suspension was autoclaved at 15 lb. pressure (120°) for 45 minutes. To the cooled solution was then added 100 ml. of ethanol and 100 g. of Fleischmann bakers' yeast. The *p*H of the reaction mixture was adjusted to 4.5–5.0 by the addition of dilute sulfuric acid, the yeast cell mass was dispersed and mechanical agitation, sufficiently slow so that anaerobic conditions were maintained, was commenced and continued for 48 hours. Hourly adjustment of the *p*H of the medium to 4.5–5.0 by the addition of dilute ammonium hydroxide was carried on during the first 12 hours. Subsequently *p*H determination and adjustment was made every eight hours.

At the end of the reaction period the mixture was centrifuged for one hour and the supernatant liquid was separated. The remaining cell mass was extracted by refluxing for one-half hour with two 1-l. portions of methanol. The combined methanolic extracts and supernatant liquid were concentrated *in vacuo* to 200 ml. and 400 ml. of water was added. The aqueous solution was then extracted three times with ethylene dichloride, and the combined ethylene dichloride extracts were washed neutral and dried. The solvent was removed *in vacuo* and the residue was crystallized from acetone–hexane solution; yield 0.28 g. (62%), m.p. 177–180°, $[\alpha]^{25}D$ +182.4° (1% in acetone).

B. **Bromination and Dehydrobromination of Etiocholan-17β-ol-3,11-dione (X).**—To a solution of 0.61 g. (0.002 mole) of X in 20 ml. of glacial acetic acid containing one drop of 0.28 *N* hydrogen bromide in acetic acid was added, dropwise, with mechanical stirring, 0.33 g. of bromine in 10 ml. of glacial acetic acid at such a rate that the color of the bromine solution was discharged as fast as it was added. Stirring was continued for five minutes, whereupon the reaction mixture was diluted with water and extracted with methylene chloride. The combined methylene chloride extracts were washed neutral with water and aqueous sodium carbonate and dried over magnesium sulfate.

The dried solution was evaporated to dryness and the residual oil was taken up in 30 ml. of glacial acetic acid. To the stirred solution, under a carbon dioxide atmosphere, was added a solution of 0.28 g. of semicarbazide hydrochloride and 0.20 g. of sodium acetate in 2 ml. of water and 2 ml. of acetic acid. After ten minutes 2.4 ml. of 1 *N* sodium acetate in acetic acid was added and stirring was continued for ten minutes. Then the stirring and carbon dioxide atmosphere were discontinued, 0.58 g. of pyruvic acid (91%) in 1 ml. of water and 3 ml. of acetic acid was added and the resulting solution was refluxed for ten minutes. The solution was cooled to room temperature, diluted with water and extracted with methylene chloride. After the methylene chloride extracts were washed neutral with aqueous sodium carbonate they were dried over magnesium sulfate and concentrated to about 40 ml. The resulting solution was then chromatographed on Florisil (15 g.) and the column was eluted first with methylene chloride and thereafter with methylene chloride containing 1% of methanol. All the crystalline fractions (0.43 g.) were combined and recrystallized from acetone–hexane, yielding 0.26 g. (43%) of VII, m.p. 177–180°. A sample recrystallized for analysis melted at 181–182.4°, $[\alpha]^{25}D$ +177.8° (1% in acetone), ϵ_{238} 14.4 × 10^3 (ethanol).

Anal. Calcd. for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.31; H, 8.52.

Mixture melting point of samples from A and B showed no depression.

BLOOMFIELD, N. J.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION OF SCHERING CORP.]

11-Oxygenated Steroids. II. The Reduction of 11-Carbonyl to 11α-Hydroxyl in the Etiocholane Series

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Reduction with sodium and propanol-1 has been shown to convert 11-carbonyl to 11α-hydroxyl and 17-carbonyl to 17β-hydroxyl in several etiocholane derivatives. The 11α-hydroxyl group is shown to resist oxidation by N-bromoacetamide in aqueous acetone under conditions where the 3α- and 17β-hydroxyl groups are oxidized to the corresponding carbonyl groups.

The reduction of 11-ketosteroids to 11β-hydroxysteroids has been effected by catalytic hydrogenation using a platinum catalyst in acetic acid,[1,2] by lithium aluminum hydride,[3] by lithium borohydride[4] and by sodium borohydride.[5]

No satisfactory, general method has been described whereby an 11-ketosteroid can be converted to an 11α-hydroxysteroid.[6,6a] Comparatively few 11α-hydroxysteroids are known; among these are sarmentogenin and its degradation products,[7] the products derived from the Wolff–Kishner reductions of 11-(α and β)-hydroxy-12-ketocholanic acid[8-10] and 12β-hydroxy-11-ketocholanic acid[8,11,12] and the 11α-hydroxyallopregnanes and derived steroids prepared by Djerassi and co-workers[13] from $\Delta^{7,9(11)}$-allopregnadien-3β-ol-20-one acetate by performic acid oxidation, followed by alkaline rearrangement of the resulting 9α,11α-epoxide.[13a]

(1) A. Lardon and T. Reichstein, *Helv. Chim. Acta*, **26**, 586 (1943).

(2) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 1949, p. 655.

(3) L. H. Sarett, M. Feurer and K. Folkers, THIS JOURNAL, **73**, 1777 (1951).

(4) N. L. Wendler, Huang-Minlon and M. Tishler, *ibid.*, **73**, 3818 (1951).

(5) H. Heymann and L. F. Fieser, *ibid.*, **73**, 5252 (1951).

(6) F. Sondheimer, R. Yashin, G. Rosenkranz and C. Djerassi in a recent communication (*ibid.*, **74**, 2696 (1952)) noted that the carbonyl group and the double bond conjugated with it in Δ^8-22-isoallospirosten-3β-ol-11-one propionate are both reduced to yield the saturated 11α-ol with the aid of lithium, liquid ammonia and alcohol.

(6a) NOTE ADDED IN PROOF.—Following the submission of the preliminary communication describing part of this work (H. L. Herzog, E. P. Oliveto, M. A. Jevnik and E. B. Hershberg, THIS JOURNAL, **74**, 4470 (1952)) a paper by H. Heusser, R. Anliker and O. Jeger appeared (*Helv. Chim. Acta*, **35**, 1537 (1952)) which reported the reduction of $\Delta^{22,23}$-ergosten-3β-ol-11-one acetate to the corresponding 3β,11α-diol with sodium and propanol-1. In that paper the hypothesis is suggested that the reduction of an 11-ketone to an 11α-ol may proceed through the 11β-ol which then epimerizes. The reduction of etiocholan-3α,11β-diol-17-one (X) to etiocholan-3α,11β,17β-triol (V), described by us, makes this explanation unsatisfactory for the etiocholane series.

(7) Katz, *Helv. Chim. Acta*, **31**, 993 (1948).

(8) T. F. Gallagher and W. P. Long, *J. Biol. Chem.*, **162**, 521 (1946).

(9) T. F. Gallagher and V. P. Hollander, *ibid.*, **162**, 533 (1946).

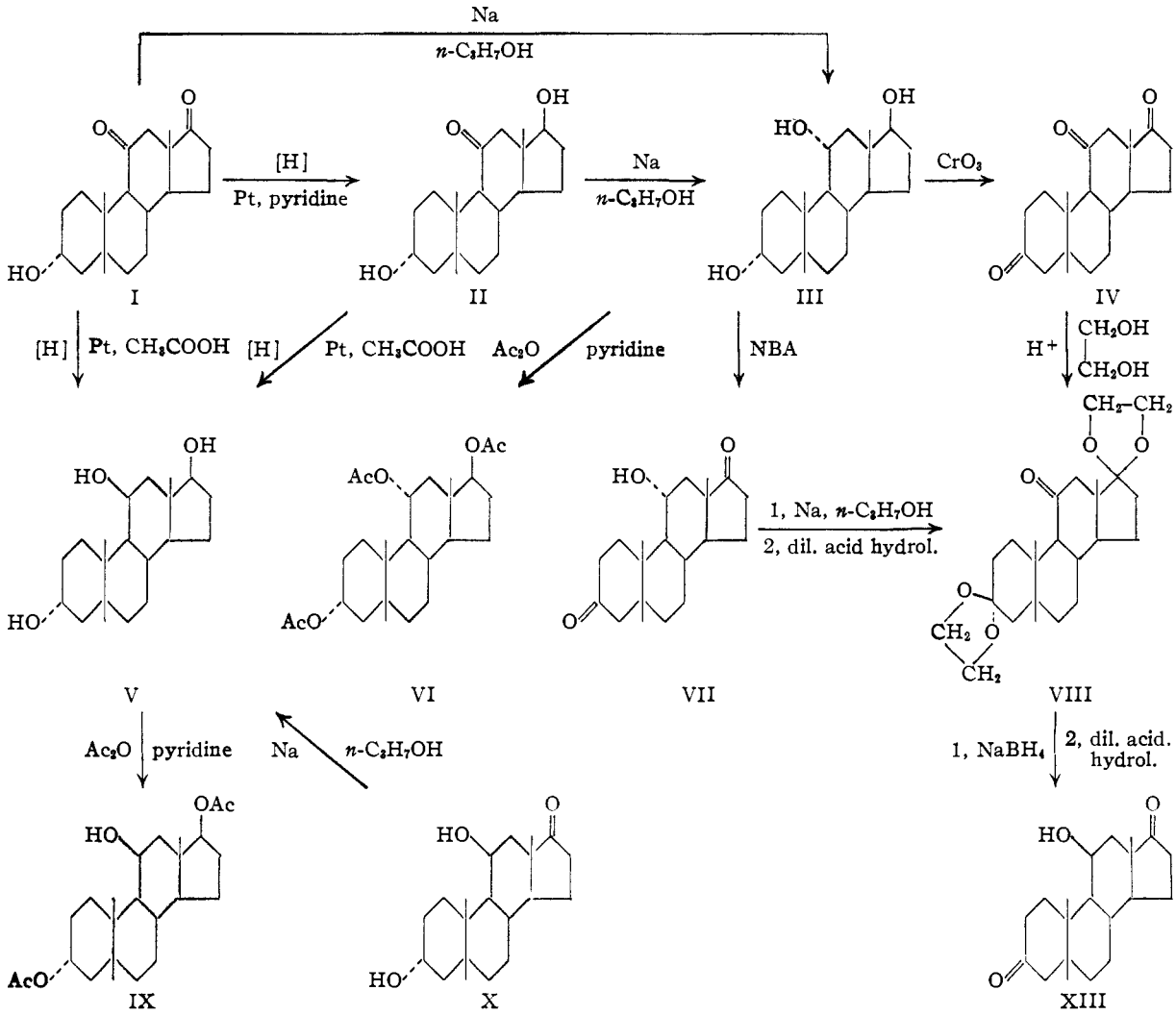
(10) W. P. Long and T. F. Gallagher, *ibid.*, **162**, 511 (1946).

(11) T. F. Gallagher, *ibid.*, **162**, 539 (1946).

(12) O. Wintersteiner, M. Moore and K. Reinhardt, *ibid.*, **162**, 707 (1946).

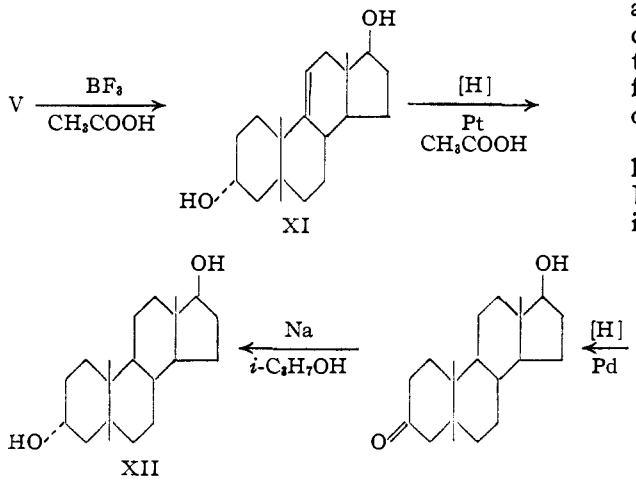
(13) C. Djerassi, O. Mancera, G. Stork and G. Rosenkranz, THIS JOURNAL, **73**, 4496 (1951); C. Djerassi, E. Batres, J. Romo and G. Rosenkranz, *ibid.*, **74**, 3634 (1952).

(13a) NOTE ADDED IN PROOF.—Recently microbiological methods for the direct introduction of the 11α-hydroxyl group have been described: see D. H. Peterson and H. C. Murray, *ibid.*, **74**, 1872 (1952); J. Fried, R. W. Thoma, J. R. Gerke, J. E. Herz, M. N. Donin and D. Perlman, *ibid.*, **74**, 3962 (1952).



Etiocholan-3α-ol-11,17-dione (I) and etiocholan-3α,11β-diol-17-one (X)[14] have now been employed in a study of the hydrogenation of the 11- and 17-carbonyl functions in the etiocholane series, and a method has been devised for converting 11-carbonyl groups to the corresponding 11α-hydroxyl groups. Catalytic hydrogenation of I with Adams platinum catalyst in methanol containing a trace of pyridine gave etiocholan-3α,17β-diol-11-one (II), while the use of Adams catalyst in glacial acetic acid resulted in complete reduction of I to etiocholan-3α,11β,17β-triol (V). Catalytic hydrogenation of II under acid conditions also resulted in the formation of V, indicating that the configuration of the 17-hydroxyl group is the same in II and V.

This configuration was established as β by relating V to testosterone in the following manner. Dehydration of V with boron trifluoride etherate in glacial acetic acid[5] gave $\Delta^{9,11}$-etiocholen-3α,17β-diol (XI), which was transformed by catalytic hydrogenation with Adams catalyst in glacial acetic acid to etiocholan-3α,17β-diol (XII). Butenandt and co-workers have isolated XII from urine and have proved its structure by synthesis from testosterone.[15]



Fieser and Fieser have generalized from the few available examples that catalytic hydrogenation of 11-ketosteroids in glacial acetic

(14) H. L. Herzog, M. A. Jevnik, P. L. Perlman, A. Nobile and E. B. Hershberg, THIS JOURNAL, **75**, 266 (1953).

(15) A. Butenandt, K. Tscherning and H. Dannenberg, *Z. physiol. Chem.*, **248**, 205 (1937).

acid leads to 11β-hydroxysteroids.[16] The assignment of the β-configuration to the 11-hydroxyl group in V was based upon its ready dehydration to XI, which reaction is characteristic of an hydroxyl possessing this configuration.[5] Furthermore, the triol V forms only a diacetate (IX) on treatment with acetic anhydride and pyridine, the 11β-hydroxyl group resisting acetylation as reported.[2,17] In contrast with the preceding observations, the reduction of I with sodium and propanol-1 resulted in the formation of a new triol, etiocholan-3α,11α,17β-triol (III). The same triol was also formed in this manner from II, which indicated that the difference between III and V lies only in the configuration at the 11-position, and that this type of reduction converts 17-ketosteroids in the etiocholane series predominantly to 17β-hydroxysteroids. Further evidence for these structural assignments was supplied by the formation of V by the sodium and propanol-1 reduction of etiocholan-3α,11β-diol-17-one (X).[14]

Confirmation of the α-configuration at the 11-position in the triol III resulted from the preparation of a triacetate VI with acetic anhydride and pyridine.[2] In order to prove that no rearrangement of oxygen atoms had occurred during the sodium and alcohol reduction of I, III was oxidized to the known triketone, etiocholan-3,11,17-trione (IV), with chromic acid.

The 11α-hydroxyl group in III resisted oxidation with N-bromoacetamide (NBA) in aqueous acetone at 5–10° and from this reaction was isolated etiocholan-11α-ol-3,17-dione (VII), the structure of which was established by synthesis from IV. Treatment of IV with excess ethylene glycol and *p*-toluenesulfonic acid in benzene gave etiocholan-3,11,17-trione 3,17-bisdioxolane (VIII). Reduction of VIII with sodium and propanol-1 yielded etiocholan-11α-ol-3,17-dione 3,17-bisdioxolane, which was hydrolyzed to the desired VII. The corresponding 11β-hydroxysteroid, etiocholan-11β-ol-3,17-dione, (XIII) was prepared by reduction of the 11-carbonyl group in VIII by sodium borohydride, followed by hydrolysis of the protective dioxolane groups.

TABLE I

MOLECULAR ROTATIONS

	M_D	$M_D^\beta - M_D^\alpha$
Etiocholane		
3α,11β,17β-Triol (V)	160	
3α,11α,17β-Triol (III)	40	120
11β-ol-3,17-Dione (XIII)	355	
11α-ol-3,17-Dione (VII)	218	137
Cholanic acid		
3α,11β-Diol[1]	206	
3α,11α-Diol[6,8]	86	120

A comparison of M_D values of epimers (Table I) provides a further substantiation that the α-configuration of the 11-hydroxyl group is correctly ascribed to III and VII. In each instance $M_D^\beta - M_D^\alpha$ is in agreement, within experimental error, with the value reported for the epimeric 3α,11-dihydroxycholanic acids.

Experimental[18,19]

Etiocholan-3α,17β-diol-11-one (II).—To a solution of 1 g. of I in 75 ml. of methanol containing one drop of pyridine was added 0.2 g. of Adams platinum oxide catalyst and the resulting mixture was hydrogenated at atmospheric pressure until hydrogen absorption ceased. The catalyst was removed by filtration and the resulting solution was concentrated to a small volume. Upon cooling, 0.7 g. (69.5%) of etiocholan-3α,17β-diol-11-one (II) crystallized as needles, m.p. 252–253°, $[\alpha]^{25}D$ + 68.4° (1% in ethanol). An additional 0.2 g. (20%), m.p. 248–252°, was obtained from the mother liquor by addition of water.

Anal. Calcd. for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 74.57; H, 9.90.

Etiocholan-3α,11α,17β-triol (III) from I.—To a solution of 0.2 g. of I in 20 cc. of refluxing propanol-1, 2.0 g. of sodium was added in one portion. The solution was allowed to reflux spontaneously and when the initial vigorous reaction had subsided, refluxing was maintained by heating until sodium *n*-propoxide began to precipitate. Methanol was added cautiously to the hot mixture to react with the undissolved sodium and to dissolve the precipitate. After the sodium had been destroyed, water was added to the hot solution and the bulk of the alcohol was removed by distillation. Etiocholan-3α,11α,17β-triol (III) crystallized from the boiling solution. Filtration of the cooled mixture gave 0.2 g. (99%) of III, m.p. 242–244°. Recrystallization from methanol–water raised the m.p. to 245–247°, $[\alpha]^{26}D$ +13.1° (0.5% in ethanol).

Anal. Calcd. for $C_{19}H_{32}O_3$: C, 73.98; H, 10.46. Found: C, 73.82; H, 10.72.

III from II.—The reaction was carried out as described for the conversion of I to III except that II was employed in place of I. The precipitated etiocholan-3α,11α,17β-triol (III) melted 243–246° and a mixture melting point with III prepared from I showed no depression.

Etiocholan-3,11,17-trione (IV) from III.—A solution of 0.220 g. (0.0022 mole) of chromium trioxide in 10 ml. of acetic acid, 1.5 ml. of water and 0.02 ml. of concentrated sulfuric acid was added dropwise to a solution of 0.310 g. (0.001 mole) of III in 10 ml. of acetic acid and 1 ml. of water maintained at 7–10°. The resulting green-brown solution was allowed to stand for ten minutes after completion of the addition and was then poured into 100 ml. of ice-water. The mixture was extracted thoroughly with methylene chloride and the extract was washed neutral with water. Concentration of the dried methylene chloride solution left an oily residue which crystallized partially upon treatment with ether; yield of IV, 0.060 g. (20%), m.p. 130–133.5°. The sample gave no depression of melting point in mixture with an authentic sample[14] of IV.

Etiocholan-3α,11β,17β-triol (V) from I.—A solution of 1.0 g. of I in 25 ml. of glacial acetic acid, to which had been added 0.2 g. of Adams platinum catalyst, was hydrogenated at atmospheric pressure until hydrogen absorption ceased. Since absorption was slow it was most convenient to allow the reaction to proceed overnight. The catalyst was filtered from the solution and the filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in methanolic potassium hydroxide, the resulting solution was refluxed for one-half hour and finally several volumes of water were added. An ethereal extract of the resulting mixture was dried with magnesium sulfate and concentrated. Crystallization of the residue from acetone–hexane gave 0.9 g. (89%) of V in the form of prisms, m.p. 200–201.5°.

Examination of the infrared spectrum of V crystallized as previously noted, revealed the presence of acetone of crystallization, with a pronounced carbonyl absorption

(16) Reference 2, p. 410.

(17) L. H. Sarett, *J. Biol. Chem.*, **173**, 185 (1948), has described a triol, etiocholan-3α,11β,17α-triol, and the corresponding diacetate, obtained from the catalytic reduction of etiocholan-3α-ol-11,17-dione 3-acetate, which appear to be identical with V and IX, respectively.

(18) All melting points are corrected.

(19) The authors are indebted to Mr. Edwin Conner, Mrs. Thomas Barrella, Mrs. Raymond McEntire and Miss Joan Mustachio for the microanalyses and rotations, and to Dr. William Tarpley, Miss Cecelia Vitiello and Miss Betty Blasko for the measurement and interpretation of the infrared spectra.

band. When a sample of V with acetone of crystallization was dissolved in ethanol and the resulting solution was evaporated to dryness, there was obtained an amorphous solid, m.p. 200–201.5°, which had no carbonyl absorption band in the infrared; $[\alpha]^{26}D$ +51.9° (1% in ethanol).

Anal. Calcd. for $C_{19}H_{32}O_3$: C, 73.98; H, 10.46. Found: C, 74.23; H, 10.45.

V from II.—The reaction was carried out as described for the conversion of I to V except that II was employed in place of I. Etiocholan-3α,11β,17β-triol (V), m.p. 200–201°, was isolated from the acetone–hexane crystallization. The melting point of a mixture of samples of V derived from both I and II showed no depression.

Etiocholan-3α,11α,17β-triol Triacetate (VI).—A solution of 0.45 g. of III in 10 ml. of pyridine and 3 ml. of acetic anhydride was allowed to stand overnight at room temperature. The resulting solution was diluted with hexane and washed with ice-water, dilute sulfuric acid and again with water. The hexane solution was dried over magnesium sulfate and chromatographed on Florisil. Elution with 20% ether in hexane in five 50-ml. fractions removed successively 0.04 g., m.p. 156.5–158°; 0.31 g., m.p. 160.5–161.5; 0.06 g., m.p. 153–157°; and insignificant amounts of residue in the last two fractions. Recrystallization of the second fraction from hexane resulted in VI, m.p. 161–162°, $[\alpha]^{26}D$ −1.9° (0.9% in ethanol).

Anal. Calcd. for $C_{25}H_{38}O_6$: C, 69.09; H, 8.81. Found: C, 69.31; H, 8.94.

Etiocholan-11α-ol-3,17-dione (VII) from III.—To a solution of 0.540 g. (0.00175 mole) of III in 40 ml. of acetone, 10 ml. of methanol and 10 ml. of water at room temperature was added 1.93 g. (0.014 mole) of *N*-bromoacetamide. After standing for three hours in the dark at 5–10° the colorless solution had become orange. The reaction mixture was poured into 100 ml. of 5% aqueous sodium sulfite and the product was extracted with methylene chloride. The dried methylene chloride solution was concentrated and the residual oil was crystallized from ether–hexane; yield of VII, 0.440 g. (82.5%) of colorless needles, m.p. 136–140.5°. A sample which had been recrystallized from ether melted at 143–144°, $[\alpha]^{25}D$ +71.9° (1% in acetone).

Anal. Calcd. for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.87; H, 9.24.

Etiocholan-3,11,17-trione 3,17-Bisdioxolane (VIII).—A solution containing 2.0 g. of IV, 10 ml. of ethylene glycol and 0.2 g. of *p*-toluenesulfonic acid in 100 ml. of benzene was refluxed for 18 hours. The water which was present initially, and which formed during the reaction, was separated continuously with a trap. The cooled solution was washed with dilute aqueous sodium carbonate, dried over magnesium sulfate and evaporated to dryness under reduced pressure. Crystallization of the residual oil from hexane yielded 1.35 g. (52%) of VIII as colorless needles, m.p. 118–121°. Second and third crops of 0.35 g., m.p. 118–120°, and 0.21 g., m.p. 110–119°, respectively, raised the total yield to 73.5%. Recrystallization from hexane raised the melting point of VI, to 122–123°, $[\alpha]^{25}D$ +29.5° (1% in chloroform).

Anal. Calcd. for $C_{23}H_{34}O_6$: C, 70.73; H, 8.77. Found: C, 70.75; H, 9.07.

Crystallization of VIII from methanol–water gave prisms, m.p. 94–95° dec. Recrystallization of the solvate from hexane removed the solvent of crystallization and the product then melted at 122–123°.

Etiocholan-11α-ol-3,17-dione (VII) from VIII.—To a solution of 0.500 g. of VIII in 50 ml. of refluxing propanol-1, 5.0 g. of sodium was added in one portion. Following the solution of the sodium, which was accelerated in the manner described in the preparation of III from I, the reaction mixture was diluted with water and extracted with methylene chloride. The residual oil from the concentration of the methylene chloride solution was dissolved in a solution of 40 ml. of methanol, 20 ml. of acetone and 5 ml. of 4.5 *N* hydrochloric acid and refluxed for one hour. After cooling, the solution was diluted with water, extracted with methylene chloride and the extracts were washed with water until neutral. Concentration of the dried solution left a semi-crystalline residue which was dissolved in ether–hexane and from which crystallized 0.200 g. (51.5%) of VII, m.p. 139–142.8°. The melting point of a mixture with VII prepared by NBA oxidation of III showed no depression.

Etiocholan-3α,11β,17β-triol 3,17-Diacetate (IX).—A solution of 0.300 g. of V in 5 ml. of pyridine and 2 ml. of acetic anhydride was allowed to stand overnight at room temperature. The reaction mixture was diluted with methylene chloride and washed with water, dilute sulfuric acid and again with water. Concentration of the dried solution left an oil which was taken up in hexane and from which crystallized 0.23 g. (60%) of IX, m.p. 162–162.5°, $[\alpha]^{25}D$ +52.7° (1% in ethanol). A mixture with VI (m.p. 161–162°) melted at 140–150°.

Anal. Calcd. for $C_{23}H_{36}O_5$: C, 70.37; H, 9.24. Found: C, 70.56; H, 9.52.

Etiocholan-3α,11β,17β-triol (V) from X.—To a solution of 0.100 g. of X in 20 ml. of refluxing propanol-1 was added 1.0 g. of sodium. Following the solution of the sodium, which was accelerated in the manner described in the preparation of III from I, the reaction mixture was diluted with water and the product was extracted with ether. The dried ethereal solution was concentrated and the residue was crystallized from acetone–hexane; yield of V, 0.095 g. (94%), m.p. 199–201°. The melting point of a mixture with a sample of V prepared from I showed no depression.

$\Delta^{9,11}$-Etiocholen-3α,17β-diol (XI) from V.—A solution of 0.11 g. of V in 10 ml. of acetic acid containing 0.4 ml. of boron trifluoride etherate was allowed to stand overnight at room temperature. The reaction mixture was diluted with ether and washed with ice-water. The residue left after evaporation of the ether solution was refluxed for an hour with methanolic potassium hydroxide and the resulting solution was diluted with water and extracted with ether. Concentration of the dried ethereal solution left an oily residue which crystallized readily on trituration with hexane; yield 0.07 g. (67.5%), m.p. 225–227°. Recrystallization from methanol–water raised the m.p. to 228–229.5°, $[\alpha]^{25}D$ +36.6° (0.5% in ethanol).

Anal. Calcd. for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.71; H, 10.26.

Employing the same procedure as described previously, IX was also converted to XI. From 0.24 g. of IX there was obtained 0.15 g. (84.5%) of XI, m.p. 226–228°.

Etiocholan-3α,17β-diol (XII).—A solution of 0.04 g. of XI in 50 ml. of acetic acid containing 0.2 g. of Adams platinum catalyst was hydrogenated at atmospheric pressure until absorption of hydrogen ceased. It was found convenient to allow the reaction to proceed overnight. The catalyst was removed by filtration, the reaction mixture was concentrated *in vacuo*, and the residue was refluxed for one hour with methanolic potassium hydroxide. The methanol was then removed by vacuum distillation and water was added to the residue. The undissolved solid was collected with suction and recrystallized from methanol–water mixture; yield 0.02 g. (50%), m.p. 228.5–230°, $[\alpha]^{26}D$ +30.2° (0.2% in ethanol). Butenandt and co-workers[14] report XII, m.p. 232°, $[\alpha]^{20}D$ +26.5° (in alcohol) (synthetic substance), $[\alpha]^{18}D$ +29.7° (in alcohol) (isolated from urine).

Etiocholan-11β-ol-3,17-dione (XIII).—A solution of 2.68 g. of VIII in 70 ml. of methanol was refluxed for 5.5 hours with 1.25 g. of sodium borohydride and 5.1 ml. of 50% aqueous sodium hydroxide and was then allowed to stand overnight at room temperature. The reaction mixture was diluted with methylene chloride and the resulting solution was washed neutral with water and evaporated to dryness. To a solution of the residue in 70 ml. of methanol was added 5 ml. of 4.5 *N* hydrochloric acid and the reaction mixture was refluxed for ten minutes. The reaction mixture was again diluted with methylene chloride, washed with water until neutral and dried over magnesium sulfate. Concentration of the dried solution followed by addition of ether induced crystallization; first crop of XIII, 1.18 g. (57%), m.p. 205–211°; second crop, 0.30 g. (14%), m.p. 195–208°. Recrystallization from the same solvent mixture gave XIII, m.p. 211–213°, $[\alpha]^{26}D$ +116.9° (1.6% in acetone).

Anal. Calcd. for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 75.15; H, 9.62.

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