fect in the case of the third methoxyl group, and the C8–O5 bond is accordingly long [1.399 (4) Å]. All three methoxyl groups adopt staggered conformations about the methyl–oxygen bond.

A projection down the *c* axis (Figure 2; the *a* axis is horizontal and the *b* axis vertical) shows the molecular packing. The shortest intermolecular distance is 2.21 (5) Å, between H4 and H9. The shortest intermolecular distance between nonhydrogen atoms (O7 and C11) is 3.325 (5) Å.

Registry No.—5′-Demethoxy-β-peltatin A methyl ether, 32970-80-2.

Acknowledgments.—We thank Drs. E. Bianchi and J. R. Cole of our Pharmacy Department for providing crystals, Drs. L. L. Reed and Paul Johnson for helpful advice, the Computer Center of the University of Arizona for computer time, and the National Cancer Institute (CA-10944) and Sloan Foundation (fellowship to R. B. B.) for financial aid.

Reduction of α,β-Oxido Ketones with Chromous Acetate. Synthesis of 3β,5β,17β,19-Tetrahydroxy-5β-androstane, a Degradation Product of Strophanthidin[1,2]

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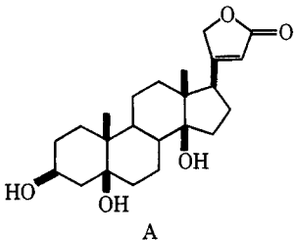
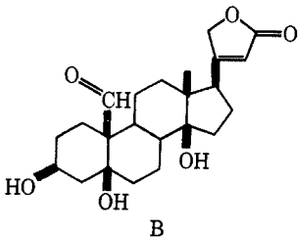
Received July 22, 1971

The reaction of steroidal α,β-oxido ketones with chromous acetate has been studied, using a variety of solvents, as a potential route to the A/B ring system of some cardiac-active steroids. These reductions generate β-hydroxy ketones with retention of configuration at the β-carbon atom, along with the corresponding α,β-unsaturated ketones. The β-hydroxy ketone formed in the reaction is stable to the reaction conditions. Steroidal 4β,5β-oxido-3 and 4α,5α-oxido-3 ketones give respectively 5β-hydroxy- and 5α-hydroxy-3-oxo steroids on reduction with chromous acetate, while 6α,7α-oxido-4-cholesten-3-one generates the biosynthetically interesting 7α-hydroxy-4-cholesten-3-one. Yields of β-hydroxy ketone are approximately 50% in the cases studied. The reaction has been used to prepare 3β,5β,17β,19-tetrahydroxy-5β-androstane, a degradation product of strophanthidin.

In a search for new ways to generate the 3β,5β-dihydroxy system found in cardiac-active steroids such as periplogenin (A) and strophanthidin (B), we con-

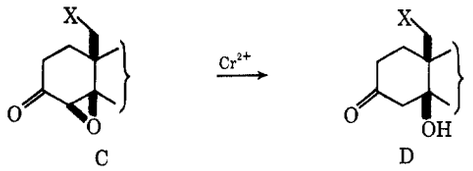


A



B

sidered the possibility of reduction of an α,β-oxido ketone (as C) with chromous ion. Cleavage of the C–O bond α to the ketone should occur, giving the required stereochemistry for the resulting tertiary hydroxyl group at the β carbon. Furthermore, α,β-oxido ketones are readily available by the action of alkaline hydrogen peroxide on the corresponding α,β-unsaturated ketones. If X were hydrogen or an oxygenated function, subsequent reduction of the carbonyl group in D to an axial alcohol would provide the re-



C D

quired A/B ring system found in such compounds as periplogenin and strophanthidin.

(1) Abstract 158, 23rd International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971.

(2) This work was supported, in part, by U. S. Public Health Service Grants HE-08913, AM-07422, and GM 16492.

Numerous examples of the reaction of α,β-oxido ketones with chromous chloride can be found in the literature.[3,4] These reactions, however, invariably generate the α,β-unsaturated ketone in high yield, as illustrated[3a] by the conversion of 4,5β-oxidocholestan-3-one to 4-cholesten-3-one with chromous chloride. The conversions[5] of steroidal 16α,17α-oxido-20 ketones to the corresponding 16α-hydroxy-20 ketones using chromous acetate in acetic acid represent the only reported examples of β-hydroxy ketone formation from α,β-oxido ketone with chromous ion. These observations, coupled with the fact that the reported chromous chloride reactions all involve strongly acid solutions (which might convert any β-hydroxy ketone to the conjugated ketone), encouraged us to study reduction of the model compound 4β,5β-oxidocholestan-3-one (1) (Chart I) with chromous acetate.

Studies were carried out with a variety of solvents (dimethylformamide, *N*-methylpyrrolidinone, tetrahydrofuran, diglyme, ethanol, aqueous acetone, acetic acid–sodium acetate) at room temperature, under an atmosphere of carbon dioxide, using up to a tenfold excess of chromous acetate. Conversion of the oxido ketone **1** to the 5β-hydroxy ketone **2** was best effected (*ca.* 50% yield of isolated pure product) by use of a large excess (5–10 molar equiv) of freshly prepared chromous acetate in absolute ethanol or, better,

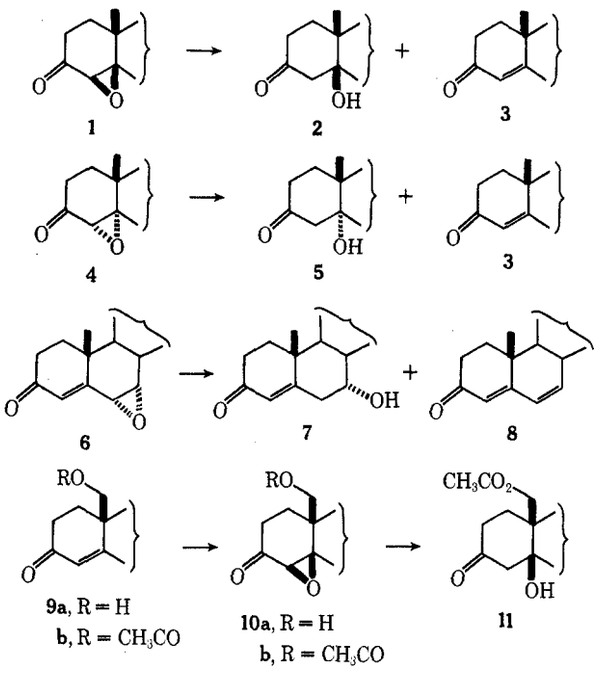
(3) *Cf.* (a) W. Cole and P. L. Julian, *J. Org. Chem.*, **19**, 131 (1954); (b) D. Arigoni, D. H. R. Barton, E. J. Corey, and O. Jeger, *Experientia*, **16**, 41 (1960); (c) A. Akisanya, C. W. L. Bevan, T. G. Halsall, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc.*, 3705 (1961).

(4) For a recent review of reductions of organic compounds with chromous salts, see J. R. Hanson and E. Premuzic, *Angew. Chem., Int. Ed. Engl.*, **7**, 247 (1968).

(5) V. Schwarz, *Collect. Czech. Chem. Commun.*, **26**, 1207 (1961). See also R. Neher, P. Desaulles, E. Vischer, P. Wieland, and A. Wettstein, *Helv. Chim. Acta*, **41**, 1667 (1958), as well as ref 3 and 4.

in aqueous acetone. In the latter case, buffering with sodium acetate–acetic acid had a beneficial effect[6] because work-up was easier. The balance of the reaction product was invariably the α,β-unsaturated ketone **3**. Lowering the reaction temperature to $-60°$ had essentially no effect on the ratio of products **2** and **3**. Because compound **3** can be reconverted to oxido ketone **1** in yields of better than 90%, the reduction of **1** to 5β-hydroxy ketone **2** can be accomplished efficiently if recycling of **3** is undertaken.

CHART I
CHOLESTANE SERIES



We had supposed originally that the conjugated ketone **3** arose by dehydration of β-hydroxy ketone **2**. However, the formation of **3** in closely similar proportions in both ethanol and the buffered aqueous acetone system seems to contradict this notion. Furthermore, when β-hydroxy ketone **2** was subjected to the chromous acetate–ethanol reaction conditions, it was recovered unchanged. Thus, **2** and **3** appear to be formed from the oxido ketone **1** by different pathways. Such paths might include delivery of electrons from chromous ion directly into the C-3 carbonyl, with eventual formation of a 5β-hydroxy-Δ^3-enol, or attack by chromous ion at C-4 with oxide opening to produce a C-4 organochromium intermediate.

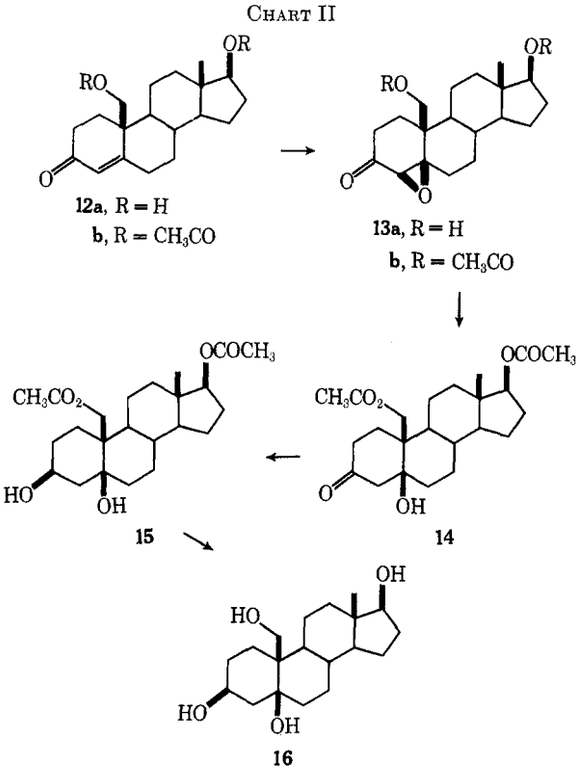
Two other steroidal oxido ketones were then studied. When the 4α,5α-oxido-3 ketone[7] **4** was reduced with chromous acetate in ethanol, the 5α-hydroxy-3 ketone **5** was obtained pure in 46% yield, along with the conjugated ketone **3**.

The γ,δ-oxido-α,β-unsaturated ketone[8] **6** gave, on reduction with chromous acetate in aqueous acetone, 7α-hydroxy-4-cholesten-3-one[9] (**7**) in 50% yield, as well as the dienone[10] **8**. The 7α-hydroxy compound **7** has been of considerable interest in connection with bile acid biosynthesis, and its synthesis[9,11] has hitherto been difficult. The present method offers a simple route from readily available starting material.

In the above cases, as well as in the reported[5] reductions of the 16α,17α-oxido-20-oxo steroid system to 16α-hydroxy-20 ketone with chromous acetate, stereochemical integrity is retained at the carbon bearing the new hydroxyl group.

We now turned to C-19-oxygenated steroids, and converted 19-hydroxytestosterone[12] (**12a**) (Chart II)

CHART II



to the 4β,5β-oxido compound **13a** and thence to the corresponding 17β,19-diacetate **13b**. The analytical and spectroscopic data were consistent with the structures and stereochemistry shown, and the β orientation of the oxido group was further confirmed by CD measurements.[13,14] Reduction of compounds **13a** and **13b** with chromous acetate in aqueous acetone gave interesting and unexpected results. In contrast to our earlier observations with C-10 methyl steroids, the 4β,5β-oxido diol **13a** gave a quantitative yield of 19-hydroxytestosterone, with *none* of the expected 5β-hydroxy ketone. On the other hand, the 4β,5β-oxido diacetate **13b** behaved as expected, and gave 5β,17β,19-trihydroxyandrostan-3-one 17β,19-diacetate (**14**) in

(6) We thank Dr. K. H. Overton (Glasgow University) for kindly providing unpublished details of chromous acetate reductions in buffered aqueous acetone in the triterpene series.

(7) E. P. Oliveto, C. Gerold, and E. B. Hershberg, *J. Amer. Chem. Soc.*, **79**, 3596 (1957).

(8) A. Nickon and J. F. Bagli, *ibid.*, **83**, 1498 (1961).

(9) H. Danielsson, *Acta Chem. Scand.*, **15**, 242 (1961).

(10) L. Mandell, *J. Amer. Chem. Soc.*, **78**, 3199 (1956).

(11) I. Björkhem, H. Danielsson, C. Issidorides, and A. Kallner, *Acta Chem. Scand.*, **19**, 2151 (1965).

(12) M. Ehrenstein and K. Otto, *J. Org. Chem.*, **24**, 2006 (1959).

(13) *Cf.* K. Kuriyama, H. Tada, Y. K. Sawa, S. Ito, and I. Itoh, *Tetrahedron Lett.*, 2539 (1968).

(14) We thank Dr. G. Snatzke (Bonn) for the circular dichroism data reported in this paper.

over 60% yield, under exactly the same conditions. The structure and stereochemistry of **14** followed from the analytical and spectroscopic data, including CD. In addition, 19-hydroxytestosterone diacetate (**12b**) was isolated from the chromous acetate reduction of **13b**.

Exactly analogous observations were made in the cholestane series. Thus, whereas the 19-hydroxy-4β,5β-oxido-3 ketone **10a** gave 19-hydroxy-4-cholesten-3-one (**9a**) quantitatively on reduction with chromous acetate, the corresponding 19-acetoxy-4β,5β-oxido compound **10b** gave the 5β-hydroxy-3 ketone **11** under the same conditions. This difference between 10-methyl- and 19-acetoxy-4β,5β-oxido-3 ketones on the one hand and the corresponding 19-hydroxy compounds on the other is interesting. If, as suggested by our earlier experiments, conjugated ketone formation occurs by a different path than does β-hydroxy ketone formation, the presence of a 19-hydroxyl apparently assists the former process. The C-19 hydroxyl group may act as a ligand to chromium, and may then facilitate intramolecular electron delivery.

Returning now to the 5β-hydroxyandrostane derivative **14**, it remained only to reduce the C-3 carbonyl to an axial hydroxyl group, in order to secure the 3β,5β,19-triol system. Model experiments carried out with 5β-hydroxycholestan-3-one showed that, of a variety of reducing agents (sodium borohydride–methanol, lithium aluminum tri-*tert*-butoxyhydride, lithium aluminum hydride–methanol–tetrahydrofuran, trimethylamine–borane in diglyme, W-2 Raney nickel in ethanol) only W-2 Raney nickel in refluxing ethanol favored reduction to axial alcohol at C-3, giving predominantly cholestane-3β,5β-diol. The 5β-hydroxyandrostane derivative **14** was then reduced at C-3 with W-2 Raney nickel in refluxing ethanol to give, in 70% yield, the desired 3β,5β,17β,19-tetrahydroxyandrostane 17β,19-diacetate (**15**). This product (**15**) could be oxidized back to the starting ketone **14** with chromium trioxide–acetone–sulfuric acid, and the nmr spectrum of **15** attested to the axial nature of the newly introduced C-3 hydroxyl group. Finally, basic hydrolysis of compound **15** yielded 3β,5β,17β,19-tetrahydroxyandrostane (**16**) which proved to be identical with an authentic sample obtained[15] by degradation of strophanthidin. The sequence of reactions outlined above seems to have promise as a route to 3β,5β-dihydroxy steroids, with or without C-19 oxygenation. More generally, the chromous acetate method appears to be useful for reduction of α,β- and vinylogous α,β-oxido ketones to the often difficultly accessible β- and vinylogous β-hydroxy ketones.

Experimental Section[16]

5β-Hydroxycholestan-3-one (2) by Chromous Acetate Reduction of 4,5β-Oxidocholestan-3-one (1). A.—To a stirred solution of 4,5β-oxidocholestan-3-one (1, 509 mg) in ethanol (50 ml) at room temperature, under an atmosphere of carbon dioxide, was added freshly prepared chromous acetate[17] (1.9 g) and after 1 hr the mixture was evaporated *in vacuo* at 30°. Water was added, the mixture was extracted with ethyl acetate, and the organic extract was filtered through Celite. The filtered ethyl acetate solution was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. Preparative tlc of the residue (chloroform–ethyl acetate, 92.5:7.5) gave (a) 264 mg of 4-cholesten-3-one (**3**) identical with an authentic specimen as judged by melting point, mixture melting point, tlc, and infrared comparison and (b) 232 mg of 5β-hydroxycholestan-3-one[18] (**2**), identical with an authentic sample by melting point, mixture melting point, tlc, and infrared comparison.

B.—To a stirred solution of 4,5β-oxidocholestan-3-one (1, 15.4 mg) in acetone (3.1 ml) and water (0.5 ml) under an atmosphere of carbon dioxide was added freshly prepared chromous acetate (32 mg). After 10 min a further portion (26 mg) of chromous acetate was added, and stirring was continued for another 15 min. The reaction mixture was evaporated under a jet of nitrogen, and the residue was triturated with water and extracted with chloroform. The chloroform extract was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. Preparative tlc (solvent system as in A above) gave 4-cholesten-3-one (**3**, 7 mg) and 5β-hydroxycholestan-3-one (**2**, 7 mg), each compound being identified by melting point, mixture melting point, tlc, and infrared comparison with authentic samples.

5α-Hydroxycholestan-3-one (5) by Chromous Acetate Reduction of 4,5α-Oxidocholestan-3-one (4).—4,5α-Oxidocholestan-3-one (**4**, 140 mg) in ethanol (15 ml) was allowed to react with freshly prepared chromous acetate (560 mg) for 30 min, exactly as for the preparation of compound **2** above, except that the product was extracted with benzene. Preparative tlc (chloroform–ethyl acetate, 9:1) gave (a) 4-cholesten-3-one (**3**, 37 mg) identical with an authentic sample as judged by melting point, mixture melting point, tlc, and infrared comparison; (b) 5α-hydroxycholestan-3-one[19] (**5**, 65 mg), identity with an authentic specimen proved by melting point, mixture melting point, tlc, and infrared comparison.

Reduction of 6α,7α-Oxido-4-cholesten-3-one (6) with Chromous Acetate to Give 7α-Hydroxy-4-cholesten-3-one (7).—To a stirred solution of the oxido ketone **6** (160 mg) in acetone (36 ml) was added a solution of sodium acetate trihydrate (1.47 g) in water (4.0 ml) and acetic acid (1.0 ml) followed by chromous acetate (500 mg) in one portion. After 25 min the reaction mixture was evaporated *in vacuo* at 25°, and the residue was triturated with water and extracted with ethyl acetate. The organic extracts were washed with water, dried (Na_2SO_4), and evaporated *in vacuo* at 25°, and the crude product was chromatographed on silica gel (9.5 g). Elution with benzene–chloroform (3:7) gave 4,6-cholestadien-3-one[10] (**8**, 54 mg) identical with authentic material[20] as judged by melting point, mixture melting point, infrared spectra, and tlc comparison.

Elution with benzene–chloroform (1:1) gave crude 7α-hydroxy-4-cholesten-3-one (**7**, 80 mg) which was freed from minor impurities by preparative tlc (chloroform–ethyl acetate, 49:1), giving pure 7α-hydroxy-4-cholesten-3-one[11] (**7**, 60 mg), mp 179–182° (undepressed on admixture with authentic material[21] of mp 180–182°), identical with authentic material by infrared and tlc comparison.

Although the above experiment was carried out using sodium acetate buffer, a subsequent experiment using acetone–water (9:1) alone as the reaction medium gave closely comparable results.

(15) M. Ehrenstein and M. Dünnenberger, *J. Org. Chem.*, **21**, 774 (1956).

(16) Melting points were measured on the Kofler block. Optical rotations were measured in chloroform solution and circular dichroism measurements were made with the Roussel–Jouan dichrograph using dioxane solutions (0.5–0.6 mg/g) at 20°. Nmr chemical shifts are given in parts per million on the δ scale (TMS = 0), and infrared spectra were recorded using chloroform solutions unless otherwise specified. For tlc, silica gel GF254 was used in 0.25-mm layers for analytical purposes and in 2-mm layers for preparative work.

(17) Chromous acetate was obtained by reaction of air-free sodium acetate solution with aqueous chromous chloride, under an atmosphere of carbon dioxide, essentially as described by J. H. Balthis and J. C. Bailar, *Inorg. Syn.*, **1**, 122 (1939). The precipitated chromous acetate was filtered off and washed successively with deoxygenated water, absolute ethanol, and ether, all operations being carried out under an atmosphere of carbon dioxide. The brick red precipitate was dried by suction on the filter, still in the absence of air, and was then used immediately. Prolonged drying in a vacuum desiccator often resulted in decomposition of the chromous acetate, and such drying was therefore avoided.

(18) P. A. Plattner, H. Heusser, and A. B. Kulkarni, *Helv. Chim. Acta*, **31**, 1822 (1948).

(19) P. A. Plattner, A. Fürst, F. Koller, and W. Lang, *ibid.*, **31**, 1455 (1948).

(20) We thank Dr. A. Nickon, Johns Hopkins University, for kindly supplying an authentic specimen of 4,6-cholestadien-3-one.

(21) We thank Dr. H. Danielsson, Karolinska Institute, for kindly supplying an authentic sample of 7α-hydroxy-4-cholesten-3-one.

4β,5β-Oxido-19-hydroxycholestan-3-one (10a).—Ice-cold 30% aqueous hydrogen peroxide (8.5 ml) was added dropwise to a stirred ice-cooled solution of 19-hydroxy-4-cholesten-3-one[22] (**9a**, 1.67 g) in dioxane (100 ml) and aqueous sodium hydroxide (5 *N*, 8.5 ml). The reaction mixture was allowed to warm to 25°, and stirring was continued for 20 hr at 25°. Acetic acid (2 ml) was then added, followed by water, and the mixture was extracted three times with methylene chloride. The organic extract was washed successively with aqueous ferrous sulfate solution and water, dried (Na_2SO_4), and evaporated *in vacuo*, giving the crude product (1.73 g). Crystallization from ethyl acetate–petroleum ether (bp 30–60°) gave pure oxido ketone **10a** (1.14 g): mp 160–162°; $[\alpha]D$ +123°; ν_{max} 3660, 3510, 1715 cm^{-1}; nmr ($CDCl_3$) δ 0.73 (s, 3, C-18 CH_3), 2.91 (s, 1, C-4 H), 3.98 (2 d, 2, J = 11 Hz, C-19 CH_2OH); mass spectrum m/e 416 (M^+), 400, 398, 386, 385, 370.

Anal. Calcd for $C_{27}H_{44}O_3$: C, 77.83; H, 10.65. Found: C, 77.79; H, 10.65.

4β,5β-Oxido-19-hydroxycholestan-3-one 19-Acetate (10b).—The oxido compound **10a** (100 mg) was acetylated in pyridine and acetic anhydride at room temperature for 16 hr in the usual manner. The crude product was an uncrystallizable glass: ν_{max} 1739, 1718, 1242 cm^{-1}; nmr ($CDCl_3$) δ 0.68 (s, 3, C-18 CH_3), 2.1 (s, 3, acetate CH_3), 2.87 (s, 1, C-4 H), 4.45 (2 d, 2, J = 11 Hz, C-19 CH_2OAc); mass spectrum m/e 458 (M^+), 442, 416, 400, 398, 370.

Reduction of 4β,5β-Oxido-19-hydroxycholestan-3-one 19-Acetate (10b) with Chromous Acetate.—The 19-acetate **10b** (115 mg) in ethanol (40 ml) was allowed to react with chromous acetate (768 mg) for 10 min exactly as in the preparation of compound **2** above. Preparative tlc (petroleum ether–ethyl acetate, 4:1) gave pure 19-acetoxy-4-cholesten-3-one (**9b**, 38 mg), identified by comparison (melting point, mixture melting point, tlc, infrared) with authentic material prepared by acetylation of 19-hydroxy-4-cholesten-3-one (**9a**). In addition, 70 mg of 5β, 19-dihydroxycholestan-3-one 19-acetate (**11**) was obtained, contaminated with the Δ^4-3 ketone **9b**. This material was again subjected to preparative tlc [chloroform–ethyl acetate (9:1)] and gave 5β-hydroxy compound **11** as an uncrystallizable glass, ν_{max} 3630, 1730 (broad), 1242 cm^{-1}. This glass, when treated with a saturated solution of sodium hydrogen carbonate in 95% ethanol under reflux for 0.5 hr, was converted quantitatively to 19-hydroxy-4-cholesten-3-one (**9a**), identical with authentic material by melting point, mixture melting point, tlc, and infrared comparison.

4β,5β-Oxido-17β,19-dihydroxyandrostan-3-one (13a).—A stirred solution of 19-hydroxytestosterone (**12a**, 584 mg) in 95% ethanol (60 ml) was cooled in ice, and ice-cold sodium hydroxide solution (5 *N*, 2.4 ml) was added quickly, followed by dropwise addition of ice-cold hydrogen peroxide (30%, 2.4 ml). Stirring was continued, and the solution was maintained at 0–5° for 3.5 hr. The reaction mixture was worked up exactly as for compound **10a** above. The crude product was chromatographed on silica gel (60 g), and elution with chloroform–ethanol (97:3) gave the 4β,5β-oxido ketone **13a** (412 mg) as a colorless glass: ν_{max} 3650, 3510, 1720 cm^{-1}; nmr ($CDCl_3$) δ 0.77 (s, 3, C-18 CH_3), 2.92 (s, 1, C-4 H), 4.0 (2 d, 2, J = 11 Hz, C-19 CH_2OH); mass spectrum m/e 320 (M^+), 304, 302, 290, 289, 274, 273.

4β,5β-Oxido-17β,19-dihydroxyandrostan-3-one 17β,19-Diacetate (13b).—The foregoing dihydroxy oxido ketone **13a** (219 mg) was acetylated with pyridine–acetic anhydride at room temperature for 16 hr, giving pure diacetate **13b** (185 mg): mp 133–135° (from aqueous methanol); CD λ_{max} 335 nm ($\Delta\epsilon$ + 1.50), 321 (+3.78), 310 (+4.42), and 300 nm (+3.86); ν_{max} 1745–1739 (broad), 1250 cm^{-1}; nmr ($CDCl_3$) δ 0.82 (s, 3, C-18 CH_3), 2.03 and 2.13 (s, each 3, C-17 and C-19 acetate CH_3), 2.90 (s, 1, C-4 H), 4.43 (2 d, 2, J = 12 Hz, C-19 CH_2); mass spectrum m/e 404 (M^+), 388, 376, 375, 362, 361, 347, 344, 316.

(22) H. Dannenberg, H. G. Neumann, and D. D. v. Dressler, *Justus Liebigs Ann. Chem.*, **674**, 152 (1964).

Anal. Calcd for $C_{28}H_{32}O_6$: C, 68.29; H, 7.97. Found: C, 68.49; H, 8.04.

Reduction of 4β,5β-Oxido-17β,19-dihydroxyandrostan-3-one 17β,19-Diacetate (13b) with Chromous Acetate.—The oxido ketone **13b** (370 mg) in acetone (83 ml) containing sodium acetate trihydrate (3.38 g), water (9.2 ml), and acetic acid (2.3 ml) was reduced for 25 min with freshly prepared chromous acetate (1.18 g) exactly as in the preparation of compound **6** above. The residue (323 mg) was chromatographed on silica gel (384 g) using chloroform–ethyl acetate (1:1) as eluent and taking 10-ml fractions with an automatic fraction collector. The early fractions contained 17β,19-diacetoxy-4-androsten-3-one (**12b**, 85 mg), which was crystallized from ether–petroleum ether to give pure **12b** (35 mg), mp 124–126°, identical with authentic material[23] as judged by melting point, mixture melting point, and infrared comparison. Later fractions contained 5β,17β,19-trihydroxyandrostan-3-one 17β,19-diacetate (**14**, 242 mg) which was crystallized from ether–petroleum ether to give the analytical sample of **14**: mp 151–153°; CD λ_{max} 307 nm ($\Delta\epsilon$ −0.27), 299 (−0.41), 289 (−0.46); ν_{max} 3580, 1712, 1240 cm^{-1}; nmr ($CDCl_3$) δ 0.82 (s, 3, C-18 CH_3), 2.05 and 2.08 (s, each 3, C-17 and C-19 acetate CH_3), 4.48 (s, 2, C-19 CH_2); mass spectrum m/e 388 (M − H_2O), 346, 328, 316.

Anal. Calcd for $C_{23}H_{34}O_6$: C, 67.95; H, 8.43. Found: C, 68.15; H, 8.20.

Oxidation of 3β,5β,17β,19-Tetrahydroxyandrostane 17β,19-Diacetate (15) Back to 5β,17β,19-Trihydroxyandrostan-3-one 17β,19-Diacetate (14) with Jones Reagent.—The tetrol diacetate **15** (5 mg) in acetone (1.0 ml) was oxidized with Jones reagent, giving the crude 3 ketone **14** (4.5 mg), identical with authentic material by melting point, mixture melting point, infrared, and tlc comparison.

3β,5β,17β,19-Tetrahydroxyandrostane 17β,19-Diacetate (15).—5β,17β,19-Trihydroxyandrostan-3-one 17β,19-diacetate (**14**, 170 mg) was reduced with W-2 Raney nickel in refluxing ethanol (1 hr). Preparative tlc (chloroform–ethyl acetate, 3:2) gave pure tetrol diacetate **15** (140 mg) as a colorless glass: ν_{max} 1740, 1245 cm^{-1}; nmr ($CDCl_3$) δ 0.78 (s, 3, C-18 CH_3), 2.03 and 2.07 (s, each 3, C-17 and C-19 acetate CH_3), 3.33 (s, 2, OH), 4.13 (s, $W_{1/2}$ = 8 Hz, 1, C-3 H), 4.38 (s, 2, C-19 CH_2); mass spectrum m/e 408 (M^+), 390, 372, 348, 336, 330.

3β,5β,17β,19-Tetrahydroxyandrostane (16).—The tetrol diacetate **15** was hydrolyzed in 1% methanolic potassium hydroxide solution (18 hr reflux), giving pure tetrol **16**: mp 204–207° (from acetone–hexane), undepressed on admixture with an authentic sample[24] of **16** of mp 205–208°; $[\alpha]D$ +44° (chloroform–ethanol, 9:1) [lit 38° (solvent "chloroform (2 ml) containing 1 drop of ethanol")];[15] mass spectrum m/e 306 (M − 18), 288, 276, 270, 258, 252, indistinguishable from the mass spectrum of the authentic sample.

Registry No.—**10a**, 33066-33-0; **10b**, 33065-66-6; **11**, 33065-67-7; **13a**, 23463-01-6; **13b**, 30517-97-6; **14**, 33065-70-2; **15**, 33065-71-3; **16**, 33065-72-4; chromous acetate, 628-52-4.

Acknowledgments.—We thank Sharon Cylus for excellent technical assistance. Our best thanks are also due to Dr. A. Nickon and Syntex Corporation for generous gifts of steroids. We also thank Drs. D. P. Hollis and C. C. Fenselau for 100-MHz nmr spectra and mass spectra, respectively.

(23) *Cf.* M. Ehrenstein and K. Otto, *J. Org. Chem.*, **24**, 2006 (1959). The authentic sample was prepared by acetylation of 19-hydroxytestosterone with pyridine–acetic anhydride at room temperature.

(24) The authentic sample of **16** was provided by the late Dr. M. Ehrenstein, University of Pennsylvania.