SOLVOLYTIC REARRANGEMENTS IN 4β,5-CYCLOPROPANO-5β-ANDROSTANE-3β,17β,19-TRIOL 3-ACETATE 17-BENZOATE 19-*p*-TOLUENESULFONATE*

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The title tosylate *V* was prepared from the tosylate *III* by Simmons–Smith methylenation. Its acetolysis afforded three products with modified steroid skeletons: The diene *VIII*, the olefin *XI*, and the pentacyclic diacetate *XIII*. The 3-oxo derivatives *XIV*, *XVI*, *XVII*, and *XIX* — compounds of potentional biological interest — were prepared as follows: Oxidation of the monoacetate *X* followed by hydrolysis yielded the testosterone analogue *XIV* and oxidation of the diol *IX* gave the dione *XVI*. Using similar reaction sequence the triol diester *XII* afforded the oxo compounds *XVII* and *XIX*.

In our previous paper[1] we dealt with solvolysis of 19-*p*-toluenesulfonate of 4β,5-cyclopropano-5β-cholestane-3β,19-diol. The reaction afforded three main products all of them having a modified steroid skeleton. The new structures have been carefuly established by spectroscopic means and labelling experiments as well and the mechanisms which gave rise to the products were discussed in detail[2]. In our systematic search for biologically active steorids we have now carried out similar studies in the androstane series in order to obtain new structures of potential biological activity. Since an analogous course of the solvolytic rearrangements and formation of analogous products can be safely assumed in the both series, we did not consider it necessary to repeat here the labelling and mass spectral experiments.

The starting tosylate *II* was prepared from the previously[3] described alcohol *I* by standard procedure. Reduction with sodium borohydride in ethyl acetate–methanol yielded the allylic alcohol *III* which was submitted to the Simmons–Smith methylenation to afford the cyclopropano derivative *IV*. The beta configuration of the cyclopropane ring was assigned by analogy with the known course of this reaction in allylic and homoallylic alcohols where the cyclopropane ring adopts always *cis* configuration to the participating hydroxyl group[4]. Acetylation of the alcohol *IV* yielded the acetate *V* which was submitted to the acetolytic conditions (1 h reflux

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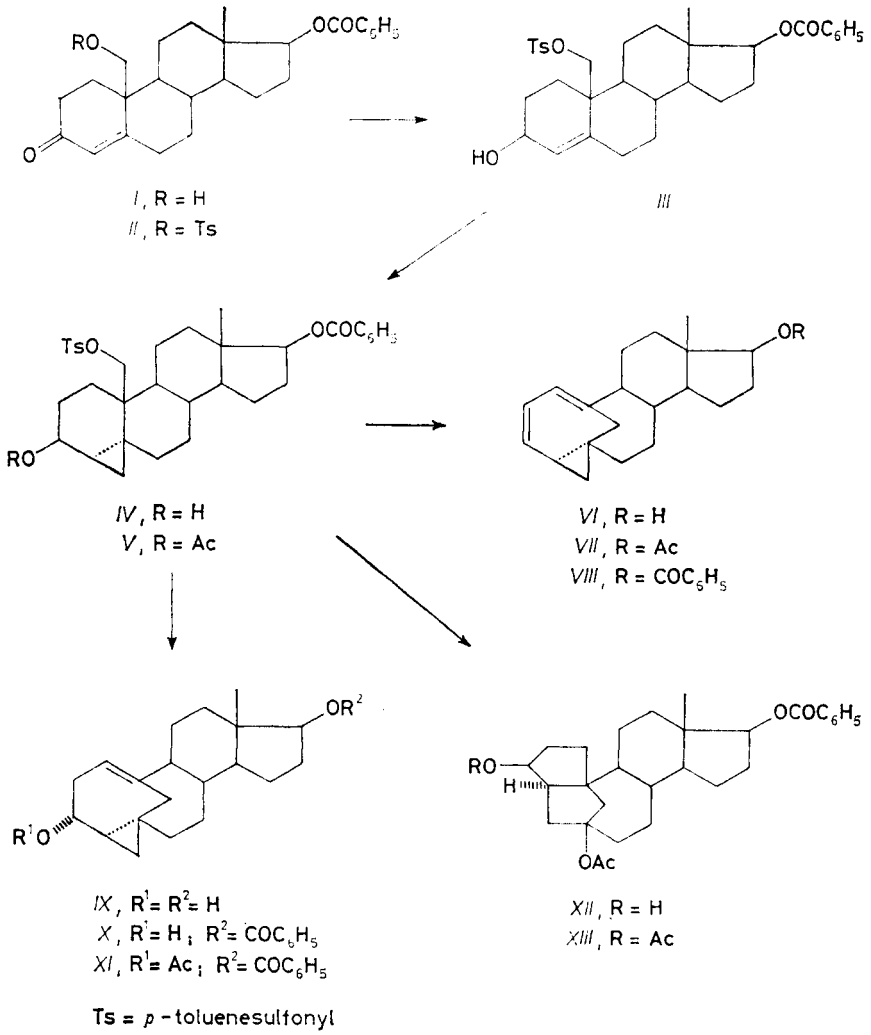
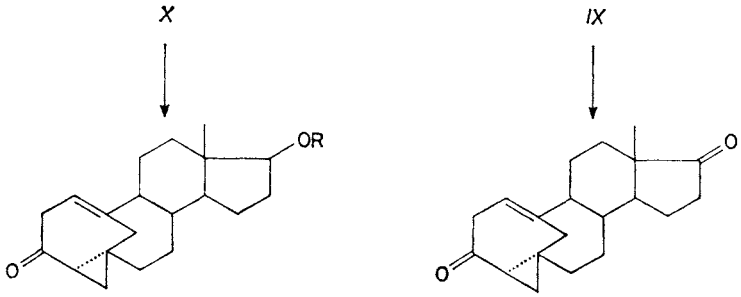
in acetic acid–acetic anhydride–potassium acetate). Similarly to the cholestane series, the reaction mixture consisted of three main components (TLC in benzene) which were separated by column chromatography on silica gel.



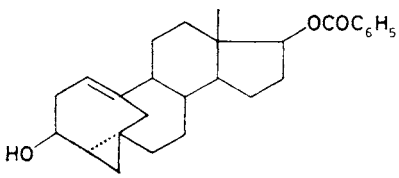
The most lipophilic component which was isolated from the reaction mixture was the conjugated diene *VIII* with the preserved cyclopropane ring as shown by spectral evidence. It was characterised after hydrolysis and subsequent acetylation also as the corresponding alcohol *VI* and acetate *VII*. The reaction product of medium polarity was identified as an unsaturated acetoxy derivative *XI*. In analogy to the cholestane

series and on the basis of the mechanism discussed elsewhere[2] we assign 3α-configuration to the acetoxy group in this compound. Partial hydrolysis of the diester *XI* afforded the alcohol *X* which on Jones' oxidation gave the ketone *XV* and, after hydrolysis, the hydroxy ketone *XIV* in which the presence of the cyclopropane ring was detected by infrared spectra. Also similarly to the cholestane series, reduction of the ketone *XV* with tri-tert-butoxyaluminium hydride afforded the 3-hydroxy derivative *XX*; the 2β-configuration was deduced from the levorotatory shift of its molecular optical rotation as compared to the 3α-epimer (in agreement with observation in the cholestane series). Complete hydrolysis of the diester *XI* led to the diol *IX* which on subsequent oxidation with Jones' reagent gave the dione *XVI*.



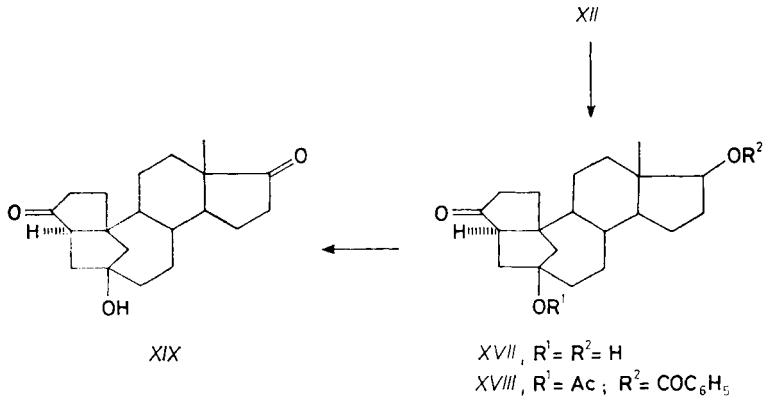
XIV, R = H
XV, R = COC_6H_5

XVI



XX

To the most polar product of the solvolysis of the tosylate *V* was ascribed a structure of the diacetate *XIII*. The absence of the cyclopropane ring in this compound follows from its IR spectrum and can be interpreted by a rearrangement of the A/B ring system to a new saturated tricyclic ring structure, to the pentacyclic diacetate *XIII*, in analogy to the observation in the cholestane series[1]. Partial hydrolysis resulted in the formation of the alcohol *XII* which was subsequently oxidized to the ketone *XVIII*. Further transformation of the latter compound yielded the diol *XVII* and the dione *XIX*.



XIX *XVII*, $R^1 = R^2 = H$
XVIII, $R^1 = Ac$; $R^2 = COC_6H_5$

EXPERIMENTAL

Melting points were determined on a Kofler block. Optical rotations were carried out in chloroform unless otherwise stated with an error of $\pm 2°$. The infrared spectra were recorded on the Zeiss UR 20 spectrometer in tetrachloromethane. Wavenumbers are given in cm^{-1}. Mass spectra were recorded on a Jeol D-100 double-focussing spectrometer (75 eV, 300 μA, 3 kV). The samples were introduced to the ion source via a direct probe heated to the lowest temperature enabling evaporation (100° to 150°C). Accurate *m/z* values of ions were determined by the peak matching technique with perfluorokerosene as internal standard. The identity of the samples prepared by different routes was checked by thin-layer chromatography (TLC, silica gel G Woelm, detection with sulfuric acid) and by infrared spectra. Working up of a reaction mixture means extraction of the product with an organic solvent and washing the extract with 5% aqueous hydrochloric acid, water, 5% aqueous sodium hydrogen carbonate, water, drying over magnesium sulfate, and evaporation of the solvent in vacuo at 50°C. Ligroin refers to the fraction of b.p. 40°–60°C.

17β,19-Dihydroxyandrost-4-en-3-one 17-Benzoate 19-*p*-Toluenesulfonate (*II*)

The alcohol *I* (20 g) in pyridine (150 ml) was treated at +5°C with *p*-toluenesulfonyl chloride (20 g) and allowed to stand at room temperature for 24 h. The mixture was decomposed with ice and water and the product was taken into ether. Usual working up yielded after evaporation of the solvent an oily residue which was chromatographed on a silica gel column (800 g) in benzene–ether 19 : 1. Working up and crystallisation from methanol afforded 18·5 g (67%) of the tosylate *II*, m.p. 162–164°C, $[\alpha]_D^{20}$ +141° (*c* 1·4). IR spectrum: 1 721, 1 277 (benzoate); 1 682, 1 623 (O=C–C=C); 1 370, 1 192, 1 181 (tosylate). For $C_{33}H_{38}O_6S$ (562·7) calculated: 70·43% C, 6·80% H, 5·69% S; found: 70·67% C, 7·00% H, 5·71% S.

4-Androstene-3β,17β,19-triol 17-Benzoate 19-*p*-Toluenesulfonate (*III*)

The ketone *II* (3·8 g) in ethyl acetate (150 ml) and methanol (30 ml) was treated under stirring at 15°C with sodium borohydride (1 g) added in three portions within 30 min. Stirring was then

continued at the same temperature for another 1 h. The excess hydride was decomposed with acetic acid, water was added (100 ml) and the organic solvents were distilled off in vacuo. The product was extracted into ether, and the solution was worked up. Evaporation left 3·7 g of a product which was chromatographed over silica gel (300 g) in benzene–ether (3 : 1). The fractions with the desired product were combined, solvents removed, and the residue was crystallized, from ether–ligroin to afford 3·25 g (85%) of the allylic alcohol *III*, m.p. 83—85°C (decomposition), $[\alpha]_D^{20}$ +90° (*c* 1·6). IR spectrum: 3 620, 3 605 (hydroxyl); 1 721, 1 278 (benzoate); 1 660 (double bond; 1 370, 1 190, 1 180 (tosylate). For $C_{33}H_{40}O_6S$ (564·7) calculated: 70·18% C, 7·14% H, 5·68% S; found: 70·02% C, 7·11% H, 5·39% S.

4β,5-Cyclopropano-5β-androstane-3β,17β,19-triol 17-Benzoate 19-*p*-Toluenesulfonate (*IV*)

The 0·5% Zn–Cu couple was prepared form zinc dust (29·3 g) with cupric acetate monohydrate (500 mg) in acetic acid (200 ml) as described for the Simmons–Smith methylenation in our previous paper[1]. Similar treatement with iodine (80 mg) and diiodomethane (30 ml) afforded the organozinc intermediate which on reaction with the olefin *III* (9·2 g) in ether (100 ml) underthe described[1] conditions and analogous working up gave 10·7 g of a crude product which was chromatographed on a silica gel column (500 g) in benzene–ether (7 : 1) to yield 3·3 g of pure*IV*. Fractions which were contaminated with the starting material (5·43 g) were dissolved in chloroform (140 ml) and treated with an ethereal solution of perphthalic acid (2 g in 50 ml). After 20 h at room temperature the acids were extracted into 5% aqueous sodium carbonate and the organic layer was worked up. The residue (5·25 g) was chromatographed over silica gel (250 g) in benzene–ether (7 : 1) to afford 3·8 g of the pure *IV*. Both crops were combined and crystallized from acetone to yield 6·7 g (71%) of the cyclopropano derivative *IV*, m.p. 148—150°C $[\alpha]_D^{20}$ +32° (*c* 1·8). IR spectrum: 3 620 (hydroxyl); 1 721, 1 246 (benzoate); 1 371, 1 189, 1 179 (tosylate). Mass spectrum, *m/z*: $M^{+\cdot}$ 578. For $C_{34}H_{42}O_6S$ (578·7) calculated: 70·56% C, 7·31% H, 5·54% S; found: 70·35% C, 7·37% H, 5·33% S.

4β,5-Cyclopropano-5β-androstane-3β,17β,19-triol 3-Acetate
17-Benzoate 19-*p*-Toluenesulfonate (*V*)

The alcohol *IV* (22 g) in pyridine (80 ml) was treated with acetic anhydride (65 ml) and allowed to stand at room temperature for 20 h. The reaction mixture was decomposed with ice and water and the product was isolated with ethyl acetate. Usual working up yielded a crude product which on crystallization from acetone gave 18·5 g (78%) of *V*, m.p. 139—141°C, $[\alpha]_D^{20}$ −1° (*c* 1·7). For $C_{36}H_{44}O_7S$ (620·8) calculated: 69·65% C, 7·14% H, 5·16% S; found: 69·70% C, 7·07% H, 5·08% S.

4β,5-Cyclopropano-5(10a)-homo-19-nor-5β-androsta-1(10),2-dien-17β-ol (*VI*)

The benzoate *VIII* (500 mg) in methanol (80 ml) was treated with a solution of potassium hydroxide (1 g) in water (2 ml) and in methanol (20 ml) and heated to 55°C for 6 h. The excess alkali was neutralized with acetic acid and methanol was distilled off in vacuo. The product was taken into ethyl acetate and the solution was worked up as usual. The crude product after evaporation of the solvent was chromatographed over silica gel (20 g) in ligroin–ether (20 : 1). Crystallization from acetone afforded 270 mg (74%) of the diene *VI*, m.p. 129—130°C, $[\alpha]_D^{20}$ +440° (*c* 1·2). IR spectrum: 3 625 (hydroxyl); 3 060, 3 010 (cyclopropane); 1 637, 1 607, 714 (diene). Mass spectrum, *m/z*: $M^{+\cdot}$ 284. For $C_{20}H_{28}O$ (284·4) calculated: 84·45% C, 9·92% H; found 84·27% C, 9·81% H.

4β,5-Cyclopropano-5(10a)-homo-19-nor-5β-androsta-1(10),2-dien-17β-ol 17-Acetate (*VII*)

A solution of *VI* (250 mg) in pyridine (2 ml) was treated with acetic anhydride (1·5 ml) and allowed to stand at room temperature for 18 h. Uusual working up with ether and crystallization from methanol gave 180 mg (63%) of the acetate *VII*, m.p. 142–144°C, $[\alpha]_D^{20}$ +395° (*c* 1·4). IR spectrum: 3 065 (cyclopropane); 1 741, 1 250, 1 047, 1 023 (acetate); 1 639, 1 606, 715 (diene). Mass spectrum, *m/z*: $M^{+\cdot}$ 326. For $C_{22}H_{30}O_2$ (326·5) calculated: 80·93% C, 9·26% H; found: 81·20% C, 9·47% H.

4β,5-Cyclopropano-5(10a)-homo-19-nor-5β-androsta-1(10),2-dien-17β-ol 17-Benzoate (*VIII*)

Acetic acid (210 ml) and acetic anhydride (18 ml) were refluxed with freshly fused potassium acetate (18 g) for 1 h. The tosylate *V* (20 g) was then added and refluxed for 4 h. The boiling reaction mixture was treated with water (5 ml) and refluxed for additional 30 min. The acetic acid was distilled off in vacuo and the residue was taken into ethyl acetate and the solution was worked up in the usual way. The crude product (14 g) consisted according to the TLC of three components. It was chromatographed on a silica gel column (1 kg) in ligroin–ether (9 : 1). Fractions containing the most lipophilic component were combined, solvent removed and the residue was crystallized from methanol to afford 6·1 g (49%) of the diene *VIII*, m.p. 102–104°C, $[\alpha]_D^{20}$ +256° (*c* 1·3). IR spectrum: 3 060 (cyclopropane); 1 723, 1 275 (benzoate); 1 641, 1 608, 715 (diene). Mass spectrum, *m/z*: $M^{+\cdot}$ 388. For $C_{27}H_{32}O_2$ (388·5) calculated: 83·46% C, 8·30% H; found: 83·29% C, 8·20% H.

4β,5-Cyclopropano-5(10a)-homo-19-nor-5β-androst-1(10)-ene-3α,17β-diol (*IX*)

The diester *XI* (180 mg) in methanol (25 ml) was treated with a solution of potassium carbonate (200 mg) in water (2·5 ml) and refluxed for 1 h. The excess alkali was neutralized with acetic acid and methanol was distilled off in vacuo. The product was taken into ethyl acetate and the extract was worked up in the usual way. The residue was crystallized from methanol to yield 115 mg (95%) of the diol *IX*, m.p. 162–163°C, $[\alpha]_D^{20}$ +78° (*c* 1·5). IR spectrum: 3 060 (cyclopropane); 3 020 (double bond); 3 610, 1 046, 1 035 (hydroxyl). Mass spectrum, *m/z*: $M^{+\cdot}$ 302. For $C_{20}H_{30}O_2$ (302·4) calculated: 79·42% C, 10·00% H; found: 79·31% C, 9·89% H.

4β,5-Cyclopropano-5(10a)-homo-19-nor-5β-androst-1(10)-ene-3α,17β-diol 17-Benzoate (*X*)

The diester *XI* (2·4 g) in methanol (250 ml) was treated with a solution of potassium carbonate (1.5 g) in water (18 ml) and allowed to stand at 35°C for 4 h and further processed as described for compound *IX*. The residue (2·28 g) was chromatographed on a silica gel column (260 g) in ligroin–ether (2 : 1) to afford after crystallization from methanol 1·4 g (64%) of the alcohol *X*, m.p. 175–176°C, $[\alpha]_D^{20}$ +112° (*c* 1·4). IR spectrum: 3 620, 1 032 (hydroxyl); 1 722, 1 275 (benzoate). Mass spectrum, *m/z*: $M^{+\cdot}$ 406. For $C_{27}H_{34}O_3$ (406·5) calculated: 79·76% C, 8·43% H; found: 79·63% C, 8·39% H.

4β,5-Cyclopropano-5(10a)-homo-19-nor-5β-androst-1(10)-ene-3α,17β-diol 3-Acetate 17-Benzoate (*XI*)

Further elution of the column after isolation of the diene *VIII* with the same solvent mixture afforded the product of medium polarity which was repurified by chromatography over silica gel (300 g) in ligroin–ether (9 : 1) to yield 2·9 g (20%) of the oily diester *XI* $[\alpha]_D^{20}$ +88°(*c* 1·5).

IR spectrum: 1 731, 1 249 (acetate); 1 728, 1 276 (benzoate). Mass spectrum, *m/z*: M^+ 448. For $C_{29}H_{36}O_4$ (448·6) calculated: 77·64% C, 8·09% H; found: 77·49% C, 8·00% H.

4β,10β-Cyclo-5(10a)-homo-19-nor-5β-androstane-3β,5,17β-triol 5-Acetate 17-Benzoate (*XII*)

The triester *XIII* (1 g) in methanol (100 ml) was treated with a solution of potassium carbonate (600 mg) in water (10 ml), allowed to stand at 35°C for 4 h and worked up as described for compound *IX*. The crude product was chromatographed over silica gel (150 g) in ligroin–ether (3 : 1) to afford 520 mg of a product which on crystallization from methanol–water gave 420 mg (46%) of *XII*, m.p. 134–136°C, $[\alpha]_D^{20}$ +35° (*c* 1·3). IR spectrum: 3 625 (hydroxyl); 1 728, 1 251 (acetate); 1 728, 1 275 (benzoate). Mass spectrum, *m/z*: $M^{+\cdot}$ 466. For $C_{29}H_{38}O_5$ (466·6) calculated: 74·65% C, 8·21% H; found: 74·47% C, 8·19% H.

4β,10β-Cyclo-5(10a)-homo-19-nor-5β-androstane-3β,5,17β-triol 3,5-Diacetate 17-Benzoate (*XIII*)

Continued elution of the column after isolation of the diene *VIII* and the olefin *XI* afforded the most polar product of the solvolysis. The crude product (1·9 g) was rechromatographed on a silica gel column (200 g) in ligroin–ether (10 : 1) to afford 1·1 g (7%) of the oily triester *XIII*, $[\alpha]_D^{20}$ +7° (*c* 1·4). IR spectrum: 1 740, 1 251 (acetate); 1 727, 1 277 (benzoate). Mass spectrum, *m/z*: M^+ 508. For $C_{31}H_{40}O_6$ (508·6) calculated: 73·20% C, 7·93% H; found: 73·04% C, 7·82% H.

17β-Hydroxy-4β,5-cyclopropano-5(10a)-homo-19-nor-5β-androst-1(10)-en-3-one (*XIV*)

The benzoate *XV* (150 mg) in methanol (300 mg) was treated with a solution of potassium hydroxide (200 mg) in water (1 ml), allowed to stand at 50°C for 10 h and worked up as described for compound *IX*. The residue gave on chromatography over silica gel (10 g) in ligroin–ether (3 : 1) and crystallization from acetone 95 mg (43%) of *XIV*, m.p. 162–163°C, $[\alpha]_D^{20}$ −170° (*c* 1·1). IR spectrum: 3 625, 1 072, 1 054, 1 034 (hydroxyl); 3 070 (cyclopropane); 3 035 (double bond) 1 692 (carbonyl). Mass spectrum, *m/z* (rel. intensity): 300 ($M^{+\cdot}$, $C_{20}H_{28}O_2$, 67), 282(5), 273 (6), 272 (31), 257 (10), 244 (14), 239 (10), 91 (100). For $C_{20}H_{28}O_2$ (300·4) calculated: 79·95% C, 9·39% H; found: 79·80% C, 9·29% H.

17β-Hydroxy-4β,5-cyclopropano-5(10a)-homo-19-nor-5β-androst-1(10)-en-3-one 17-Benzoate (*XV*)

A) The alcohol *X* (300 mg) in acetone (20 ml) was treated with excess Jones' reagent. After 7 min at room temperature the excess reagent was removed with methanol and most of the solvents were distilled off in vacuo. The residue was treated with water and ethyl acetate and the organic layer was worked up. The residue after evaporation of the solvent was chromatographed on a silica gel column (15 g) in ligroin–ether (9 : 1) to yield 220 mg of a crude product which was crystallized ffom methanol to afford 180 mg (60%) of the ketone *XV*, m.p. 196–198°C, $[\alpha]_D^{20}$ −74° (*c* 1·1). IR spectrum: 1 722, 1 277 (benzoate); 1 692 (carbonyl); 1 642 (double bond). For $C_{27}H_{32}O_3$ (404·5) calculated: 80·16% C, 7·97% H; found: 80·02% C, 7·85% H.

B) The reaction was performed with the alcohol *XX* (40 mg) as described under *A*); yield (after crystallization from methanol) 28 mg (70%) of the ketone *XV*, m.p. 197–198°C, $[\alpha]_D^{20}$ −72° (*c* 1·0).

4β,5-Cyclopropano-5(10a)-homo-19-nor-5β-androst-1(10)-ene-3,17-dione (*XVI*)

A solution of the diol *IX* (100 mg) in acetone (15 ml) was treated with excess Jones' reagent and alowed to stand at room temperature for 10 min. The excess reagent was removed with methanol, water (7 ml) was added and the solvents were distilled off in vacuo. The product was dissolved in ethyl acetate, the solution was worked up and the residue after evaporation of the solvent was chromatographed over silica gel (8 g) in ligroin–ether (4 : 1). Working up of the relevant fractions and crystallization from ligroin (b.p. 60—80°C) afforded 65 mg (66%) of the dione *XVI*, m.p. 169—170°C, $[\alpha]_D^{20}$ −89° (*c* 1·3). IR spectrum: 3 035 (double bond); 3 065 (cyclopropane); 1 745, 1 693 (carbonyl). Mass spectrum, *m/z* (rel. intensity): 298 ($M^{+\cdot}$, $C_{20}H_{26}O_2$, 62), 270 (31), 255 (10), 243 (7), 242 (22), 241 (11), 213 (16), 199 (11), 173 (15), 131 (33), 91 (100). For $C_{20}H_{26}O_2$ (298·4) calculated: 80·49% C, 8·78% H; found: 80·35% C, 8·71% H.

5,17β-Dihydroxy-4β,10β-cyclo-5(10a)-homo-19-nor-5β-androstan-3-one (*XVII*)

A solution of the diester *XVIII* (180 mg) in methanol (40 ml) was treated with a solution of potassium hydroxide (400 mg) in water (1 ml) and methanol (5 ml), heated to 50°C for 6 h and worked up as described for compound *IX*. The residue after evaporation of the solvent afforded on crystallization from ethyl acetate 90 mg (73%) of the diol *XVII*, m.p. 190—191°C, $[\alpha]_D^{20}$ −63° (*c* 1·1). IR spectrum (KBr): 3 450, 3 420, 1 068 (hydroxyl); 1 721 (carbonyl). Mass spectrum, *m/z* (rel. intensity): 318 ($M^{+\cdot}$, $C_{20}H_{30}O_3$, 48), 300 (14), 276 (6), 246 (13), 165 ($C_{10}H_{13}O_2$, 100) 137 ($C_8H_9O_2$, 58), 109 ($C_7H_9O + C_8H_{13}$, 53). For $C_{20}H_{30}O_3$ (318·4) calculated: 75·43% C, 9·50% H; found: 75·20% C, 9·43% H.

5,17β-Dihydroxy-4β,10β-cyclo-5(10a)-homo-19-nor-5β-androstan-3-one
5-Acetate 17-Benzoate (*XVIII*)

The alcohol *XII* (140 mg) in acetone (5 ml) was oxidized with Jones' reagent as described for the preparation of the ketone *XVI*. Similar working up and crystallization from methanol afforded 115 mg (83%) of the ketone *XVIII*, m.p. 137—139°C, $[\alpha]_D^{20}$ −34° (*c* 1·7). IR spectrum: 1 741, 1 252 (acetate); 1 726, 1 277 (benzoate); 1 712 shoulder (carbonyl). Mass spectrum, *m/z*: $M^{+\cdot}$ 464. For $C_{29}H_{36}O_5$ (464·6) calculafed: 74·97% C, 7·81% H; found: 74·79% C, 7·80 H.

5-Hydroxy-4β,10β-cyclo-5(10a)-homo-19-nor-5β-androstane-3,17-dione (*XIX*)

The alcohol *XVII* (100 mg) in acetone (40 mg) was oxidized with excess Jones' reagent as described for the preparation of the ketone *XVI*. Usual working up and crystallization from ethyl acetate gave 62 mg (62%) of the dione *XIX*, m.p. 230—232°C, $[\alpha]_D^{20}$ +24 (*c* 1·1). IR spectrum: 3 600, 1 049, 1 042 (hydroxyl); 1 736 (carbonyl). Mass spectrum, *m/z*: $M^{+\cdot}$ 316. For $C_{20}H_{28}O_3$ (316·4) calculated: 75·91% C, 8·92% H; found: 75·79% C, 8·83% H.

4β,5-Cyclopropano-5(10a)-homo-19-nor-5β-androst-1(10)-ene-3β,17β-diol
17-Benzoate (*XX*)

The ketone *XV* (200 mg) in tetrahydrofuran (5 ml) was treated with solid tri-tert-butoxyaluminium hydride (500 mg) and allowed to stand at room temperature for 1 h. The reaction mixture was diluted with ethyl acetate and poured into 5% hydrochloric acid. The organic layer was worked up in the usual way and the solvent was distilled off under reduced pressure. The residue contained according to the TLC traces of the 3α-hydroxy derivative *X* next to the main product, the alcohol *XX*. It was chromatographed on a silica gel column (25 g) in ligroin–ether (20 : 1) to yield after

working up of the corresponding fractions and crystallization from methanol 405 mg (81%) of the alcohol *XX*, m.p. 102–103°C, $[\alpha]_D^{20}$ +78° (*c* 1·3). IR spectrum: 3 610, 1 042 (hydroxyl); 1 720, 1 280 (benzoate). Mass spectrum, *m/z*: $M^{+\cdot}$ 406. For $C_{27}H_{34}O_3$ (406·5) calculated: 79·76% C, 8·43% H; found 79·55% C, 8·41% H.

The analyses were carried out in the Analytical Laboratory of this Institute by Mrs E. Sýkorová and Mrs E. Šípová under the direction of Dr V. Pechanec. The IR *spectra were recorded by Mrs K. Matoušková under the direction of Dr J. Smolíková. The mass spectra were recorded by Dr F. Tureček.*

REFERENCES

1. Joska J., Fajkoš J., Tureček F.: Collect. Czech. Chem. Commun. *52*, 2991 (1987).
2. Joska J., Fajkoš J., Tureček F.: Tetrahedron Lett. *28*, 2901 (1987).
3. Joska J., Fajkoš J.: Collect. Czech. Chem. Commun. *47*, 2423 (1982).
4. Ginsing R., Cross A. D.: J. Am. Chem. Soc. *87*, 4629 (1965).

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