[Contribution from the Lederle Laboratories Division, American Cyanamid Company]

$\Delta^{5,7}$-STEROIDS. VII.[1] THE CONVERSION OF $\Delta^{5,7}$- TO $\Delta^{5,7,9}$-STEROIDAL HORMONES

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In the previous publication of this series,[1] detailed procedures were presented for the preparation of $\Delta^{5,7}$-steroidal hormones. As is well known the $\Delta^{5,7}$-steroid system lends itself to numerous transformations, namely, hydrogenation, dehydrogenation, rearrangement, oxidation, etc. (1). Consequently, we have undertaken a systematic study of four $\Delta^{5,7}$-steroids, $\Delta^{5,7}$-androstadiene-3β-ol-17-one, $\Delta^{5,7}$-androstadiene-3β, 17β-diol, $\Delta^{5,7}$-pregnadiene-3β-ol-20-one, and $\Delta^{5,7}$-pregnadiene-3β,21-diol-20-one, and have carried out a number of such transformations. In this publication, we wish to report on the dehydrogenation of $\Delta^{5,7}$-steroids by mercuric acetate to give $\Delta^{5,7,9}$-steroids.

The method of synthesis and mode of characterization may be illustrated by the following. $\Delta^{5,7}$-androstadiene-3β-ol-17-one acetate (III) was dehydrogenated with mercuric acetate in alcohol acidified with glacial acetic acid according to the method of Windaus and Linsert (2), and gave in 33% yield the expected $\Delta^{5,7,9}$-androstatriene-3β-ol-17-one acetate (XII). Hydrolysis with alcoholic potash gave the free steroid (XI), which on acetylation gave back XII, and on benzoylation gave XIII.

In a similar manner, $\Delta^{5,7,9}$-androstatriene-3β,17β-diol (XIV), and $\Delta^{5,7,9}$-pregnatriene-3β-ol-20-one (XVII) were prepared and characterized. We have also succeeded in preparing $\Delta^{5,7,9}$-pregnatriene-3β,21-diol-20-one diacetate (XXI). The latter compound on hydrolysis gave the diol (XX) which was incompletely characterized.

All of the $\Delta^{5,7,9}$-steroids (XI–XXI) display highly positive optical rotations characteristic of compounds containing such a double bond system (2, 3). These compounds likewise possess a characteristic ultraviolet absorption spectrum. In this connection, we have examined the ultraviolet absorption spectra of $\Delta^{5,7,9}$-cholestatriene-3β-ol (VII) (3), its acetate (VIII) (3) and benzoate (IX), and dehydroergosteryl acetate (X) (2, 4). The latter compound was prepared in 54% yield by a modified procedure. In general (conclusions based on spectra of fifteen compounds), a $\Delta^{5,7,9}$-steroid has three absorption maxima in the ultraviolet at about 310–312, 323–325, and 335–341 mμ. The principal maximum is at 323–325 mμ; occasionally, the other two maxima appear as inflections (in one case the 335–341 mμ maximum appeared as a plateau). The order of the magnitude of the molecular extinction coefficients is $\epsilon_{323-325} > \epsilon_{310-312} > \epsilon_{335-341}$. Morton, *et al.* (5) have noted that dehydroergosterol has three maxima, $\lambda_{max.}$ 311, 325, and 342 mμ, with an inflection at 296–297 mμ. We have observed that the

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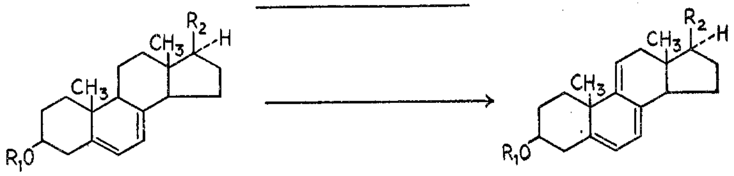
[1] Paper VI. Antonucci, Bernstein, Giancola, and Sax, *J. Org. Chem.*, **16**, preceding paper.

degree of inflection at 296–297 mμ may be considered as a criterion of the purity of the $\Delta^{5,7,9}$-steroid. A pure $\Delta^{5,7,9}$-steroid has a minor change in the slope of the curve in this region. The presence of a sharp inflection (or maximum) indicates contamination with $\Delta^{5,7}$-steroid.

Further transformations products of $\Delta^{5,7}$ and $\Delta^{5,7,9}$-steroidal hormones will be the subject matter of future publications from this laboratory.

FLOWSHEET I



I $R_1 = H$; $R_2 = C_8H_{17}$
II $R_1 = Ac$; $R_2 = C_9H_{17}$
III $R_1 = Ac$; $R_2(H) = O$
IV $R_1 = Ac$; $R_2 = OAc$
V $R_1 = Ac$; $R_2 = COCH_3$
VI $R_1 = Ac$; $R_2 = COCH_2OAc$

VII $R_1 = H$; $R_2 = C_8H_{17}$
VIII $R_1 = Ac$; $R_2 = C_8H_{17}$
IX $R_1 = Bz$; $R_2 = C_8H_{17}$
X $R_1 = Ac$; $R_2 = C_9H_{17}$
XI $R_1 = H$; $R_2(H) = O$
XII $R_1 = Ac$; $R_2(H) = O$
XIII $R_1 = Bz$; $R_2(H) = O$
XIV $R_1 = H$; $R_2 = OH$
XV $R_1 = Ac$; $R_2 = OAc$
XVI $R_1 = Bz$; $R_2 = OBz$
XVII $R_1 = H$; $R_2 = COCH_3$
XVIII $R_1 = Ac$; $R_2 = COCH_3$
XIX $R_1 = Bz$; $R_2 = COCH_3$
XX $R_1 = H$; $R_2 = COCH_2OH$
XXI $R_1 = Ac$; $R_2 = COCH_2OAc$

EXPERIMENTAL

Absorption spectra. All spectra were determined with a Beckman quartz spectrophotometer (National Technical Laboratories, South Pasadena, California), and were determined, unless otherwise stated, in commercial absolute alcohol.

Melting points. All m.p.'s are uncorrected, and were determined with uncalibrated Anschütz thermometers (total immersion). Many of the m.p.'s were dependent on the rate of heating and on the temperature of the bath at which the sample was inserted; generally, the sample was inserted in the bath about 5–10 degrees below its anticipated m.p.

Optical rotations. The sample was dissolved in chloroform (unless otherwise stated) to make a 2-ml. solution, and the rotation was determined in a 1-dcm. semi-micro tube.

All reactions and distillations were carried out in a nitrogen atmosphere.

$\Delta^{5,7,9}$-Cholestatriene-3β-ol[2] (VII). 7-Dehydrocholesterol (25 g.) (I) in 100 ml. of carbon tetrachloride and 500 ml. of alcohol was dehydrogenated with 71 g. of mercuric acetate in 600 ml. of alcohol acidified with 26 ml. of acetic acid in the manner described below for de-

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[2] Windaus, Deppe, and Roosen-Runge (3): free sterol, m.p. 112°, $[\alpha]_D^{20}$ +146°, λ_{max} 313 mμ; acetate, m.p. 88–89°, $[\alpha]_D^{20}$ +220°. These investigators, likewise, found the free sterol to be solvated.

hydroergosteryl acetate (X). The crude product was an oil which on being cooled and worked with methanol gave crystals, wt. 6.4 g., m.p. 99–109°. Several recrystallizations from acetone-methanol gave 3.2 g., m.p. 119–121° (solvent evolution at 88–95°, resolidification), λ_{max} 312, 325, and 339 mμ, ϵ 10,100, 12,800, and 7,950 resp., $[\alpha]_{\mathrm{D}}^{30}$ +168°, $[\alpha]_{\mathrm{Hg}}^{30}$ +306° (31.6 mg., α_{D} +2.65°, α_{Hg}[3] +3.25°) $\alpha_{\mathrm{Hg}}/\alpha_{\mathrm{D}}$ 1.23; $[\mathrm{M}]_{\mathrm{D}}$ +642 (solvation ignored).

Anal. Calc'd for $C_{27}H_{42}O$ (382.61): C, 84.75; H, 11.07.
$C_{27}H_{42}O \cdot H_2O$ (400.62): C, 80.94; H, 11.07.
Found: C, 81.10; H, 10.65.

$\Delta^{5,7,9}$-*Cholestatriene-3β-ol acetate* (VIII). Compound VII (230 mg.) in 2 ml. of pyridine was acetylated in the usual manner with 0.4 ml. of acetic anhydride. Crystallization from a very small volume of methanol gave 0.17 g. of VIII, m.p. 89–90.5°. Recrystallization from dilute methanol gave 0.13 g., m.p. 88.5–90.5°, λ_{max} 311, 324–325, and 340 mμ, ϵ 10,300, 11,900, and 7,450 resp., $[\alpha]_{\mathrm{D}}^{28}$ +226°, $[\alpha]_{\mathrm{Hg}}^{28}$ +281° (16.1 mg., α_{D} +1.82°, α_{Hg} +2.26°) $\alpha_{\mathrm{Hg}}/\alpha_{\mathrm{D}}$ 1.24; $[\mathrm{M}]_{\mathrm{D}}$ +958.

$\Delta^{5,7,9}$-*Cholestatriene-3β-ol benzoate* (IX). Compound VII (0.1 g.) in 2 ml. of pyridine was benzoylated in the usual manner with 0.1 ml. of benzoyl chloride. Several recrystallizations of the crude product gave 80 mg. of pure IX, m.p. 140–141.5°, 145.5°, $\lambda_{\mathrm{max}}^{1\%\mathrm{CA}}$[4] 311–312, 325, and 341 mμ (no 229 mμ maximum), ϵ 11,500, 13,500, and 8,000 resp., $[\alpha]_{\mathrm{D}}^{25}$ +194°, $[\alpha]_{\mathrm{Hg}}^{25}$ +242° (30.2 mg., α_{D} +2.94°, α_{Hg} +3.64°). $\alpha_{\mathrm{Hg}}/\alpha_{\mathrm{D}}$ 1.24; $[\mathrm{M}]_{\mathrm{D}}$ +943.

Anal. Calc'd for $C_{34}H_{46}O_2$ (486.71): C, 83.90; H, 9.53.
Found: C, 83.70; H, 9.62.

Dehydroergosteryl acetate[5] ($\Delta^{5,7,9,22}$-*ergostatetraene-3β-ol acetate*) (X). To a refluxing solution of 150 g. of ergosteryl acetate (II) in 2.5 liters of carbon tetrachloride and 4 liters of alcohol was added a hot solution of 356 g. of mercuric acetate in 2.7 liters of alcohol acidified with 130 ml. of glacial acetic acid. The mixture was refluxed for 1.3 hours, and allowed to stand for 0.75 hour. The hot solution was filtered and treated with water. The cooled mixture was transferred to a separatory-funnel, and the carbon tetrachloride layer was separated. The water layer was extracted several times with additional carbon tetrachloride. The combined extracts were washed with water, dried with magnesium sulfate, treated with Norit, and filtered. The filtrate was evaporated *in vacuo*, and the residue was crystallized from acetone-methanol. This gave 78.5 g., m.p. 147.5–149.5°. Recrystallization from acetone-methanol gave 66.4 g. of pure X, m.p. 147.5–149.5°, λ_{max} 311, 325, and 340–341 mμ, ϵ 10,500, 12,100, and 7,500 resp. From the mother liquors by concentration and addition of methanol there were obtained two additional fractions, wt. 13.15 g., m.p. 147–149°; and wt. 1.75 g., m.p. 146.5–150°. The total wt. of X was 81.3 g. (54%).

$\Delta^{5,7,9}$-*Androstatriene-3β-ol-17-one acetate* (XII). *A*. To a refluxing solution of 1.64 g. of III in alcohol was added a hot solution of 4.8 g. of mercuric acetate in alcohol acidified with 2 ml. of glacial acetic acid. (The total volume of alcohol used was 100 ml.) The mixture was refluxed for 1.5 hours, cooled and filtered. The filtrate was added to about twice its volume of water and the product was worked up in carbon tetrachloride. The extract was washed twice with dilute acetic acid, and with water, dried with magnesium sulfate, treated with Norit, and filtered through Celite. Evaporation *in vacuo* gave a yellow viscous oil which was dissolved in methanol. This solution on being cooled (−80°) and worked gave crystals which were removed, and were washed with methanol previously cooled to −80°; wt. 0.49 g., m.p. 145–154° with previous softening. Three recrystallizations from methanol gave 0.22 g. of XII, m.p., 162–164°, λ_{max} 311–311.5 (inflection) 323, and 338–339 (inflection) mμ;

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[3] This refers to the usual mercury line, 5461 Å.

[4] 1% CA = 1% chloroform-absolute alcohol, *i.e.* the weighed sample was dissolved in 1 ml. of reagent chloroform, and this solution was rapidly diluted to 100 ml. with commercial absolute alcohol.

[5] Windaus and Linsert (2), m.p. 146°; Bergmann and Stevens (4), m.p. 143–146°, yield 50%; Morton, *et al.* (5), m.p. 146°; Callow and Rosenheim, *J. Chem. Soc.*, 387 (1933), m.p. 145–147°.

ϵ 9,900, 11,100, and 6,900 resp.; $[\alpha]_D^{30}$ +388°, $[\alpha]_{Hg}^{30}$ +491° (16.0 mg., α_D +3.10°, α_{Hg} +3.93°) α_{Hg}/α_D 1.27; $[M]_D$ +1265.

Anal. Calc'd for $C_{21}H_{26}O_3$ (326.42): C, 77.27; H, 8.03.
Found: C, 77.20, 77.59; H, 8.52, 8.49.

In another run with 5.0 g. of II in 25 ml. of alcohol, and 15 g. of mercuric acetate in 25 ml. of alcohol acidified with 3 ml. of glacial acetic acid (reflux 1 hour, allowed to stand *ca.* 1 hour, worked up in carbon tetrachloride) after recrystallization from methanol there was obtained 1.63 g. of XII, m.p. 162–164°, 33% yield.

B. Compound XI (9.8 mg.) in 0.5 ml. of pyridine was acetylated in the usual manner with 0.1 ml. of acetic anhydride. Recrystallization of the crude product from methanol gave 5 mg. of XII, m.p. 162–162.5°, ϵ_{324} 11,300.

$\Delta^{5,7,9}$-*Androstatriene-3β-ol-17-one* (XI). To 1.57 g. of the $\Delta^{5,7,9}$-acetate (XII) in 20 ml. of alcohol was added 0.4 g. of potassium hydroxide in 0.25 ml. of water and 40 ml. of alcohol. The mixture was refluxed for ½ hour, cooled, and treated with ice. This gave crystals, wt. 1.07 g., m.p. 166.5–168.5°. Recrystallization from acetone-petroleum ether (b.p. 64–66°) gave 0.78 g. of XI, m.p. 169–171.5°, λ_{max} 310–311 (inflection), 322, and 338–339 (inflection) mμ; ϵ 9,650, 10,800, 6,800, resp., $[\alpha]_D^{30}$ +346°, $[\alpha]_{Hg}^{30}$ +438° (14.9 mg., α_D +2.58, α_{Hg} +3.26°) α_{Hg}/α_D 1.26; $[M]_D$ +983.

Anal. Calc'd for $C_{19}H_{24}O_2$ (284.38): C, 80.24; H, 8.51.
Found: C, 80.58; H, 8.43.

$\Delta^{5,7,9}$-*Androstatriene-3β-ol-17-one benzoate* (XIII). A solution of 52 mg. of XI in 2 ml. of pyridine was benzoylated in the usual manner with 0.12 ml. of benzoyl chloride. Recrystallization of the crude benzoate from acetone gave 20 mg. of pure XIII, m.p. 243–245.5° (with previous softening at 240° and d.), λ_{max} 227, 311, 323, and 335–336 mμ, ϵ 17,350, 11,600, 12,850, 8,100 resp., $[\alpha]_D^{29}$ +337°, $[\alpha]_{Hg}^{29}$ +425° (10.55 mg., α_D +1.78°, α_{Hg} +2.24°) α_{Hg}/α_D 1.26; $[M]_D$ +1308.

Anal. Calc'd for $C_{26}H_{28}O_2$ (388.48): C, 80.38; H, 7.26.
Found: C, 80.39; H, 7.53.

$\Delta^{5,7,9}$-*Androstatriene-3β,17β-diol* (XIV). To a refluxing solution of 5.5 g. of $\Delta^{5,7}$-diacetate (IV) in 30 ml. of alcohol was added a hot solution of 16 g. of mercuric acetate in 125 ml.of alcohol acidified with 4 ml. of acetic acid. The mixture was refluxed for 70 minutes, filtered while still hot, and the product was worked up in carbon tetrachloride after the addition of water. The extract was washed with dilute acetic acid, and water, dried with magnesium sulfate, treated with Norit and filtered through Celite. The carbon tetrachloride solution was evaporated *in vacuo*, and the oily residue was dissolved in methanol. All attempts to crystallize the material failed. An ultraviolet absorption analysis showed that no $\Delta^{5,7}$-diacetate (IV) was present.

One-half of the methanol solution was hydrolyzed for 45 minutes with 50 ml. of 5% methanolic potash in the usual manner; this caused the solution to darken considerably. It was poured with stirring into an ice-slurry, and the colored precipitate was collected, taken up in acetone, and filtered after the addition of Norit. Concentration and addition of water gave an oil. The mixture was poured into an ice-slurry, and the resulting solid was collected by filtration through Celite. The solid was separated from the Celite with the aid of acetone. The resulting turbid, brown solution was treated with Norit and filtered. The yellow filtrate on concentration and cooling (ice-acetone bath) gave 0.78 g. of crude XIV, m.p. 178–187° with much previous softening. Recrystallization from acetone gave 0.34 g. of XIV, m.p. 188–191°, λ_{max} 312, 324, 339 mμ, ϵ 11,230, 12,680, 7,950 resp. $[\alpha]_D^{28}$ +246°, $[\alpha]_{Hg}^{28}$ +307° (25.1 mg., absolute alcohol, α_D +3.09°, α_{Hg} +3.85°) α_{Hg}/α_D 1.25; $[M]_D$ +704 (solvation ignored).

Anal. Calc'd for $C_{19}H_{26}O_2$ (286.40): C, 79.68; H, 9.15.
Found:[6] C, 77. 64, 78.07; H, 9.60, 9.64.

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[6] The compound was solvated or hydrated. Attempts to obtain an anhydrous compound were unsuccessful.

The remaining half of the diacetate (XV) in 100 ml. of methanol was refluxed for two hours with 2.2 g. of sodium carbonate in 15 ml. of water, poured into water, and filtered. Five recrystallizations from acetone gave 0.16 g. of XIV, m.p. 189–191°, λ_{max} 312, 324, and 339 mμ, ϵ 9,040, 10,250, 6,370 resp.

Found: C, 74.76; H, 9.48.

$\Delta^{5,7,9}$-*Androstatriene-3β,17β-diol diacetate* (XV) (*?*). A solution of 100 mg. of $\Delta^{5,7,9}$-diol (XIV) in 1 ml. of pyridine was treated in the cold with 0.25 ml. of acetic anhydride. The mixture was worked up in ether in the usual manner. Evaporation of the ether gave an oil, λ_{max} 312, 324, and 339 mμ, ϵ 9,900, 10,300, 6,400 resp. Attempts to crystallize the material from various solvents were unsuccessful. Also, neither chromatography nor evaporative distillation gave a crystalline product.

$\Delta^{5,7,9}$-*Androstatriene-3β,17β-diol dibenzoate* (XVI). The diol (XIV) (100 mg.) in 4 ml. of pyridine was benzoylated in the usual manner with 1.8 ml. of benzoyl chloride. Recrystallization of the crude benzoate from methanol gave 50 mg. of pure XVI, m.p. 202–205° d., λ_{max} 228–229, 312, 324, and 340 mμ, ϵ 30,250, 11,300, 12,700, 8,100 resp., $[\alpha]_D^{29}$ + 180°,$[\alpha]_{Hg}^{29}$ +235° (15.9 mg., α_D +1.43°, α_{Hg} +1.87°) α_{Hg}/α_D 1.31; $[M]_D$ +889.

Anal. Calc'd for $C_{33}H_{34}O_4$ (494.60): C, 80.13; H, 6.93.

Found: C, 79.77, 79.86; H, 6.93, 6.81.

$\Delta^{5,7,9}$-*Pregnatriene-3β-ol-20-one acetate* (XVIII). *A*. To a refluxing solution of 10 g. of $\Delta^{5,7}$-acetate (V) in 50 ml. of alcohol was added a hot solution of 30 g. of mercuric acetate in 250 ml. of alcohol acidified with 5 ml. of glacial acetic acid. The mixture was refluxed for 80 minutes, filtered, and poured into 2 volumes of water. The product was worked up in carbon tetrachloride, and the extract was washed with dilute acetic acid and water, dried, and filtered. Evaporation *in vacuo*, and treatment of the residue with methanol gave 4.22 g., m.p. 142–145°. Recrystallization from methanol gave 3.77 g. of pure XVIII, m.p. 144–146°, λ_{max} 312, 324, and 339 mμ; ϵ 11,500, 12,800, 7,700 resp., $[\alpha]_D^{29}$ +317°, $[\alpha]_{Hg}^{29}$ +400° (12.0 mg., α_D +1.90°, α_{Hg} +2.40°) α_{Hg}/α_D 1.26; $[M]_D$ +1122; 38% yield.

Anal. Calc'd for $C_{23}H_{30}O_3$ (354.47): C, 77.93; H, 8.53.

Found: C, 78.07; H, 8.75.

B. A solution of 0.25 g. of $\Delta^{5,7,9}$-*pregnatriene-3β-ol-20-one* (XVII) in 7.5 ml. of pyridine was acetylated in the usual manner with 1 ml. of acetic anhydride. Recrystallization of the crude acetate from dilute methanol gave 0.20 g. of pure XVIII, m.p. 145.5–147.5°, λ_{max} 312, 324, and 339 mμ; ϵ 10,700, 12,200, 7,520 resp.

Anal. Found: C, 78.24; H, 8.88.

$\Delta^{5,7,9}$-*Pregnatriene-3β-ol-20-one* (XVII). The $\Delta^{5,7,9}$-acetate (XVIII) (3.7 g.) in 75 ml. of methanol was refluxed for 2 hours with 3.0 g. of potassium carbonate, cooled, and treated with water. The resulting crystals were washed with water and methanol, wt. 2.7 g., m.p. 220–221.5°. Recrystallization from benzene-methanol, and chloroform-petroleum ether (b.p. 66–68°) gave 1.52 g. of pure XVII, m.p. 221–225°, $\lambda_{max}^{1\%CA}$ 311–312 (inflection), 323 and 337–339 (inflection) mμ, ϵ 10,200, 11,550, 7,400 resp. $[\alpha]_D^{30}$ +304°, $[\alpha]_{Hg}^{30}$ +378° (24.3 mg., pyridine, α_D +3.69°, α_{Hg} +4.59°) α_{Hg}/α_D 1.24; $[M]_D$ +948.

Anal. Calc'd for $C_{21}H_{28}O_2$ (312.43): C, 80.73; H, 9.03.

Found: C, 80.61; H, 9.25.

Development of the mother liquors with chloroform-petroleum ether (b.p. 66–68°), acetone-petroleum ether (b.p. 66–68°), and with acetone gave a second fraction of XVII, wt. 0.61 g., m.p. 217.5–224°, $\lambda_{max}^{1\%CA}$ 311–312 (inflection), 324 and 339–340 (inflection) mμ; ϵ 10,500, 11,600, 7,250 resp.

$\Delta^{5,7,9}$-*Pregnatriene-3β-ol-20-one benzoate* (XIX). Compound XVII (100 mg.) in 5 ml. of pyridine was benzoylated in the usual manner with 0.3 ml. of benzoyl chloride. Recrystallization of the crude benzoate from dilute methanol and dilute acetone gave 60 mg. of pure XIX, m.p. 196.5–199°, λ_{max} 227.5–228, 312, 324, and 338–339 mμ; ϵ 16,900, 11,450, 12,900, 8,000 resp., $[\alpha]_D^{29}$ +290°, $[\alpha]_{Hg}^{29}$ +368° (17.5 mg., α_D +2.54°, α_{Hg} +3.22°) α_{Hg}/α_D 1.27; $[M]_D$ +1206.

Anal. Calc'd for $C_{28}H_{32}O_3$ (416.54): C, 80.73; H, 7.75.

Found: C, 80.58; H, 8.04.

$\Delta^{5,7,9}$-*Pregnatriene-3β,21-diol-20-one diacetate* (XXI). To a refluxing solution of 190 mg. of $\Delta^{5,7}$-pregnadiene-3β,21-diol-20-one diacetate (VI) in alcohol was added a hot solution of 0.6 g. of mercuric acetate in alcohol containing 0.25 ml. of glacial acetic acid. The total volume of alcohol was 15 ml. The mixture was refluxed for 2 hours, cooled, and the mercurous acetate was separated. Evaporation *in vacuo* gave a crystalline residue which was recrystallized from methanol, wt. 22 mg., m.p. 144–146°, λ_{max} 311–312, 325, and 337–340 (plateau) mμ; ε 10,500, 11,900, 7,400 resp. $[\alpha]_D^{29}$ +295° (10.1 mg., α_D +1.49°); $[M]_D$ +1215.

Anal. Calc'd for $C_{25}H_{32}O_5$ (412.51): C, 72.79; H, 7.82.
Found: C, 72.57; H, 8.19.

In another run with 2.35 g. of VI, 7.5 g. of mercuric acetate, 60 ml. of alcohol, and 2.5 ml. of glacial acetic acid by essentially the same procedure there was obtained after recrystallization from methanol, dilute methanol, and methanol, 0.56 g. of XXI, m.p. 142–143.5°, ϵ_{324} 11,800; 24% yield.

$\Delta^{5,7,9}$-*Pregnatriene-3β,21-diol-20-one* (XX) (*?*). The diacetate (XXI, 560 mg.) was refluxed for 2 hours with 0.50 g. of potassium carbonate in 25 ml. of methanol containing several drops of water. The mixture was poured into ice-water and filtered. The product was dissolved in acetone, and the solution was concentrated with the simultaneous addition of water. The crystals so obtained had m.p. 174–178° (due to solvation a low m.p. was first obtained, sample was cooled after melting, and m.p. was redetermined), λ_{max} 312–313 (inflection), 323.5–324, and 337–339 (inflection) mμ; ε 9,400, 10,500, 6,700 resp. Further lengthy recrystallization from acetone-petroleum ether (b.p. 64–66°) and dilute acetone to approximately constant m.p. and constant ultraviolet absorption gave a very poor yield of diol (XX), 5 mg., m.p. 187–189.5° (yellow melt, with previous shrinkage); λ_{max} 310–311, 324, and 338–339 mμ; ε 9,300, 10,700, and 6,660 resp., $[\alpha]_D^{26}$ +224°, $[\alpha]_{Hg}^{23}$ +279° (3.3 mg., α_D +0.37°, α_{Hg} +0.46°) α_{Hg}/α_D 1.24.

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SUMMARY

Several $\Delta^{5,7,9}$-steroidal hormones have been prepared from the corresponding $\Delta^{5,7}$-steroids by the Windaus mercuric acetate method.

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