ANALOGUES OF ANDROGENS WITH THE OPEN RING A*

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The synthesis of the A-nor-3,5-seco analogue of dehydroepiandrosterone (*VII*) is based on different acylation and oxidation rates of the hydroxyl groups in A-nor-3,5-seco-5-androsten--3,17β-diol (*I*). The methyl ester of 5-oxo-17β-pivaloyloxy-A-nor-3,5-secoandrostan-3-oic acid (*X*), accessible from testosterone pivalate, was converted to 4,5-seco analogues of testosterone and methyltestosterone (compounds *XVII* and *XXIII*).

In the past, the structures of physiologically active substances have been submitted to a series of modifications with the aim of preparing substances with a usefully modified activity. One of such structural modifications is the cleavage of the ring in the molecule of the original substance. The recent synthesis[1] of compound *I* opened the way to 3,5-seco analogues of steroid hormones which could assume the same conformation as these hormones, and compete with them in target tissues.

The hydroxyl groups in compound *I* are of different natures and their reactivities can be differentiated. Etherification with triphenylmethyl chloride took place on the 3-hydroxy group only, under formation of compound *IV* which after oxidation and regeneration of the 3-hydroxy group afforded 3-hydroxy-A-nor-3,5-seco-5-androsten--17-one (*VII*). This compound could also be obtained by partial acetylation of diol *I*, followed by oxidation and hydrolysis of the acetoxy ketone *V*. However, in the case of acetylation the differentiation of the reactivities of both hydroxyl groups in compound *I* was not as unambiguous as in the preceding case. The simplest procedure for the synthesis of compound *VII* consists in partial oxidation of diol *I* with pyridinium chlorochromate, affording 45% of the required hydroxy ketone. This result can be further improved by recycling the by-products (*i.e.* 30% of the starting diol *I* and 20% of a mixture of monohydroxy derivatives).

For the preparation of 4,5-seco analogues the following shorter sequence was made use of: 5-oxo-17β-pivaloyloxy-A-nor-3,5-secoandrostan-3-oic acid[2] (*IX*), obtainable from testosterone pivalate, was esterified with methanol and converted[3] to corresponding benzylthioenol ether *XI*. It is known that the course of the reduction with Raney nickel depends on the solvent used[4]: If the reduction of compound *XI* was

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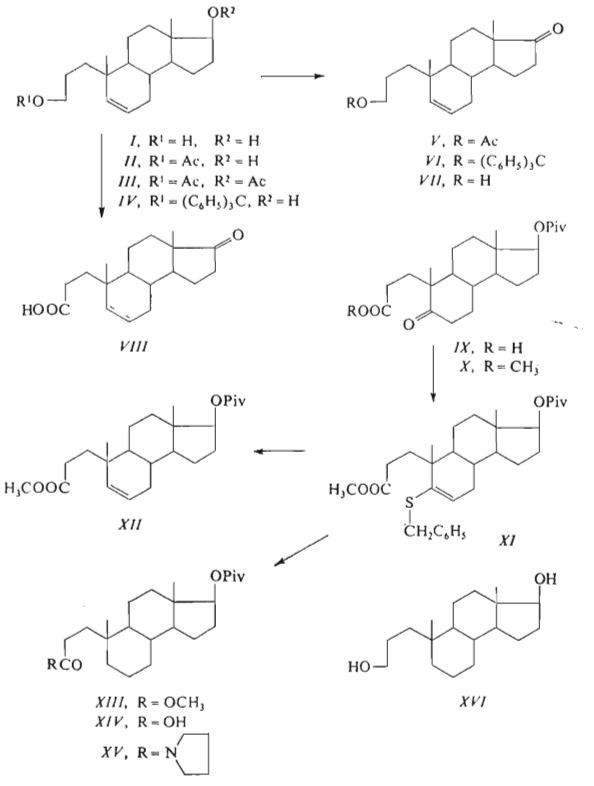
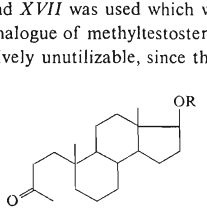
carried out in ethanol, the product was saturated ester *XIII*, without a detectable amount of dehydro product *XII*. For further synthetic purposes compound *XIII* seemed more suitable than *I*, since it directly offered the possibility of introducing various substituents into both physiologically relevant positions (3, 17). The methoxycarbonyl group in compound *XIII* was hydrolysed with lithium bromide in lutidine[5] and the resulting acid *XIV* was converted to the corresponding lithium salt. The action of methyllithium[6] on this salt gave the required 4,5-secotestosterone (*XVII*) which

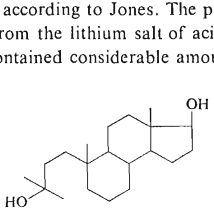


was characterized as acetate *XVIII*. The by-product contained only hydroxy groups in the molecule (IR spectrum), as well as an additional methyl group (^{1}H-NMR spectrum), so that structure *XIX* could be assigned to it. In order to decrease the yield of compound *XIX* in the product after reaction with methyllithium, ester *XIII* was aminolysed and amide *XV* was submitted to the reaction with methyllithium; however, the resulting mixture contained both products in a similar ratio.

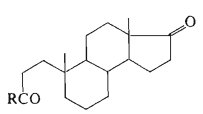
For the preparation of the analogue of androstenedione, *i.e.* compound *XXII*, compound *XVII* was used which was oxidized according to Jones. The preparation of the analogue of methyltestosterone *XXIII* from the lithium salt of acid *XX* was preparatively unutilizable, since the product contained considerable amounts of di-



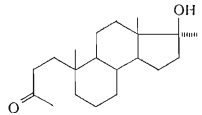
XVII, R = H
XVIII, R = Ac



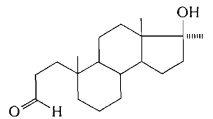
XIX



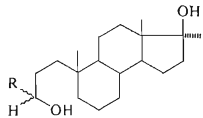
XX, R = OH
XXI, R = H
XXII, R = CH_3



XXIII



XXV



XXIV, R = H
XXVI, R = CH_3

Ac = CH_3CO, Piv = $(CH_3)_3CCO$

ketone *XXII*. We could avoid these problems, due evidently to the low solubility of the lithium salts in the reaction medium, in the following manner: Diol *XVI* was submitted to oxidation with pyridinium chlorochromate[7], affording 17-oxo-A-nor--3,5-secoandrostan-3-al (*XXI*), and 2 molecules of methyllithium were then added

to this compound. The main product of addition, compound *XXVI*, was oxidized according to Jones, affording the required 17β-hydroxy-17-methyl-4,5-secoandrostan--3-one (*XXIII*). The by-products of the reaction of the aldehyde with methyllithium were identified as compounds *XXIII* and *XXIV*; compound *XXIV* can be considered as a product of reduction of the transitorily formed aldehyde *XXV* either with the reagent[8] or with compound *XXVI*.

The biological tests with the analogues described, *VII*, *XVII*, *XXII* and *XXIII*, will be published later.

TABLE I

Characteristic Parameters of the ^{1}H-NMR Spectra

The spectra were measured on a Tesla 60 instrument in deuteriochloroform with tetramethylsilane as internal standard. Chemical shifts are given in the δ-scale (ppm).

Compound	18-H[a]	19-H[a]	3-H	17-H[b]	Other signals
II	0·75	0·88	4·02[c]	3·65	2·02[a], 5·26[d], 5·58[e]
III	0·79	0·88	4·00[c]	4·60	2·02[a], 5·26[d], 5·59[e]
IV	0·75	0·87	3·02[c]	3·65	5·26[d], 5·57[e], 7·32[f]
V	0·92	0·88	4·01[c]	—	5·32[d], 5·63[e], 2·03[a]
VII	0·93	0·89	3·50[c]	—	5·34[d], 5·63[e]
VIII	0·95	0·88	—	—	5·29[d], 5·59[e]
X	0·85	1·10	—	4·58	1·18[g], 3·64[a]
XI	0·79	1·07	—	4·55	1·18[g], 3·83[h], 5·57[i], 7·28[f], 3·63[a]
XII	0·83	0·93	—	4·56	1·18[g], 3·63[a], 5·27[d], 5·63[e]
XIII	0·78	0·86	—	4·54	1·17[g], 3·64[a]
XIV	0·78	0·87	—	4·55	1·18[g]
XV	0·79	0·89	—	4·57	1·18[g], 3·43[j]
XVI	0·71	0·84	3·60[c]	3·60	
XVII	0·72	0·86	—	3·63	2·13[a]
XVIII	0·76	0·84	—	4·58	2·02[a], 2·13[a]
XIX	0·72	0·86	—	3·63	1·18[k]
XX	0·90	0·86	—	—	
XXI	0·88	0·85	—	—	9·78[l]
XXII	0·89	0·86	—	—	2·15[a]
XXIII	0·88	0·85	—	—	1·20[a], 2·15[a]
XXIV	0·84	0·84	3·67[m]	—	1·20[a]
XXVI	0·85	0·88	3·70[n]	—	1·19[o], 1·21[a]

[a] Singlet, 3 protons; [b] triplet, $J = 8$ Hz, 1 proton; [c] triplet, $J = 6$ Hz, 2 protons; [d] $C_{(5)}$-proton signal, $J_{5,6} = 10$ Hz, $J_{5,7} = 1$ Hz; [e] $C_{(6)}$-proton signal, $J_{5,6} = 10$ Hz, $J_{6,7} = 4$ Hz; [f] multiplet, aromatic protons; [g] singlet, 9 protons; [h] singlet, 2 protons; [i] broad doublet, $J = 5$ Hz, 1 proton; [j] multiplet, 4 protons, $W_{1/2} = 11$ Hz; [k] singlet, 6 protons; [l] triplet, $J = 1{\cdot}6$ Hz, 1 proton; [m] multiplet, 2 protons; [n] multiplet, 1 proton; [o] doublet, $J = 6$ Hz, 3 protons.

EXPERIMENTAL

The melting points were measured on a Kofler block and they are not corrected. The infrared spectra and specific rotations were measured in chloroform solution, unless stated otherwise, the ^{1}H-NMR spectra in deuteriochloroform. The identity of the samples prepared in various ways was proved by comparison of the infrared spectra and on the basis of mixture melting point determinations.

Partial Acetylation of A-Nor-3,5-seco-5-androsten-3,17β-diol

The dihydroxy derivative *I* (350 mg) was dissolved in a mixture of benzene (4 ml) and pyridine (5 ml) and acetic anhydride (2 ml) was added to the solution at room temperature. After 90 min standing the excess of anhydride was decomposed by addition of methanol (3 ml). After 1 h the volatile components were evaporated in a vacuum and the residue was applied on a silica gel thin layer, which was then developed in benzene containing 20% of ether. The most unpolar component was 3,17β-diacetoxy-A-nor-3,5-seco-5-androstene (*III*, 122 mg), $[\alpha]_D^{20}$ −28 (*c* 1·1), IR spectrum (CCl_4): 1743, 1730, 1245, 1043, 1036 (CH_3COO groups) and 1659, 3065 (C=C double bond) cm^{-1}; for $C_{22}H_{34}O_4$ (362·5) calculated: 72·78% C, 9·45% H; found: 72·98% C, 9·74% H. Further components (in order of increasing polarity) were: 3-Acetoxy-A-nor-3,5-seco-5-androsten-17β-ol (*II*, 185 mg), $[\alpha]_D^{20}$ −27° (*c* 0·9). IR spectrum (CCl_4): 3625, 1057 (OH group), 1744, 1728, 1243, 1040 (CH_3COO group) and 3065, 1660 (C=C double bond) cm^{-1}; for $C_{20}H_{32}O_3$ (320·5) calculated: 74·95% C, 10·07% H; found: 74·67% C, 9·95% H. A-Nor-3,5-seco-5-androsten-3,17β-diol (*I*, 55 mg), R_F and the melting point was identical with the values for an authentic specimen of compound *I*.

3-Triphenylmethoxy-A-nor-3,5-seco-5-androsten-17β-ol (*IV*)

Dihydroxy derivative *I* (100 mg) was reacted with triphenylmethyl chloride (100 mg) in pyridine (1·5 ml) at 100°C. After 2 h the solvent was evaporated under reduced pressure and the residue applied on a thin layer of silica gel. After development in a mixture of 10% of ether in benzene the product was eluted with ether. Yield, 114 mg, $[\alpha]_D^{20}$ −18° (*c* 0·9). For $C_{37}H_{44}O_2$ (520·7) calculated: 85·34% C, 8·52% H; found: 85·11% C, 8·79% H.

3-Acetoxy-A-nor-3,5-seco-5-androsten-17-one (*V*)

Hydroxy compound *II* (160 mg) was oxidized in acetone with Jones's reagent, the mixture was poured into an aqueous potassium hydrogen carbonate solution and the product was extracted with ether. The extract was washed with water, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by thin-layer chromatography on silica gel (10% ether in benzene), m.p. 66–67°C (methanol), $[\alpha]_D^{20}$ +32° (*c* 1·2). For $C_{20}H_{30}O_3$ (318·5) calculated: 75·43% C, 9·50% H; found: 75·16% C, 9·19% H.

3-Hydroxy-A-nor-3,5-seco-5-androsten-17-one (*VII*)

a) *From acetate* V: Hydrochloric acid (0·2 ml) was added to a solution of compound *V* (210 mg) in 6 ml of methanol and 0·6 ml of chloroform and the mixture was allowed to stand at 37°C for 24 h. The solution was diluted with water, the precipitated material was extracted with ether and the extract washed with aqueous potassium hydrogen carbonate solution, and with water. After drying over sodium sulfate and evaporation the residue was crystallized from acetone

and heptane to afford 115 mg of pure compound of m.p. 102–104°C, $[\alpha]_D^{20}$ +36° (*c* 1·0). IR spectrum (CCl_4): 1744 (keto group), 3635, 1058, 1019 (hydroxy group) cm^{-1}. For $C_{18}H_{28}O_2$ (276·4) calculated: 78·21% C, 10·21% H; found: 77·95% C, 10·40% H.

b) *From triphenylmethoxy derivative* IV: 65 mg of compound *IV* were oxidized according to Jones and the crude product was heated with 10 ml of 90% aqueous acetic acid at 90°C for 10 min. The solution was evaporated in a vacuum and the residue chromatographed on a thin layer of silica gel (40% of ether in benzene). The more polar component of the mixture, eluted with ether, was found identical with the compound prepared under *a*) (30 mg).

c) *From diol* I: A suspension of compound *I* (20 mg) and pyridinium chlorochromate (80 mg) in 1·5 ml of dichloromethane was stirred at 25°C for 6 min, then poured onto a column of silica gel (2 g) and the organic material was eluted with 70 ml of 20% acetone in light petroleum. The eluate was evaporated in a vacuum and the residue chromatographed on a thin layer of silica gel. The main product was found identical in all respects with ketone *VII* (8·6 mg, 43%, or 62% per the reacted compound *I*).

17-Oxo-A-nor-3,5-seco-5-androsten-3-oic Acid (*VIII*)

Dihydroxy derivative *I* (40 mg) was oxidized according to Jones at room temperature, the product was extracted with ether, washed with water and dried by filtration through a column of sodium sulfate. The product was crystallized from acetone and heptane, m.p. 157–159°C (24 mg), $[\alpha]_D^{20}$ +35° (*c* 1·2); IR spectrum: 1739 (17-oxo group), 1712 (carboxyl group), 1661 (C=C double bond) cm^{-1}. For $C_{18}H_{26}O_3$ (290·4) calculated: 74·44% C, 9·03% H; found: 74·63% C, 9·16% H.

Methyl Ester of 5-Oxo-17β-pivaloyloxy-A-nor-3,5-secoandrosten-3-oic Acid (*X*)

The acid *IX* (9 g) (ref.[2]) was dissolved in 15 ml of dichloromethane and 85 ml of methanol, hydrochloric acid (2 ml) was added to the solution and the mixture was allowed to stand at 40°C for 48 h. The larger part of the solvents was evaporated in a vacuum and the product was precipitated by addition of water. The dried product crystallized from methanol at −70°C, m.p. 75–76°C, $[\alpha]_D^{20}$ +50° (*c* 0·8); IR spectrum (CCl_4): 1710, 1740, 1438, 1165, 1730, 1286 cm^{-1}. For $C_{24}H_{38}O_5$ (406·5) calculated: 70·90% C, 9·42% H; found: 71·06% C, 9·51% H.

Methyl 5-Benzylthio-17β-pivaloyloxy-A-nor-3,5-seco-5-androsten-3-oate (*XI*)

A solution of ketone *X* (9 g) and *p*-toluenesulfonic acid (0·5 g) in benzene (150 ml) and benzyl mercaptan (6 ml) was refluxed and the water formed was bound with a molecular sieve (60 g) placed in the Soxhlet adapter. After 48 h the mixture was cooled and washed with a 10% potassium hydroxide solution (totally 800 ml) and water and dried over sulfate. After evaporation the product was chromatographed on 300 g of silica gel using 10% ether in light petroleum for elution. The main product (7·5 g) crystallized from methanol, m.p. 79–81°C. $[\alpha]_D^{20}$ −20° (*c* 1·2); IR spectrum: 1712, 1295, 1173 (pivaloyloxy group), 1603, 1585 (benzyl group), 1722, 1173, 1438 (methoxycarbonyl group), 1628 (C=C double bond) cm^{-1}. For $C_{31}H_{44}O_4S$ (512·7) calculated: 72·61% C, 8·65% H; found: 72·81% C, 6·36% H.

Methyl 17β-Pivaloyloxy-A-nor-3,5-seco-5-androsten-3-oate (*XII*)

Freshly prepared Raney nickel (30 g) was stirred in 130 ml of boiling acetone. A solution of thio derivative *XI* (0·9 g) in acetone was then poured to the above stirred suspension and the mixture

was then refluxed for another 12 h. The inorganic material was filtered off and the filtrate concentrated *in vacuo*. The residue was purified by chromatography on silica gel (with 10% ether in light petroleum). M.p. 63–65°C (methanol, 0·3 g), $[\alpha]_D^{20}$ −23° (*c* 0·9). IR spectrum: 1730, 1288, 1165 (pivaloyloxy group), 1740, 1438 (methoxycarbonyl group) cm^{-1}. For $C_{24}H_{38}O_4$ (390·5) calculated: 73·81% C, 9·81% H; found: 73·65% C, 9·71% H.

Methyl 17β-Pivaloyloxy-A-nor-3,5-secoandrostan-3-oate (*XIII*)

A solution of 9 g of benzylthio derivative *XI* in 100 ml of ethanol was poured into a stirred suspension of freshly prepared Raney nickel (250 g) in boiling ethanol (400 ml). After 6 h refluxing the mixture was worked up as in the preceding experiment and the product (5·4 g) was crystallized from methanol. M.p. 97–98°C, $[\alpha]_D^{20}$ +10° (*c* 1·1); IR spectrum (CCl_4): 1740, 1438 (methoxycarbonyl group), 1730, 1288 (pivaloyloxy group), 1165 cm^{-1} For $C_{24}H_{40}O_4$ (392·6) calculated: 73·43% C, 10·27% H; found: 73·31% C, 10·19% H.

A-Nor-3,5-seco-5-androsten-3,17β-diol (*I*)

Diester *XII* (350 mg) was refluxed with a suspension of lithium aluminum hydride (about 200 mg) in dioxane (25 ml). After 4 h the excess of hydride was decomposed by addition of a few drops of a saturated sodium sulfate solution in water and the mixture was saturated with anhydrous sodium sulfate. The the inorganic material was filtered off and washed with chloroform. The filtrate was concentrated *in vacuo* and the residue crystallized from acetone, m.p. 143–145°C (220 mg), $[\alpha]_D^{20}$ −36° (*c* 1·1). The substance was identical with a sample prepared in a different way[1].

A-Nor-3,5-secoandrostan-3,17β-diol (*XVI*)

Diester *XIII* (1 g) was reduced to diol *XVI* (0·7 g) in a similar manner. M.p. 159–161°C, $[\alpha]_D^{20}$ +11° (*c* 0·9). For $C_{18}H_{32}O_2$ (280·4) calculated: 77·09% C, 11·50% H; found: 76·94% C, 11·50% H.

N-(17β-Pivaloyloxy-A-nor-3,5-secoandrostan-3-oyl)pyrrolidine (*XV*)

A solution of diester *XIII* (1 g) in pyrrolidine (10 ml) was refluxed for 48 h. The solution was concentrated under reduced pressure and the residue was crystallized from acetone. M.p. 165 to 167°C (1·08 g), $[\alpha]_D^{20}$ +14° (*c* 1·4), IR spectrum: 1628, 1448 (amide group), 1718, 1175, 1293 (ester group) cm^{-1}. For $C_{27}H_{43}O_3N$ (429·6) calculated: 75·48% C, 10·09% H; found: 75·21% C, 10·16% H.

17β-Pivaloyloxy-A-nor-3,5-secoandrostan-3-oic Acid (*XIV*)

Diester *XIII* (0·8 g) was submitted to the action of lithium bromide (1·7 g) in boiling lutidine (40 ml) After 48 h refluxing the mixture was cooled, poured onto ice with hydrochloric acid and the separated product was extracted with chloroform. The extract was washed with water, dried and concentrated in a vacuum. The residue (0·78 g) crystallized from acetone, m.p.201–202·5°C, $[\alpha]_D^{20}$ +9° (*c* 1·4). For $C_{23}H_{38}O_4$ (378·5) calculated: 72·97% C, 10·12% H; found: 73·05% C, 10·02% H.

17-Oxo-A-nor-3,5-secoandrostan-3-oic Acid (*XX*)

Diol *XVI* (350 mg) was oxidized according to Jones in acetone at 20°C, the mixture was decomposed with saturated sodium chloride in water, the product was extracted with chloroform, washed twice with water and dried. After concentration to dryness the product crystallized from aqueous acetone, m.p. 176–177°C, $[\alpha]_D^{20}$ +83° (*c* 1·3); IR spectrum: 1736 (keto group, 1711, 2400–3400 (carxonyl grouo) cm^{-1}. For $C_{18}H_{28}O_3$ (292·4) calculated: 73·93% C, 9·65% H; found: 74·10% C, 9·81% H.

17β-Hydroxy-4,5-secoandrostan-3-one (*XVII*)

a) *From amide* XV: Amide *XV* (940 mg) was dried by azeotropic distillation with toluene and evaporation of the solvent. Methyllithium in ether (100 ml, *c* = 15 mg/ml) was added to the residue and the mixture was refluxed for 7 h. The solution was poured onto ice (about 200 g) acidified with concentrated hydrochloric acid (40 ml), the precipitated product was extracted with ether, the extract washed with aqueous sodium thiosulfate and water, dried and concentrated. Chromatography of the residue on silica gel (with 40% of ether in light petroleum) gave 420 mg of compound *XVII*, m.p. 58–60°C (cyclohexane), $[\alpha]_D^{20}$ +15° (*c* 1·2); IR spectrum (CCl_4): 3615 (hydroxy group), 1710, 1359, 1411 (keto group) cm^{-1}. For $C_{19}H_{32}O_2$ (292·4) calculated: 78·03% C, 11·03% H; found: 78·11% C, 11·17% H. The more polar admixture (*XIX*, 151 mg) crystallized from acetone and cyclohexane, m.p. 158–159°C. $[\alpha]_D^{20}$ +10° (*c* 1·3); IR spectrum (CCl_4): 3615, 1053 cm^{-1}. For $C_{19}H_{32}O_2$ (292·4) calculated: 78·03% C, 11·03% H; found: 78·11% C, 11·17% H.

b) *From acid* XX: A solution of lithium hydroxide (12·4 mg) in 0·5 ml of water was added to a solution of acid *XX* (195 mg) in 5 ml of methanol and the mixture was refluxed for 5 min. After evaporation in a vacuum the residue was dried by azeotropic distillation with toluene and evaporation and the residue was additioned with a solution of methyllithium in ether (10 ml, *c* = 19 mg/ml). The mixture was allowed to stand at room temperature for 48 h, then decomposed as in the preceding case and the products were separated chromatographically on thin layers of silica gel. The yield of compound *XVII* was 99 mg, of compound *XIX* 46 mg.

17β-Acetoxy-4,5-secoandrostan-3-one (*XVIII*)

Acetylation of hydroxy derivative *XVII* (210 mg) was carried out using acetic anhydride (1 ml) and pyridine (1 ml), at 20°C. After 18 g standing mixture was diluted with 10 ml of ethanol and evaporated in a vacuum. The residue crystallized from methanol, m.p. 50–52°C, $[\alpha]_D^{20}$ +8° (*c* 1·0); IR spectrum (CCl_4): 1739, 1250, 1043 (acetoxy group), 1721, 1360 (keto group) cm^{-1}. For $C_{22}H_{34}O_3$ (334·5) calculated: 75·40% C, 10·25% H; found: 75·31% C, 10·07% H.

4,5-Secoandrostan-3,17-dione (*XXII*)

Hydroxy ketone *XVII* (130 mg) was oxidized according to Jones at 0°C; after 5 min reaction the product was isolated. Diketone *XX* (120 mg) crystallized from methanol at −70°C, m.p. 68 to 70°C, $[\alpha]_D^{20}$ +82° (*c* 1·1); IR spectrum: 1722, 1356, 1418 (3-keto group), 1744, 1409 (17-keto group) cm^{-1}. For $C_{19}H_{30}O_2$ (290·4) calculated: 78·57% C, 10·41% H; found: 78·36% C, 10·29% H.

17-Oxo-A-nor-3,5-secoandrostan-3-al (*XIIII*)

A suspension of diol *XVI* (0·5 g) and pyridinium chlorochromate (2 g) in 70 ml of dichloromethane was stirred at 20°C for 3 h. The mixture was poured onto a column of silica gel (10 g)

which was eluted with 25% acetone in light petroleum (a total of 150 ml). The solution was concentrated in a vacuum and crystallized from acetone–heptane at −80°C. M.p. 74−75°C (0·31 g), $[\alpha]_D^{20}$ +84° (*c* 0·9); IR spectrum (CCl_4): 1746(keto group), 1732 (aldehyde group)cm^{-1}. For $C_{18}H_{28}O_2$ (276·4) calculated: 78·21% C, 10·21% H; found: 77·95% C, 10·36% H.

17β-Hydroxy-17-methyl-A-nor-4,5-secoandrostan-3-one (*XXIII*)

A solution of aldehyde *XXI* (130 mg) in 6 ml of tetrahydrofuran was added dropwise and under stirring to a solution of methyllithium in ether (20 ml, *c* = 18 mg/ml). The reaction was terminated by refluxing for 5 h. The mixture was poured into ice, the product extracted with chloroform, washed with water, dried and evaporated. Chromatography of the residue on silica gel gave 71 mg of product *XXVI*, 17 mg of a lipophilic fraction the IR spectrum of which proved the identity with compound *XXIII* and 40 mg of a hydrophilic fraction (diol *XXIV*, IR spectrum: 3615, 1085 cm^{-1}; after oxidation 3610, 1712, 1410 cm^{-1}). The main product was oxidized according to Jones, affording 17β-hydroxy-17-methyl-4,5-secoandrostan-3-one (*XXIII*, 70 mg. $[\alpha]_D^{20}$ −10° (*c* 1·1); IR spectrum: 3625, 1721, 1714 (inflexion), 1355 cm^{-1}. For $C_{20}H_{34}O_2$ (306·5) calculated: 78·38% C, 11·18% H; found: 78·11% C, 11·35% H.

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