); T. Nambara and J. Goto, *Chem. Pharm. Bull.* (Tokyo), **19**, 1937 (1971).
7) L.F. Fieser and M. Fieser, "Reagents for Orgaic Synthesis," John Wiley and Sons, Inc., New York, 1967, p. 855.

I was led to the 16β-bromo derivative (VI) *via* the enol acetate in the manner as described in the preceding paper.[3a] Being refluxed with lithium carbonate and lithium bromide in dimethylformamide VI underwent readily dehydrobromination yielding the Δ^{15}-17-ketone 3-acetate (Vb) which proved to be identical with the product obtained from Va by usual acetylation. It is to be noted that the facile dehydrobromination of the 16-bromo-17-ketone proceeds in the 13α-series but not in the common C/D-*trans* steroid. The relative ease may be ascribable to the favorable geometrical alignment of the reaction centers in the 13α-steroid.

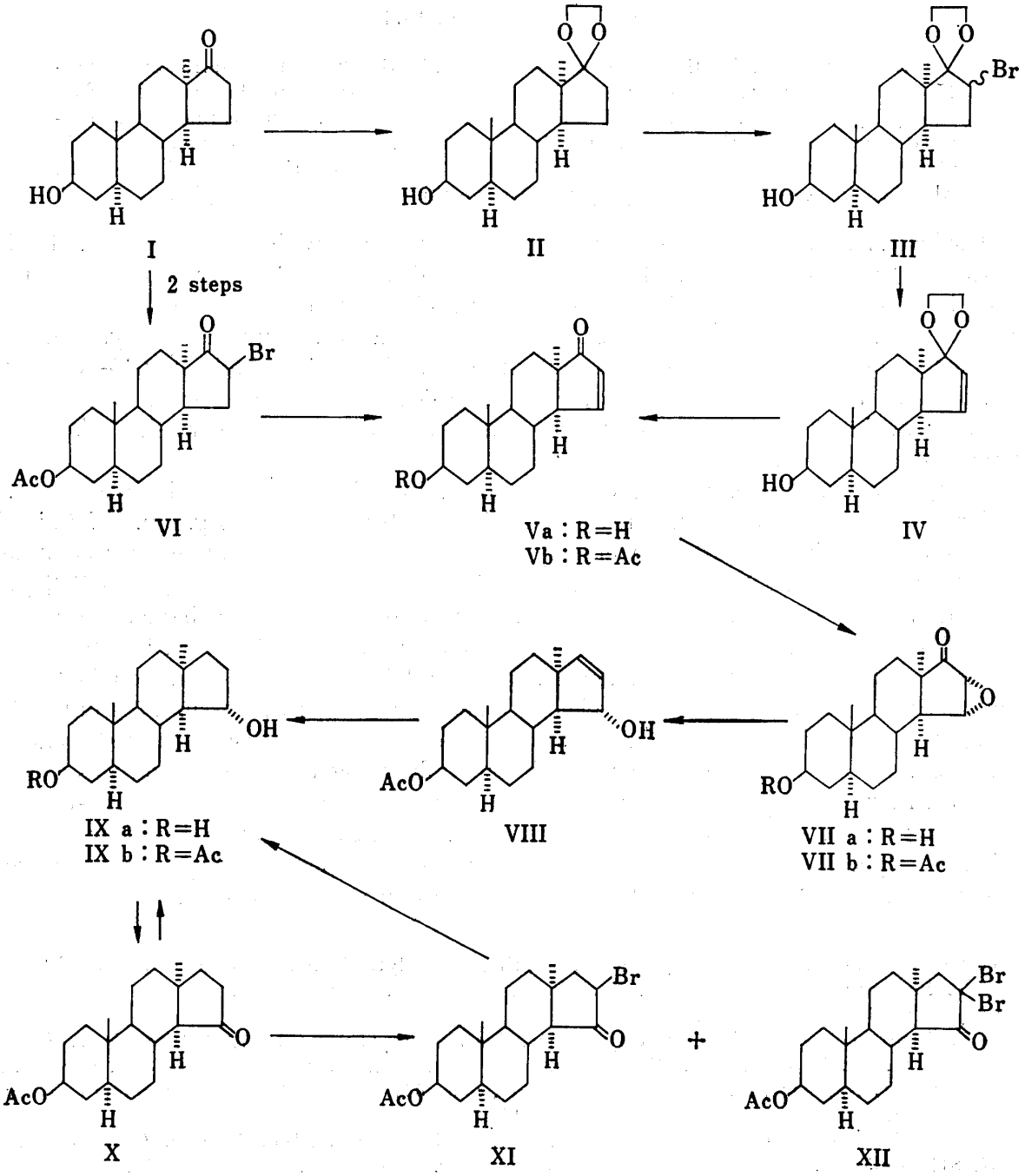

Chart 1

Upon exposure to hydrogen peroxide in the alkaline media Va was transformed into the 15α,16α-epoxy-17-ketone (VIIa). Configuration of the oxido ring was deduced to be α from the circular dichroism curve exhibiting the positive Cotton effect (for the n→π^* transition),

since the sign of Cotton effect of the epoxy ketone obeys the "reversed" octant rule and is dependent upon the sign of the octant in which the oxido oxygen is located.[8] It is of interest that epoxidation of the Δ^{15}-double bond takes place selectively at the α-side of the molecule. The 3-acetate (VIIb) was then subjected to Huang-Minlon reduction in the usual manner. As was expected the Δ^{16}-15-ol (VIII) was thus afforded in reasonable yield. The nuclear magnetic resonance (NMR) spectral data unequivocally justified the assignment of the structure allylic alcohol to VIII. Upon catalytic hydrogenation over palladium-on-charcoal VIII was reduced to the saturated compound (IXb). The configuration of the C-15 hydroxyl group in IX and hence in VIII was confirmed by the fact that a C-18 proton signal appeared at the lower field as compared with that of the parent compound due to the 1,3-diaxial interaction. It is sufficiently substantiated that the methyl group occupying position 1,3-diaxial to the hydroxyl function experiences the paramagnetic effect of the order of 0.20—0.40 ppm in pyridine relative to chloroform.[3d,9] In the present case the 15-hydroxyl group actually exerted a pyridine-induced shift of 18-proton of 0.24 ppm. Oxidation of IXb with chromium trioxide–pyridine complex gave the desired 15-ketone (X). Retention of the stereochemistry at C-14 during the oxidation step was confirmed by the metal hydride reduction by leading to the 3β,15α-diol (IXa), which proved to be identical with the hydrolyzate derived from IXb.

Treatment of X with bromine in acetic acid in the presence of hydrogen bromide gave a mixture of 16β-bromo- and 16,16-dibromo-15-ketones (XI and XII), whose separation could efficiently be attained by preparative thin-layer chromatography (TLC). The bromine atom in XI should be situated at C-16, since a NMR signal resonated at 4.27 ppm was assignable to the remaining 16-hydrogen. Application of the axial haloketone rule served to assign the β-configuration to the C_{16}-bromine bond. The monobromo ketone (XI) exhibited a positive Cotton effect with the smaller amplitude in contrast to that of the parent 15-keto steroid (X). The fact that an introduction of bromine at C-16 exerted no significant influence on the chemical shift of 18-methyl proton would also support the configurational assignment. The stereochemistry at C-14 was established by leading to the known 5α,13α-androstane-3β,15α-diol (IXa) by reductive removal of the bromine with lithium aluminum hydride.[10] The *gem*-dibromo structure of XII was evident from the elemental analysis and NMR spectrum lacking a signal of a proton attached to carbon bearing halogen.

Table I. Spectral Data of X and XI

Substance	IR		CD		[θ]
	$\nu_{max}^{CCl_4}$ cm^{-1}	$\Delta\nu$	λ_{max}^{MeOH} mμ	$\Delta\lambda$	
15-Ketone (X)	1738		297		+6000
16β-Bromo-15-ketone (XI)	1746	+8	310	+13	+2500

As summarized in Table I the spectral data of the 16β-bromo-15-ketone (XI) and the parent compound (X) demonstrate that the 16β-bromine bond possesses the quasi-axial character.

It should be now emphasized that in 13α-androstane bromination of the 15-ketone proceeds preferentially at C-16 rather than C-14. This result is in marked contrast to the behaviors of the C/D-*trans* 15-keto steroid, in which monobromination occurs solely at C-14.[11] It is well known that the direction of bromination is dependent upon that of enolization and this,

8) C. Djerassi, W. Klyne, T. Norin, G. Ohloff, and E. Klein, *Tetrahedron*, **21**, 163 (1965).
9) P.V. Demarco, E. Farkas, D. Doddrell, B.L. Mylari, and E. Wenkert, *J. Am. Chem. Soc.*, **90**, 5480 (1968).
10) T. Nambara, H. Hosoda, and T. Shibata, *Chem. Pharm. Bull.* (Tokyo), **17**, 2599 (1969).
11) C. Djerassi, J. Fajkoš, and A.R. VanHorn, *Steroids*, **6**, 239 (1965).

in turn, is determined by the relative stability of a double bond at the alternative positions. The present finding implies the greater stability of Δ^{16}- over Δ^{14}-unsaturated structure in the 13α-steroid.

Experimental[12]

17,17-Ethylenedioxy-5α,13α-androstan-3β-ol (II)——To a solution of 3β-hydroxy-5α,13α-androstan-17-one (I) (2.6 g) in toluene (80 ml) were added ethylene glycol (20 ml) and pyridine·HCl (200 mg) and refluxed for 80 hr. The resulting solution was diluted with ether, washed with H_2O and dried over anhydrous Na_2SO_4. After evaporation of solvent the oily residue obtained was chromatographed on Al_2O_3 (80 g). Elution with hexane–benzene (9:1) and recrystallization of the eluate from acetone–hexane gave II (1.6 g) as colorless needles. mp 111—112.5°. $[\alpha]_D^{20}$ −39.3° (c=0.10). *Anal.* Calcd. for $C_{21}H_{34}O_2$: C, 75.40; H, 10.25. Found: C, 75.65; H, 10.34.

16ξ-Bromo-17,17-ethylenedioxy-5α,13α-androstan-3β-ol (III)——To a solution of II (1.5 g) in THF (50 ml) was added phenyltrimethylammonium perbromide (1.5 g) under ice-cooling and allowed to stand in the refrigerator for 1 hr. The reaction mixture was poured into 5% $NaHSO_3$ and extracted with ether. The organic layer was washed with 5% $NaHCO_3$, H_2O and dried over anhydrous Na_2SO_4. After evaporation of solvent the residue obtained was recrystallized from acetone–hexane to give III (1.55 g) as colorless needles. mp 145—147°. $[\alpha]_D^{17}$ −37.1° (c=0.09). *Anal.* Calcd. for $C_{21}H_{33}O_3Br$: C, 61.01; H, 8.05. Found: C, 61.17; H, 8.23.

17,17-Ethylenedioxy-5α,13α-androst-15-en-3β-ol (IV)——To a solution of III (460 mg) in xylene (25 ml) was added *tert*-BuOK (prepared from 330 mg of metal K) and refluxed under a stream of N_2 gas for 50 min. The reaction mixture was diluted with ether, washed with H_2O and dried over anhydrous Na_2SO_4. After evaporation of solvent the residue obtained was submitted to preparative TLC using benzene–ether (4:1) as developing solvent. Elution of the adsorbent corresponding to the spot (*Rf* 0.10) and recrystallization of the eluate from acetone–hexane gave IV (260 mg) as colorless needles. mp 175—177°. $[\alpha]_D^{18}$ −174.6° (c=0.11). *Anal.* Calcd. for $C_{21}H_{32}O_2$: C, 75.86; H, 9.70. Found: C, 75.60; H, 9.50. NMR (5% solution in CCl_4) δ: 0.73 (3H, s, 19-CH_3), 0.92 (3H, s, 18-CH_3), 3.83 (4H, s, -OCH_2CH_2O-), 5.50 (1H, d, J=6 cps, 16-H), 6.12 (1H, d, d, J=6, 3 cps, 15-H).

3β-Hydroxy-5α,13α-androst-15-en-17-one (Va)——To a solution of IV (250 mg) in acetone (10 ml) was added an aq. solution (1 ml) of p-TsOH·H_2O (5 mg) and allowed to stand at room temperature for 3 hr. The resulting solution was concentrated *in vacuo* below 30° and diluted with ether. The organic layer was washed with 5% $NaHCO_3$, H_2O and dried over anhydrous Na_2SO_4. After usual work-up the crude product obtained was recrystallized from acetone–hexane to give Va (205 mg) as colorless needles. mp 174—176°. $[\alpha]_D^{20}$ −162.0° (c=0.09). *Anal.* Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.79. Found: C, 79.66; H, 9.96. NMR (5% solution in $CDCl_3$) δ: 0.69 (3H, s, 19-CH_3), 1.06 (3H, s, 18-CH_3), 3.62 (1H, m, 3α-H), 6.07 (1H, d, d, J=2, 6 cps, 16-H), 7.71 (1H, d,d, J=3, 6 cps, 15-H).

3β-Acetoxy-5α,13α-androst-15-en-17-one (Vb)——i) To a stirred solution of 3β-acetoxy-16β-bromo-5α,-13α-androstan-17-one (VI)[3a] (1 g) in DMF (30 ml) were added Li_2CO_3 (4.5 g) and LiBr (900 mg) and refluxed under a stream of N_2 gas for 1.5 hr. The resulting solution was diluted with ether, washed with H_2O and dried over anhydrous Na_2SO_4. After usual work-up the crude product obtained was recrystallized from MeOH to give Vb (440 mg) as colorless plates. mp 138—139°. $[\alpha]_D^{24}$ −156.7° (c=0.15). *Anal.* Calcd. for $C_{21}H_{30}O_3$: C, 76.31; H, 9.15. Found: C, 76.12; H, 9.39. NMR (5% solution in $CDCl_3$) δ: 0.69 (3H, s, 19-CH_3), 1.06 (3H, s, 18-CH_3), 2.00 (3H, s, 3β-$OCOCH_3$), 4.68 (1H, m, 3α-H), 6.08 (1H, d, d, J=2, 6 cps, 16-H), 7.70 (1H, d, d, J=3, 6 cps, 15-H).

ii) Treatment of Va (5 mg) with Ac_2O (0.1 ml) and pyridine (0.2 ml) in the usual manner followed by recrystallization from MeOH gave Vb (3 mg) as colorless plates. mp 138—139°. Mixed melting point on admixture with the sample obtained in i) showed no depression.

3β-Hydroxy-15α,16α-epoxy-5α,13α-androstan-17-one (VIIa)——To a solution of Va (50 mg) in MeOH (6 ml) were added 4N NaOH (0.1 ml) and 30% H_2O_2 (0.2 ml) under ice-cooling and stirred at 5° for 3 hr. After allowing to stand in the refrigerator overnight the reaction mixture was diluted with ether, washed with H_2O and dried over anhydrous Na_2SO_4. After usual work-up the crude product obtained was recrystallized from acetone–hexane to give VIIa (40 mg) as colorless prisms. mp 159—160.5°. $[\alpha]_D^{18}$ −43.8° (c=0.10). *Anal.* Calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.74; H, 9.27. NMR (5% solution in $CDCl_3$)

12) All melting points were taken on a micro hot-stage apparatus and are uncorrected. Optical rotations were measured in $CHCl_3$. NMR spectra were obtained on Hitachi Model H-60 spectrometer at 60 Mc; the chemical shifts are quoted as ppm downfield from tetramethylsilane used as an internal standard. Infrared (IR) spectra and circular dichroism measurements were carried out on Hitachi Model 225 spectrophotometer and JASCO Model ORD/UV-5 recorder, respectively. For preparative TLC silica gel H (E. Merck AG) was employed.

δ: 0.67 (3H, s, 19-CH_3), 1.14 (3H, s, 18-CH_3), 3.36 (1H,d, J=3 cps, 15β-H), 3.62 (1H, m, 3α-H), 3.82 (1H, d, J=3 cps, 16β-H). CD (c=0.10, MeOH) $[\theta]^{20}$ (mμ): 0 (342), +4000 (330), +8300 (312) (positive maximum), +5800 (300), +500 (270).

3β-Acetoxy-15α,16α-epoxy-5α,13α-androstan-17-one (VIIb)——Treatment of VIIa (470 mg) with Ac_2O (5 ml) and pyridine (10 ml) in the usual manner followed by recrystallization from MeOH gave VIIb (330 mg) as colorless needles. mp 140—141.5°. $[\alpha]_D^{20}$ −44.3° (c=0.10). *Anal.* Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 73.01; H, 8.75. NMR (5% solution in CCl_4) δ: 0.69 (3H, s, 19-CH_3), 1.09 (3H, s, 18-CH_3), 2.92 (3H, s, 3β-OCOCH_3), 3.16 (1H, d, J=3 cps, 15β-H), 3.65 (1H, d, J=3 cps, 16β-H), 4.52 (1H, m, 3α-H).

5α,13α-Androst-16-ene-3β,15α-diol 3-Acetate (VIII)——To a solution of VIb (38 mg) in iso-PrOH (2 ml) were added 80% $NH_2NH_2 \cdot H_2O$ (0.21 ml) and AcOH (0.01 ml) and allowed to stand at room temperature for 2 hr. The reaction mixture was diluted with ether, washed with H_2O and dried over anhydrous Na_2SO_4. After evaporation of solvent the oily residue obtained was submitted to preparative TLC using benzene–ether (2: 1) as developing solvent. Elution of the adsorbent corresponding to the spot (*Rf* 0.37) and recrystallization of the eluate from acetone–hexane gave VIII (6 mg) as colorless plates. mp 84—85°. $[\alpha]_D^{17}$ −11.5° (c=0.26). *Anal.* Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.66; H, 9.72. NMR (5% solution in $CDCl_3$) δ: 0.70 (3H, s, 19-CH_3), 1.15 (3H, s, 18-CH_3), 2.02 (3H, s, 3β-OCOCH_3), 4.49 (1H, d, J=2 cps, 15β-H), 4.68 (1H, m, 3α-H), 5.79 (2H, s, 16- and 17-H).

5α,13α-Androstane-3β,15α-diol (IXa)——i) To a solution of IXb (20 mg) in MeOH (2 ml) was added 5% KOH (1 ml) and refluxed for 1 hr. The resulting solution was diluted with AcOEt, washed with H_2O and dried over anhydrous Na_2SO_4. After usual work-up the crude product obtained was recrystallized from acetone–hexane to give IXa (10 mg) as colorless needles. mp 167—168°. $[\alpha]_D^{19}$ −30.0° (c=0.10). *Anal.* Calcd. for $C_{19}H_{32}O_2 \cdot \frac{1}{2}H_2O$: C, 75.70; H, 11.03. Found : C, 75.97; H, 10.85. NMR (3% solution in $CDCl_3$) δ: 0.72 (3H, s, 19-CH_3), 1.09 (3H, s, 18-CH_3), 3.62 (1H, m, 3α-H), 4.10 (1H, m, 15β-H).

ii) To a solution of X (15 mg) in anhydrous ether was added $LiAlH_4$ (30 mg) portionwise and allowed to stand at room temperature for 4 hr. To this reaction mixture was added moistened ether to decompose the excess reagent, acidified with dil. HCl and extracted with AcOEt. The organic layer was washed with K-Na tartrate solution, H_2O and dried over anhydrous Na_2SO_4. After usual work-up the crude product obtained was recrystallized from acetone–hexane to give IXa (10 mg) as colorless needles. mp 167—168.5°. Mixed melting point on admixture with the sample obtained in i) showed no depression and IR spectra of two samples were entirely identical in every respect.

iii) To a solution of XI (10 mg) in anhydrous ether was added $LiAlH_4$ (50 mg) and refluxed for 8 hr. To this reaction mixture was added moistened ether to decompose the excess reagent, acidified with dil. HCl and extracted with AcOEt. The organic layer was washed with K-Na tartrate solution, H_2O and dried over anhydrous Na_2SO_4. After usual work-up the crude product otained was submitted to preparative TLC using hexane–AcOEt (1: 1) as developing solvent. Elution of the adsorbent corresponding to the spot (*Rf* 0.32) and recrystallization of the eluate from acetone–hexane gave IXa (4 mg) as colorless needles. mp 167—168°. Mixed melting point on admixture with the sample obtained in i) showed no depression and IR spectra of two samples were entirely identical in every respect.

5α,13α-Androstane-3β,15α-diol 3-Acetate (IXb)——A solution of VIII (130 mg) in AcOEt (20 ml) was shaken with 10% Pd/C (100 mg) under a stream of H_2 at room temperature for 2 days. After removal of the catalyst by filtration the filtrate was concentrated to give the crystalline product. Recrystallization from $CHCl_3$–hexane gave IXb (80 mg) as colorless prisms. mp 149—150.5°. $[\alpha]_D^{19}$ −44.7° (c=0.20). *Anal.* Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.62; H, 10.46. NMR (5% solution in $CDCl_3$) δ: 0.73 (3H, s, 19-CH_3), 1.09 (3H, s, 18-CH_3), 2.00 (3H, s, 3β-OCOCH_3), 4.03 (1H, m, 15β-H), 4.68 (1H, m, 3α-H).

3β-Acetoxy-5α,13α-androstan-15-one (X)——To a solution of IXb (80 mg) in pyridine (2 ml) was added pyridine–CrO_3 complex (100 mg in 1 ml) and allowed to stand at room temperature for 5 hr. The reaction mixture was diluted with ether, washed with 10% AcOH, H_2O and dried over anhydrous Na_2SO_4. After usual work-up the crude product obtained was recrystallized from MeOH to give X (60 mg) as colorless prisms. mp 103—104°. $[\alpha]_D^{19}$ +8.1° (c=0.06). *Anal.* Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.80; H, 9.96. NMR (3% solution in $CDCl_3$) δ: 0.78 (3H, s, 19-CH_3), 0.91 (3H, s, 18-CH_3), 2.00 (3H, s, 3β-OCOCH_3), 4.68 (1H, m, 3α-H). CD (c=0.10, MeOH) $[\theta]^{17}$ (mμ): +600 (323), +3500 (310), +6000 (297) (positive maximum), +4400 (280), +1100 (260).

3β-Acetoxy-16β-bromo-5α,13α-androstan-15-one (XI), 3β-Acetoxy-16,16-dibromo-5α,13α-androstan-15-one (XII)——To a solution of X (100 mg) in AcOH (2 ml) were added a solution of Br_2 (69 mg) in AcOH (4 ml) and three drops of HBr-saturated AcOH and allowed to stand at room temperature for 4 hr. The reaction mixture was diluted with ether, washed with 5% $NaHSO_3$, 5% $NaHCO_3$, H_2O and dried over anhydrous Na_2SO_4. After evaporation of solvent the semi-crystalline residue obtained was submitted to preparative TLC using benzene–ether (10: 1) as developing solvent. Elution of the adsorbent corresponding to the spot (*Rf* 0.57) and recrystallization of the eluate from MeOH gave XI (72 mg) as colorless needles. mp 170—171°. $[\alpha]_D^{15}$ −12.0° (c=0.25). *Anal.* Calcd. for $C_{21}H_{31}O_3Br$: C, 61.31; H, 7.59. Found: C, 61.92; H, 7.88. NMR (5% solution in $CDCl_3$) δ: 0.80 (3H, s, 19-CH_3), 0.92 (3H, s, 18-CH_3), 2.01 (3H, s, 3β-OCOCH_3), 4.27 (1H, t, J=9 cps, 16α-H), 4.68 (1H, m, 3α-H). CD (c=0.08, MeOH) $[\theta]^{17}$ (mμ): 0 (342), +1000 (330), +2500 (310) (positive maximum), +1600 (290), +300 (260). Elution of the adsorbent corresponding to the

spot (Rf 0.68) and recrystallization of the eluate from MeOH gave XII (66 mg) as colorless needles. mp 129—130°. $[\alpha]_D^{17}$ −16.7° (c=0.18). *Anal.* Calcd. for $C_{31}H_{30}O_3Br_2$: C, 51.44; H, 6.17. Found: C, 51.61; H, 6.21. NMR (5% solution in $CDCl_3$) δ: 0.79 (3H, s, 19-CH_3), 1.19 (3H, s, 18-CH_3), 2.01 (3H, s, 3β-$OCOCH_3$), 2.87, 3.37 (2H, each d, J=16 cps, 17-H), 4.68 (1H, m, 3α-H).

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