after recrystallization of the mixture from methylene chloride–petroleum ether.

N-Carbobenzoxy-S-trityl-L-cysteine methyl ester (Vc) was prepared by carbobenzoxylation of S-trityl-L-cysteine methyl ester hydrochloride[4] in the same manner as that described for the corresponding S-benzyl derivative. The yield of the sirupy product was 80%.

Saponification.—(a) The above ester (1.5 g., 0.003 mole) was dissolved in 10 ml. of 50% aqueous dioxane (or acetone) containing 0.0033 mole of sodium hydroxide. After being allowed to stand for 1 hour at room temperature, the solution was diluted with water. Most of the organic solvent was removed *in vacuo*, the solution was acidified with sulfuric acid and extracted with ether. The ethereal extract was washed repeatedly with water until the aqueous layer was neutral to congo red paper, and finally dried over sodium sulfate. Upon addition of diethylamine to the filtrate N-carbobenzoxy-S-trityl-L-cysteine diethylammonium salt separated out. The yield was 1.4 g. (81%), m.p. 164–166°, $[\alpha]^{25}D$ 18.6° (c 4, methanol); reported[4] m.p. 168°, $[\alpha]D$ 21.4° (in methanol); *i.e.*, the product was contaminated with about 10% of the DL-form.

(b) The saponification and the isolation of the free acid were carried out in the same manner as described in (a) except that 99% methanol was used as solvent instead of 50% dioxane. N-Carbobenzoxy-S-trityl-DL-cysteine was obtained as the diethylammonium salt (83%), m.p. 161–162°.

Anal. Calcd. for $C_{34}H_{38}N_2O_4S$: N, 4.91; S, 5.61. Found: N, 4.98; S, 5.72.

β-Elimination in N-Carbobenzoxy-O-diphenylphosphoryl-DL-serine Ethyl Ester.[12]—(a) Trituration of a solution of 0.2 ml. of diethylamine and 0.5 g. (0.001 mole) of the above ester in 4 ml. of ether led to the precipitation of diethylammonium O-diphenylphosphate. The mixture was left to stand for several hours at room temperature before the salt was collected by filtration and washed with ether. The yield was 85%, m.p. 123–124°.

Anal. Calcd. for $C_{16}H_{22}NO_4P$: N, 4.33; P, 9.58. Found: N, 4.58; P, 9.65.

From the filtrate, N-carbobenzoxydehydroalanine (60%, m.p. 108–109°) was obtained in the same manner as that described for the β-elimination in I.

(b) The above ester was treated with 3 equiv. of 0.1 N NaOH in 50% ethanol and within 30 minutes the β-elimination and the saponification were complete. N-Carbobenzoxydehydroalanine (60%, m.p. 108–109°) was obtained and, in addition, a small amount of carbobenzoxy amide (m.p. 87°).

Conversion of N-Carbobenzoxy-O-tosyl-L-serine Methyl Ester (I) to N-Carbobenzoxy-S-trityl-DL-cysteine.—Triphenylthiocarbinol (0.7 g., 0.0025 mole) was dissolved in anhydrous acetone, 2.4 ml. of methanolic 1 N sodium methoxide was added and the solution was rapidly evaporated to dryness at 25–30° *in vacuo*. The sodium mercaptide thus formed was dissolved in 12 ml. of anhydrous acetone and this solution was added, in 4 equal portions, to 1 g. of I dissolved in 12 ml. of anhydrous acetone, within a period of 10 minutes. Sodium tosylate precipitated almost instantaneously and after several hours at 4° it was filtered off. The filtrate was evaporated to dryness. The residue was dissolved in ether and the solution was washed with potassium hydrogen carbonate solution. Upon concentration of the ethereal solution *in vacuo*, 0.25–0.3 g. of the starting material I was recovered. The filtrate was evaporated to dryness to give a sirupy residue consisting mostly of N-carbobenzoxy-S-trityl-DL-cysteine methyl ester (II). Saponification of the product in the same manner as that described for the corresponding L-derivative in both 50% dioxane and 99% methanol afforded N-carbobenzoxy-S-trityl-DL-cysteine which was isolated as the diethylammonium salt. The yield was 65% calculated on the basis of I used; m.p. 161–162°, undepressed upon mixing with an authentic sample of the product.

The Anthrasteroid Rearrangement. VIII.[1] The Rearrangement of Dehydroergosterol and Δ5,7,9(11)-Cholestatriene-3β-ol to Δ5,7,9,22-Anthraergostatetraen-x-ols and Δ5,7,9-Anthracholestatrien-x-ols

By Kyosuke Tsuda, Ryoichi Hayatsu, John A. Steele, Osamu Tanaka[2a] and Erich Mosettig[2b]

The acid-catalyzed rearrangement of dehydroergosteryl acetate leads in fair yields to two isomeric ring A-hydroxylated Δ5,7,9,22-tetraenes when p-toluenesulfonic acid monohydrate is employed in place of HCl gas. The secondary hydroxyl group is located either in position 2 or 3. By dehydration, two isomeric pentaene hydrocarbons are formed which contain a conjugated double bond in ring A. By catalytic hydrogenation of these Δ1(or 3),5,7,9,22-pentaenes two isomeric (at C_{14}) Δ5,7,9-anthraergostatrienes are formed. One of them is identical with the triene obtained previously by catalytic hydrogenation of Δ5,7,9,14,22-anthraergostapentaene. In an analogous manner the rearrangement of Δ5,7,9(11)-cholestatrien-3β-ol acetate, catalyzed by p-toluenesulfonic acid monohydrate, leads to two ring A-hydroxylated Δ5,7,9-anthracholestatrienols in a total yield of approximately 30%. The secondary alcohols were converted via the Δ1(or 3),5,7,9-tetraenes to 14α- and 14β-5,7,9-trienes. The former proved to be identical with the hydrocarbon obtained previously by catalytic hydrogenation of Δ5,7,9,14-anthracholestatetraene. By boiling of the steroid Δ5,7,9(11)-trienol acetates (s.ch. = C_8H_{17}) in glacial acetic acid the corresponding 14a-Δ5,7,9-trienols are obtained almost exclusively in yields of about 30%.

Tsuda and Hayatsu[3] have reported the photochemical conversion of several polyunsaturated cholesterol and ergosterol derivatives to ring A-hydroxylated anthrasteroids. This discovery appeared significant in view of the suggested mechanism of the anthrasteroid rearrangement in which the initial step is presumed to involve the creation of a double bond in ring A by loss of the hydroxyl group.[4] We have repeated the photochemical experiments according to the published directions and have consistently failed to detect any anthrasteroid material, either by ultraviolet

spectral analysis or by isolation; the only identifiable products were dehydrocholesterol peroxide and ergosterol peroxide.

However, the use of p-toluenesulfonic acid as the rearrangement catalyst[3] (rather than hydrogen chloride) enabled us to isolate ring A-hydroxylated anthrasteroids (in ca. 30% yield) from the rearrangement of steroid Δ5,7,9(11)-trienol acetates.

The work-up of the crude reaction mixture proved to be exceedingly difficult, primarily because it involved the separation of two isomeric anthrasteroid secondary alcohols which themselves, as well as their various esters, are quite similar in their physical behavior and are rather unstable insofar as they tend to eliminate their oxygen function from ring A (with the creation of a double bond) in the process of crystallization or chromatography over alumina. Therefore in the chromatographic separation Florisil was used with great advan-

(1) Paper VII, W. R. Nes and D. L. Ford, *J. Am. Chem. Soc.*, **83**, 4811 (1961).

(2) (a) Visiting Scientist, National Institutes of Health. (b) Deceased, May 31, 1962.

(3) K. Tsuda and R. Hayatsu, *J. Am. Chem. Soc.*, **77**, 3089 (1955).

(4) (a) W. R. Nes, *ibid.*, **78**, 193 (1956); (b) W. R. Nes and E. Mosettig, *ibid.*, **76**, 3182 (1954); (c) P. Bladon, *J. Chem. Soc.*, 2176 (1955); (d) A. W. Burgstahler, *J. Am. Chem. Soc.*, **79**, 6047 (1957).
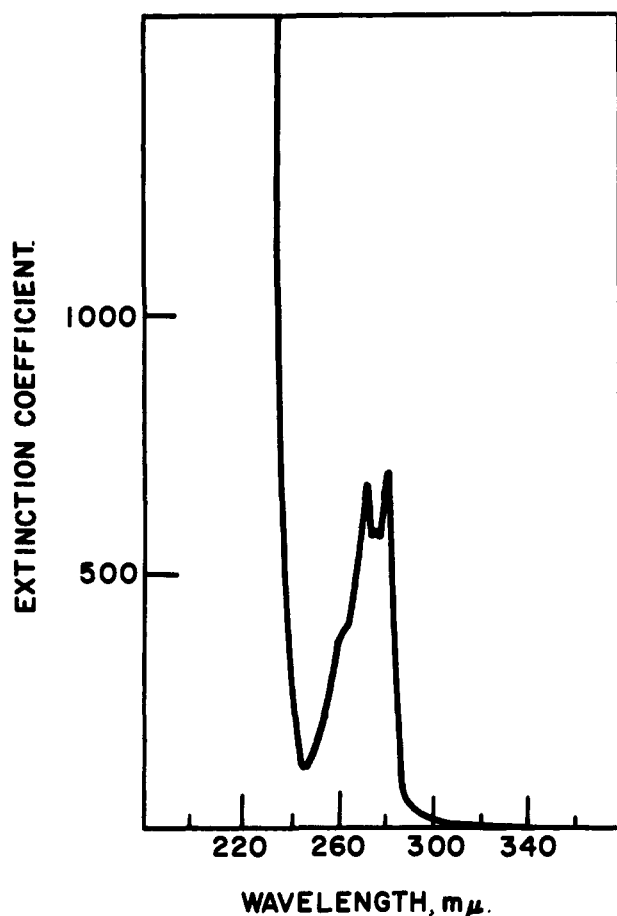
Figure 1.

Figure 2.

tage. The infrared spectra of the isomeric alcohols show only some slight differences in the fingerprint region. The ultraviolet spectra are very characteristic[5] and useful. As seen in Fig. 1 the ϵ of λ_{max} 283 mμ is slightly higher than the ϵ of λ_{max} 272.5 mμ. Also the ϵ of λ_{min} 274 mμ is very characteristic. The impurity of a given triene or trienol and its esters is readily seen in the deviation from these characteristic features as seen in Fig. 2.

When dehydroergosteryl acetate was treated with p-toluenesulfonic acid monohydrate in chloroform or dichloromethane a brownish-red oily mixture was obtained. Its infrared spectrum showed the presence of acetoxyl-group-containing components. This crude mixture was hydrolyzed with alkali and chromatographed on a Florisil column. From the first eluates 1.3% of $\Delta^{5,7,9,14,22}$-anthraergostapentaene (III)[4b] was obtained. The following eluates gave two chromatographically distinct crude products, A and B. Product A was treated with hexahydrobenzoyl chloride and the resulting ester purified by chromatography and crystallization whereby about 17% of homogeneous material was obtained. Purification of product B through the hexahydrobenzoate was not feasible since in the esterification and crystallization the oxygen function is eliminated to a certain extent and the resulting by-products cannot be removed from the ester. Treatment of B with p-chlorobenzoyl chloride, however, followed by chromatography and crystallization gave 11% of homogeneous material. By alkaline hydrolysis the hexahydrobenzoate (from A) yielded a dextrorotatory alcohol Ia, melting at 79–80°, and the p-chlorobenzoate
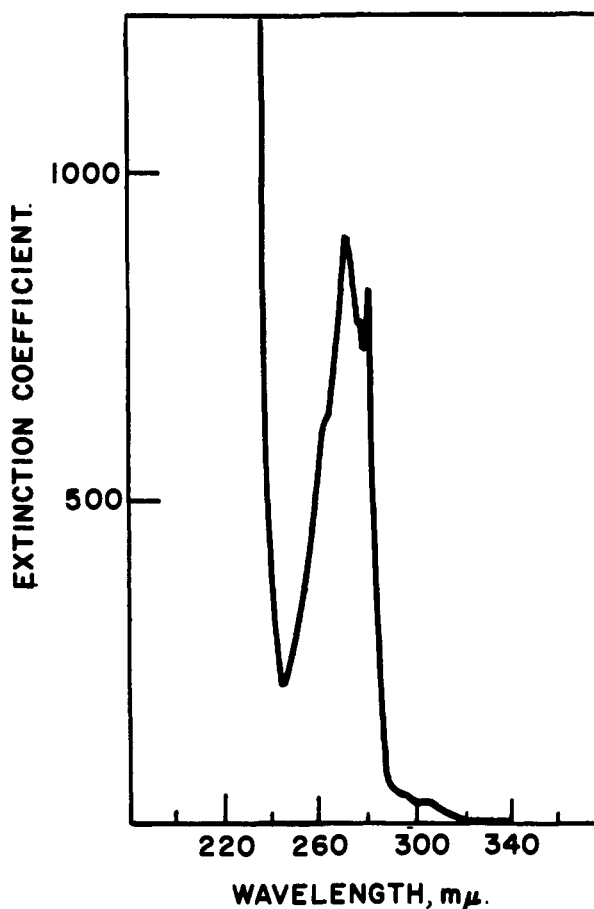
(from B) a levorotatory alcohol IIa, melting at 127–128°. Both Ia and IIa showed in their infrared spectra a strong hydroxyl band ($\lambda_{max}^{CS_2}$ 2.77 μ) and had the typical anthrasteroid triene ultraviolet spectrum (λ_{max} 282, 277, 272.5 mμ). In both alcohols the side chain double bond could be readily reduced, but only the dihydro product IIg could be obtained in crystalline state. The oily dihydro alcohol Ig gave readily a crystalline hexahydrobenzoate. Both dihydro alcohols were converted by slow distillation *in vacuo* of their intimate mixture with copper powder[6] to the corresponding ketones which showed the typical six-membered ring ketone band of 1724 cm.$^{-1}$ whereas the ultraviolet spectra demonstrated the non-conjugated carbonyl group. The tetraene alcohols Ia and IIa were also oxidized to the ketones, but more conveniently with chromic acid.

Boiling of the tosylates of Ia and IIa in collidine-xylene gave the corresponding hydrocarbons If and IIf with the new double bond at Δ^1 or Δ^3, *i.e.*, in conjugation with the aromatic ring. By catalytic hydrogenation, the conjugated and side chain double bonds were readily saturated. The anthrasteroid triene III thus obtained from IIa melted at 108–109°, $[\alpha]_D$ +21°, and was identical in every respect with the triene obtained previously by catalytic hydrogenation of $\Delta^{5,7,9,14,22}$-anthraergostapentaene.[4b] An analogous sequence of reactions led from alcohol Ia to an isomeric anthraergostatriene II, m.p. 70–71°, $[\alpha]_D$ +75°. The isomerism of these trienes must be located at the C/D ring fusion, and we assume at C_{14}. Moreover, we assume that the triene derived from $\Delta^{5,7,9,14,22}$-anthraergostapentaene has C/D *trans* juncture, and assign therefore

(5) 1. Scheer, W. R. Nes and P. B. Smeltzer, *J. Am. Chem. Soc.*, **77**, 3300 (1955); see also ref. 4b.

(6) R. E. Marker, D. L. Turner, T. S. Oakwood, E. Rohrmann and P. R. Ulshafer, *ibid.*, **64**, 720 (1942).
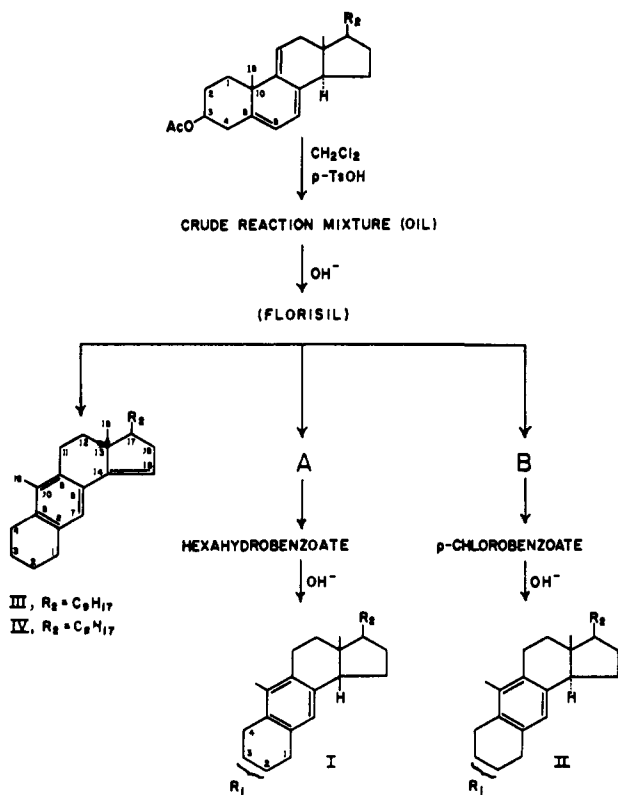
Figure 3.

to the I-derivatives the C/D-*cis* structure and to the II-derivatives the C/D-*trans* structure. We shall describe in the following paper of this series experiments supporting the above assumptions.

Because of the isomerism at C_{14} it cannot be decided whether or not the hydroxyl group in the isomeric secondary alcohols Ia and IIa occupies the same position. Since they could be oxidized to non-conjugated ketones the hydroxyl group should be located at C_2 or C_3 depending on whether in the spiro intermediate[7] the C_4 or the C_1 migrates to C_6. Position 12 cannot be excluded on experimental grounds but appears very improbable as the location of the hydroxyl group in the anthrasteroids.

It should be mentioned that the tetraenone Id and the trienone Ij not only remain stubbornly oily but give with semicarbazide rather soluble derivatives melting below 100° which makes their nature and homogeneity doubtful. On the other hand, tetraenone IId and trienone IIj and their semicarbazones appear spectroscopically (in the ultraviolet) and in regard to their physical properties quite normal. A satisfactory explanation for this different behavior is lacking at present.

The experiments in the cholesterol series proceed in an analogous manner. The crude reddish-brown oily reaction mixture obtained by treatment of $\Delta^{5,7,9(11)}$-cholestatrien-3β-ol acetate in chloroform with p-toluenesulfonic acid monohydrate was hydrolyzed and subjected to chromatography on Florisil. From the petroleum ether–benzene (19:1) eluate nearly 5% of $\Delta^{5,7,9,14}$-anthracholestatetraene (IV)[8] was obtained.[9]

By treatment with hexahydrobenzoyl chloride of the fractions eluted with benzene–petroleum ether (7:3) and benzene, the dextrorotatory secondary alcohol Ia

(7) See W. R. Nes, J. A. Steel and E. Mosettig, *J. Am. Chem. Soc.*, **80**, 5230 (1958).

(8) W. R. Nes, R. B. Kostic and E. Mosettig, *ibid.*, **78**, 436 (1956).

(9) Chloroform appears to promote to a somewhat larger extent the formation of the unsaturated hydrocarbon than does methylene chloride.

was obtained. Although homogeneous, it remained oily most stubbornly, but finally became crystalline after several months of storage. From the fractions eluted with chloroform–benzene (10:1 and 1:1 the crystalline levorotatory alcohol II could be secured by purification through the p-chlorobenzoate.

By heating the tosylates of alcohols I and II in collidine–xylene two anthracholestatetraenes were formed which thus far could not be induced to crystallize. In both tetraenes the olefinic bond is conjugated with the aromatic ring. Catalytic reduction of the tetraene derived from the levorotatory alcohol IIa yielded a crystalline triene identical in every respect with the one obtained previously by catalytic reduction of $\Delta^{5,7,9,14}$-anthracholestatetraene.[8] The corresponding triene derived from the dextrorotatory alcohol has not crystallized as yet.

TABLE I

		I (C/D-*cis*)		II (C/D-*trans*)	
R₁	R	M.p., °C.	[α]D	M.p., °C.	[α]D
OH	C_9H_{17}	79–80	+11°	127–128	−29°
OCOC₆H₁₁	C_9H_{17}	101–102	+ 8		
OCOC₆H₄p-Cl	C_9H_{17}			122–123	−12
O	C_9H_{17}	Oily	+45.1	102–103	− 1.9
NNHCONH₂	C_9H_{17}	97		218	
H (Δ¹ or Δ²)	C_9H_{17}	Oily	+76	67–68	−14.5
OH	C_9H_{19}	Oily	+34	131–132	−17
OCOC₆H₁₁	C_9H_{19}	128–128.5	+29	132–133	−10.1
OCOC₆H₄p-Cl	C_9H_{19}			137–138	+ 2
O	C_9H_{19}	Oily	+75	97–98	+ 8
NNHCONH₂	C_9H_{19}	98–99		205 dec.	
H	C_9H_{19}	70–71	+75	108–109	+21
OH	C_8H_{17}	78–80	+44.5	82–85	− 9.7
+½CH₃OH				62–64	− 9.5
OCOC₆H₁₁	C_8H_{17}	112–113	+35.2	114–115	− 4.7
OCOC₆H₄p-Cl	C_8H_{17}	68–70	+43.4	127	+ 7.7
OCOC₆H₄o-Cl	C_8H_{17}			141–142	− 1.8
Δ¹(or 3)5,7,9	C_8H_{17}	Oily	+112.8	Oily	+ 6.5
Δ⁵,⁷,⁹	C_8H_{17}	Oily	+84.0	80–82	+28.7

Also in this series it can be reasonably assumed that the isomerism of the trienes is located at C_{14}, and no conclusions can be drawn in regard to the position and configuration in ring A.

When testing qualitatively the stability of the steroid $\Delta^{5,7,9(11)}$-trien-3β-ol system in various solvents we noted with surprise that mere boiling for several hours of the steroid-5,7,9(11)-trienol acetates in acetic acid not only brought about the anthrasteroid rearrangement to the extent of about 30%, but that under these conditions the 14α-trienols were formed exclusively.

Experimental[10]

Rearrangement of Dehydroergosteryl Acetate.—To a solution of 26.0 g. of dehydroergosteryl acetate in 1.3 liters of dichloromethane was added 13.0 g. of p-toluenesulfonic acid monohydrate. The reaction mixture was allowed to remain at room temperature overnight and the resulting dark green solution extracted with 2 l. of 5% aqueous potassium bicarbonate solution. The color changed to red when all of the p-toluenesulfonic acid had been removed. The solution was washed with water, dried over sodium sulfate and evaporated under reduced pressure to dryness. The dark brown oily residue ($\lambda_{max}^{CHCl_3}$ 5.82 μ) was taken up in 1 l. of 10% alcoholic potassium hydroxide solution, and the mixture boiled for 50 minutes. After distilling off part of the ethanol and replacing it with water, the hydrolysate was extracted with ether. The ethereal solution was washed with water, dried, and evaporated *in vacuo*. The oily residue was dissolved in petroleum ether–benzene (10:1) and adsorbed on a

(10) All melting points were determined on a Kofler block and are recorded as read. Rotations were determined in chloroform in approx. 1.0–1.5% solution at 20°. Ultraviolet spectra were determined on a Cary recording spectrophotometer, model 11, in ethanol; infrared spectra on a Perkin–Elmer double beam spectrophotometer, model 21 (Mr. H. K. Miller and Mr. Richard T. Brown). Microanalyses are by the Analytical Service Laboratory of this Institute under the direction of Mr. Harold G. McCann. Woelm neutral alumina, Grades 1 and 11, was used for chromatography. The Florisil (60/100 mesh) was used as purchased from Floridin Co., Tallahassee, Fla. Petroleum ether refers to the solvent of b.p. 30–60°, purified in the conventional manner.

column of 500 g. of Florisil and eluated as: 1 and 2, 1-l. fractions of petroleum ether–benzene (10:1); 3–6, 250-ml. fractions of petroleum ether–benzene (10:1); 7–10, 250-ml. fractions of petroleum ether–benzene (1:1); 11–28, 250-ml. fractions of benzene–petroleum ether (7:3); 29 and 30, 250-ml. fractions of benzene–chloroform (8:2); 33–37, 250-ml. fractions of chloroform benzene (7:3); 41–45, 250-ml. fractions of chloroform.

Fractions 1 and 2 gave 0.3 g. of a colorless oil, which gave the characteristic ultraviolet spectrum of anthraergostapentaene.[4b] Fractions 13–25 yielded 10.3 g. of an oil (A) which showed a strong hydroxyl band ($\lambda_{max}^{CS_2}$ 2.76 μ). Fractions 29–39 gave 8.7 g. of an oil (B) which showed the same infrared absorption band. Fractions 26–28 gave 1.9 g. of an oil which was not further investigated.

14β-Δ⁵,⁷,⁹,²²-Anthraergostatetraen-x-ol Hexahydrobenzoate (Ib).—To a solution of 10.3 g. of A in 110 ml. of pyridine was added 16 ml. of hexahydrobenzoyl chloride while the temperature was kept at 0°. The mixture was allowed to stand at room temperature overnight and poured into 1 l. of ice-cold 5% aqueous potassium bicarbonate solution. The ethereal extract was washed with water, dried and evaporated *in vacuo* leaving *ca.* 15 g. of an oily residue which was dissolved in petroleum ether and absorbed on 300 g. of Florisil. Elution with petroleum ether–benzenes (10:1) gave 8.7 g. of oily material. After three crystallizations from acetone–methanol 5.05 g. of colorless, transparent, rectangular plates were obtained which melted at 101–102°, $[\alpha]$D +8°; λ_{max} 273, 277 and 288 mμ (ϵ 787, 671 and 813, respectively); λ_{min} 247 mμ (ϵ 116); $\lambda_{max}^{CS_2}$ 5.80 and 11.50 μ; λ_{max}^{Nujol} 5.76, 6.23, 6.36 and 11.50 μ.

Anal. Calcd. for $C_{35}H_{52}O_2$: C, 83.28; H, 10.38. Found: C, 83.56; H, 10.49.

14β-Δ⁵,⁷,⁹,²²-Anthraergostatetraen-x-ol (Ia).—The hexahydrobenzoate Ib was refluxed for 1 hour in 10% ethanolic potassium hydroxide, and the resulting alcohol crystallized from methanol–water; m.p. 79–80°, $[\alpha]$D +11°; λ_{max} 272, 277 and 288 mμ (ϵ 757, 654 and 813, respectively), λ_{min} 247 mμ (ϵ 103); $\lambda_{max}^{CS_2}$ 2.77 and 11.48 μ; λ_{max}^{Nujol} 3.00, 6.24, 6.36 and 11.46 μ.

Anal. Calcd. for $C_{28}H_{42}O$: C, 85.22; H, 10.73. Found: C, 85.26; H, 10.94.

14β-Δ⁵,⁷,⁹,²²-Anthraergostatetraen-x-one (Id).—To a cooled (*ca.* 5°) solution of 808 mg. of Ia in 50 ml. of acetone was added dropwise a solution of chromic acid in dilute sulfuric acid until the persistent orange-brown color indicated that oxidation was complete[11] in about 5 minutes. The reaction mixture was poured into 300 ml. of water and extracted with ether. The ethereal extracts were washed with 5% aqueous potassium bicarbonate solution, dried and evaporated. The colorless oil thus obtained was dissolved in petroleum ether and adsorbed on 50 g. of Florisil and eluted with petroleum ether containing 5% ether. About 400 mg. of oily ketonic material was obtained which could not be induced to crystallize; $[\alpha]$D +45.1°, λ_{max} 272.5 and 281.5 mμ (ϵ 1214 and 1040, respectively), λ_{min} 255 mμ (ϵ 876); $\lambda_{max}^{CS_2}$ 5.80, 10.3 and 11.33 μ. The "semicarbazone" Ic prepared in methanol with semicarbazide hydrochloride and pyridine consisted of a microcrystalline slightly discolored material and melted after two crystallizations from methanol–water at 97°; λ_{max} 271.5 and 281.0° mμ (ϵ 2065 and 2079, respectively), shoulder 312 mμ (ϵ 1362). The analytical sample was dried *in vacuo* at 50° for 3 days.

Anal. Calcd. for $C_{29}H_{43}ON_3$: C, 77.46; H, 9.64; N, 9.35. Found: C, 77.35; H, 9.56; N, 9.66.

14β-Δ¹(or 3),5,7,9,22-Anthraergostapentaene (If).—To a solution of 0.60 g. of alcohol Ia in 28 ml. of dry pyridine was added 1.5 g. of *p*-toluenesulfonyl chloride (freshly recrystallized from petroleum ether, b.p. 60–70°). The reaction mixture was allowed to stand in the dark overnight at room temperature and poured into 200 ml. of ice-cold 5% aqueous potassium bicarbonate solution. The ethereal extract was washed with water, dried and on evaporation *in vacuo* left the tosylate as a colorless oil. Without further purification it was dissolved in 20 ml. of dry xylene, and the solution added dropwise to a well-stirred refluxing mixture of 10 ml. of collidine and 30 ml. of xylene. Boiling was continued for an hour and the xylene was distilled off. Benzene was added and the mixture evaporated *in vacuo* to dryness. The unsaturated hydrocarbon was extracted with hot petroleum ether (60–70°), chromatographed on 30 g. of alumina and eluted with petroleum ether, whereby 0.48 g. of colorless oil was obtained, $[\alpha]$D +76°; λ_{max} 221, 227, 271 and 306 mμ (ϵ 19202, 18907, 9306 and 591); $\lambda_{max}^{CS_2}$ 10.30, 11.40 and 12.73 μ.

14β-Δ⁵,⁷,⁹-Anthraergostatrien-x-ol (Ig).—A solution of 4.0 g. of Ia in 272 ml. of ethyl acetate and 27 ml. of glacial acetic acid was shaken in a hydrogen atmosphere with 1.96 g. of platinum oxide. The hydrogen uptake ceased when one mole equivalent of hydrogen had been absorbed. After removal of the solvents *in vacuo*, 4.2 g. of colorless oil was obtained. Efforts to induce crystallization with various solvents and by chromatography

failed; $[\alpha]$D +34°; λ_{max} 273, 277 and 282 mμ (ϵ 720, 614 and 764, respectively); λ_{max} 247 mμ (ϵ 107); $\lambda_{max}^{CS_2}$ 2.78 and 11.47 μ.

14β-Δ⁵,⁷,⁹-Anthraergostatrien-x-ol Hexahydrobenzoate (Ih).—The hexahydrobenzoate Ic dissolved in 8 parts of ethyl acetate-glacial acetic acid (10:1) was subjected to catalytic hydrogenation as described above for the alcohol. The reduction product crystallized from acetone–methanol in transparent rectangular plates, m.p. 128–128.5°, $[\alpha]$ +29°; λ_{max} 273, 277 and 282 mμ (ϵ 740, 638 and 791, respectively); λ_{min} 247 mμ (ϵ 128); $\lambda_{max}^{CS_2}$ 5.77, 11.49 μ; λ_{max}^{Nujol} 5.76, 6.24, 6.36 and 11.51 μ.

Anal. Calcd. for $C_{35}H_{54}O_2$: C, 82.95; H, 10.74. Found: C, 82.62; H, 10.38.

14β-Δ⁵,⁷,⁹-Anthraergostatrien-x-one (Ij).—An intimate mixture of 0.49 g. of Ig and 4.0 g. of copper powder ("hydrogen reduced") was slowly heated to 250° at about 0.35 mm. The distillate (collected in the non-heated part of a horizontal wide test-tube) was dissolved in petroleum ether (b.p. 30–60°) and adsorbed in 10 g. of Florisil. By elution with petroleum ether containing 2% of ether about 0.15 g. of oily ketonic material was obtained, $[\alpha]$D +75°; λ_{max} 272.5 and 281.5 mμ (ϵ 1017 and 930, respectively), λ_{min} 260 (ϵ 825), $\lambda_{max}^{CS_2}$ 5.80 and 11.32 μ. The "semicarbazone," prepared in methanol with semicarbazide hydrochloride and pyridine, consisted of a microcrystalline slightly discolored powder and melted after crystallization from methanol–water at 98–99°; λ_{max} 281.5 and 271.5 mμ (ϵ 1826 and 1900, respectively), no defined shoulder.

Anal. Calcd. for $C_{29}H_{45}ON_3$: C, 77.11; H, 10.04; N, 9.31. For $C_{29}H_{45}ON_3 \cdot 1/4H_2O$: C, 76.35; H, 10.05; N, 9.21. Found: C, 76.29; H, 10.15; N, 9.21.

14β-Δ⁵,⁷,⁹-Anthraergostatriene (II).—Catalytic hydrogenation of the pentaene If conducted as described for the preparation of Ig or Ih, *i.e.*, one part of the pentane in eight parts of a mixture of ethyl acetate and glacial acetic acid (10:1) with a large excess of platinum oxide, yielded a crystalline product. After recrystallization from acetone it melted at 70–71°, $[\alpha]$D +75°; λ_{max} 273, 278 and 282.5 mμ (ϵ 741, 633 and 805, respectively); λ_{min} 247 mμ (ϵ 99); $\lambda_{max}^{CS_2}$ 11.54 μ.

Anal. Calcd. for $C_{28}H_{44}$: C, 88.35; H, 11.65. Found: C, 88.09; H, 11.52.

14α-Δ⁵,⁷,⁹,²²-Anthraergostatetraen-x-ol *p*-Chlorobenzoate (IIc).—The chromatographic fraction B (8.7 g.) was treated with *p*-chlorobenzoyl chloride in pyridine in the manner described for the preparation of the hexahydrobenzoate Ib. The crude ester was placed on 50 g. of alumina and eluted with 2 liters of petroleum ether–benzene (10:1) in order to remove the *p*-chlorobenzanhydride formed in the acylation. The oil thus obtained (*ca.* 11 g.) was dissolved in petroleum ether–benzene (10:1) and adsorbed on 220 g. of Florisil and eluted with 2 l. (the total of 8 fractions) of the above solvent mixture yielding 9.8 g. of colorless oily ester. Three crystallizations from acetone–ethanol gave 3.36 g. of analytically pure IIc, m.p. 122–123°, $[\alpha]$D −12°; λ_{max} 272, 275 (shoulder) and 282 mμ (ϵ 1647, 1317 and 1291, respectively); $\lambda_{max}^{CS_2}$ 5.80 μ.

Anal. Calcd. for $C_{35}H_{46}O_2Cl$: C, 78.69; H, 8.68. Found: C, 78.86; H, 8.54.

14α-Δ⁵,⁷,⁹,²²-Anthraergostatetraen-x-ol (IIa).—The hydrolysis was carried out as described in the analogous procedure for the preparation of Ia. The crystalline material obtained from methanol melted at 127–128°; $[\alpha]$D −29°; λ_{max} 273, 277 and 282 mμ (ϵ 703, 598 and 723, respectively); λ_{min} 247 mμ (ϵ 106); $\lambda_{max}^{CS_2}$ 2.77 and 11.49 μ; λ_{max}^{Nujol} 3.01, 6.23, 6.36 and 11.41 μ.

Anal. Calcd. for $C_{28}H_{42}O$: C, 85.22; H, 10.73. Found: C, 85.17; H, 10.73.

14α-Δ⁵,⁷,⁹,²²-Anthraergostatetraen-x-one (IId) was prepared by chromic acid oxidation of II in exactly the same manner as described for the conversion of Ia to Id. In this instance, however, the ketonic material obtained by chromatographic separation crystallized readily and melted at 93–97° (yield about 40%). One recrystallization from ethanol raised the m.p. to 102–103°, $[\alpha]$D −1.9°, λ_{max} 272.5 and 281.5 mμ (ϵ 713 and 671, respectively); λ_{min} 255 mμ (ϵ 356); $\lambda_{max}^{CS_2}$ 5.79, 10.3 and 11.30 μ. The analytical sample was dried under a high vacuum at 100° for 2 days whereby the m.p. was not changed.

Anal. Calcd. for $C_{28}H_{40}O$: C, 85.65; H, 10.27. Found: C, 85.57; H, 10.43.

The semicarbazone melted with decomposition at 218°, λ_{max} 271.5 and 281.5 mμ (ϵ 879 and 753), shoulder at 304 mμ (ϵ 88.9).

Anal. Calcd. for $C_{29}H_{43}ON_3$: C, 77.46; H, 9.64; N, 9.35. Found: C, 77.25; H, 9.64. N, 9.29.

14α-Δ¹(or 3),5,7,9,22-Anthraergostapentaene (IIf) was obtained by exactly the same procedures which have been described for the preparation of the pentaene If. Also here the oily intermediate was, without further purification, subjected to heating in collidine–xylene and the crude pentaene purified by chromatography and crystallization from acetone–methanol. The yield of material melting at 62–63° was 71%. Recrystallization from acetone–

(11) A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

methanol yielded long prisms melting at 67–68°, $[\alpha]$D −14.5°; λ_{max} 221, 227, 271 and 306 mμ (ϵ 24040, 26544, 9849 and 584); $\lambda_{max}^{CS_2}$ 10.32, 11.49 and 12.70 μ.

Anal. Calcd. for $C_{28}H_{40}$: C, 89.29; H, 10.71. Found: C, 89.21; H, 10.62.

14α-Δ⁵,⁷,⁹-Anthraergostatriene-x-ol (IIg).—The catalytic hydrogenation of IIa was conducted under the same conditions and the the same ratio of compound, catalyst and solvents as described for the analogous hydrogenations of Ia and Ib. Crystallization from methanol gave the trienol, m.p. 131–132°, $[\alpha]$D −17°; λ_{max} 272, 277 and 282 mμ (ϵ 674, 571 and 705, respectively); λ_{min} 247 mμ (ϵ 83); $\lambda_{max}^{CS_2}$ 2.78 and 11.47 μ.

Anal. Calcd. for $C_{28}H_{44}O$: C, 84.78; H, 11.18. Found: C, 84.72; H, 11.26.

14α-Δ⁵,⁷,⁹-Anthraergostatrien-x-ol Hexahydrobenzoate (IIh).—To a solution of 300 mg. of IIg in 10 ml. of pyridine was added 1 ml. of hexahydrobenzoyl chloride at 0° and the resulting red solution was allowed to stand overnight. By the procedure described for IIb, there were obtained colorless crystals, which after recrystallization from acetone–methanol melted at 131.5–132.5° (yield 310 mg.), $[\alpha]$D −9.7°. This material showed abnormalities in the ultraviolet spectrum: 272, 277, 282, 294 and 304 mμ (ϵ 916, 780, 838, 49 and 39, respectively); λ_{min} 214 mμ. An aliquot part of the material was subjected to catalytic hydrogenation. A small amount of hydrogen was absorbed. The ester melted after two crystallizations from acetone–methanol at 132–133°, hexagonal plates, $[\alpha]$D −10.1°; λ_{max} 272.5, 277 and 282 mμ (ϵ 688, 577, 713, respectively); λ_{min} 247 mμ (ϵ 111); $\lambda_{max}^{CS_2}$ 5.78 and 11.45 μ.

Anal. Calcd. for $C_{35}H_{54}O_2$: C, 82.95; H, 10.74. Found: C, 83.18; H, 10.55.

The mixture of the compound with the 14β-isomer IIh of m.p. 128–128.5° melted unsharply between 127 and 132°, the major part at 128–129°.

14α-Δ⁵,⁷,⁹-Anthraergostatrien-x-ol p-Chlorobenzoate (IIi).—The esterification of the alcohol IIg with p-chlorobenzoyl chloride proceeded analogously to that of (crude) IIa. The ester melted after crystallization from acetone–methanol at 137–138°, $[\alpha]$D +2°; λ_{max} 272, 275 (shoulder) and 282 mμ (ϵ 1625, 1136, and 1275, respectively); $\lambda_{max}^{CS_2}$ 5.80 μ.

Anal. Calcd. for $C_{35}H_{48}O_2Cl$: C, 78.39; H, 9.02. Found: C, 78.43; H, 9.22.

14α-Δ⁵,⁷,⁹-Anthraergostatrien-x-one (IIj) was prepared in the same manner as its 14β-isomer Ij. The crude ketone gave after chromatography on Florisil and subsequent crystallization from ethanol–water material of m.p. 97–98° in a yield of 38%, $[\alpha]$D +8°, λ_{max} 272.5 and 281.5 mμ (ϵ 714 and 663, respectively), λ_{min} 260 mμ (ϵ 439), $\lambda_{max}^{CS_2}$ 5.80 and 11.32 μ.

Anal. Calcd. for $C_{28}H_{42}O$: C, 85.22; H, 10.73. Found: C, 84.89; H, 10.97.

The semicarbazone melted after crystallization from ethanol–water at 205° with decomposition, λ_{max} 271.5 and 281.5 mμ (ϵ 1009 and 858), shoulder 304 mμ (ϵ 196).

14α-Δ⁵,⁷,⁹-Anthraergostatriene (III) was obtained by catalytic hydrogenation of the Δ¹(or ³),⁵,⁷,⁹,²²-pentaene IIf under conditions given above for the hydrogenation of the pentaene If. Crystallization from acetone gave transparent rectangular plates, m.p. 108–109°, $[\alpha]$D +21°; λ_{max} 272.5, 277 and 282.5 mμ (ϵ 675, 565 and 711, respectively); λ_{min} 247 mμ (ϵ 91); $\lambda_{max}^{CS_2}$ 11.57 μ. The hydrocarbon proved to be identical in every respect with the triene obtained previously.[4b]

Rearrangement of Δ⁵,⁷,⁹(¹¹)-Cholestatrien-3β-ol Acetate.—To a stirred solution of 10 g. of Δ⁵,⁷,⁹(¹¹)-cholestatrien-3β-ol acetate in 500 ml. of chloroform was added 5 g. of p-toluenesulfonic acid monohydrate, and the solution was allowed to stand at room temperature overnight. The solution which had turned rather dark was washed with 5% aqueous potassium bicarbonate solution and with water, dried and evaporated to dryness. The residue was dissolved in 5% aqueous potassium hydroxide solution. After boiling for 1 hour the solution was poured into water and the precipitated oil extracted with ether. The residue left by evaporation of the washed and dried ethereal solution was dissolved in petroleum ether and placed on a column of 400 g. of Florisil. The following fractions were obtained: (a) elution with 1 l. of petroleum ether; (b) with 1 l. of petroleum ether–benzene 10:1; (c) with 2.5 l. of benzene–petroleum ether 1:1, (d) with 2 l. of benzene–petroleum ether 7:3; (e) with 1 l. of benzene; (f) with 1 l. of benzene–chloroform 10:1; (g) with 1.5 l. of benzene–chloroform 1:1; (h) with 1.5 l. of chloroform.

Δ⁵,⁷,⁹,¹⁴-Anthracholestatetraene.—Evaporation of fraction b left 500 mg. of crystalline material. Recrystallization from acetone–methanol and from methanol gave a hydrocarbon melting at 118°, $[\alpha]$D −35.8°; $\lambda_{max}^{isooctane}$ 222, 227, 266, 296.5 and 308 mμ (ϵ 24,100, 25,500, 16,900, 2,430 and 1,990). It was shown by direct comparison to be identical in every respect with an authentic sample prepared previously[8] (by rearrangement in CHCl₃–HCl).

14β-Δ⁵,⁷,⁹-Anthracholestatrien-x-ol Hexahydrobenzoate (In).—Fraction e left on evaporation 2.4 g. of an oily residue which was dissolved in 50 ml. of pyridine, 4 ml. of hexahydrobenzoyl chloride added and the mixture allowed to stand at room temperature overnight. After crystallization from ethanol the ester (1.5 g.) melted at 112–113°, $[\alpha]$D +35.2°; λ_{max} 272, 277 and 281.5 mμ (ϵ 735, 622 and 765, respectively); $\lambda_{max}^{CS_2}$ 5.77 and 11.49 μ; λ_{max}^{Nujol} 5.76, 6.22, 6.34 and 11.50 μ.

Anal. Calcd. for $C_{34}H_{52}O_2$: C, 82.85; H, 10.64. Found: C, 82.68; H, 10.73.

From fraction d 1.7 g. of oily product was obtained which yielded 250 mg. of the above ester In, m.p. 111–113°.

14β-Δ⁵,⁷,⁹-Anthracholestatrien-x-ol p-Chlorobenzoate (Io).—A sample of ester In (450 mg.) was hydrolyzed by boiling in 5% ethanolic potassium hydroxide solution, and the oily alcohol ($[\alpha]$D +45.0°) obtained was treated with p-chlorobenzoyl chloride in the manner described for the preparation of In. The p-chlorobenzanhydride formed in the acylation had to be removed by chromatography on Florisil. The p-chlorobenzoate (350 mg.) crystallized from ethanol or acetone–methanol mixture melted at 68–70°, $[\alpha]$D +43.4°, $\lambda_{max}^{CS_2}$ 5.79 μ.

Anal. Calcd. for $C_{34}H_{45}O_2Cl$: C, 78.35; H, 8.70. Found: C, 78.30; H, 9.00.

14β-Δ⁵,⁷,⁹-Anthracholestatrien-x-ol (Im).—The oily alcohol was obtained by refluxing the ester In in 5% ethanolic potassium hydroxide solution for 50 minutes. The oily product ($[\alpha]$D +45°) remained subbornly oily and was re-esterified and hydrolyzed in order to ascertain its homogeneity. Eventually, when stored for several months in the cold it turned crystalline. It melted after recrystallization from minimal amounts of methanol at 78–80°. It was also obtained as a hemihydrate, m.p. 62–64°, $[\alpha]$D +44.5°; λ_{max} 273, 277.5 and 282 mμ (ϵ 736, 624 and 755, respectively); $\lambda_{max}^{CS_2}$ 2.77 and 11.50 μ; λ_{max}^{Nujol} 2.86, 6.24, 6.36 and 11.42 μ.

Anal. Calcd. for $C_{27}H_{42}O$: C, 84.75; H, 11.07. Found: C, 84.86; H, 11.25.

14β-Δ⁵,⁷,⁹-Anthracholestatriene (Ir) from Trienol Im via 14β-Δ¹(or ³),⁵,⁷,⁹-Anthracholestatetraene (Iq).—A solution of Ia (freshly prepared from 450 mg. of Ib) and 0.8 g. of freshly recrystallized tosyl chloride in 8 ml. of pyridine was allowed to stand at room temperature overnight. The reaction mixture was poured onto ice, mixed with aqueous 5% potassium carbonate and the precipitate extracted with ether. The ethereal solution was washed, dried and evaporated, and a solution of the oily tosylate in 10 ml. of xylene was added within 40 minutes to a boiling mixture of 10 ml. of xylene and 1 ml. of collidine. Refluxing was continued for 1 hour. The larger part of the xylene was distilled off under ordinary pressure, the concentrate was diluted with benzene, and the mixture evaporated to dryness *in vacuo*. The residue was extracted with ether and the solution of the hydrocarbon evaporated leaving a light brown oil. It was adsorbed on 15 g. of alumina (neutral, Grade I). By elution with 150 ml. of n-hexane 323 mg. of a colorless oil was obtained from the first fraction. The second fraction and fractions 3 and 4 (n-hexane–benzene 8:2) gave only small amounts of oily material. The oily tetraene Iq could not be induced to crystallize; $[\alpha]$D +112.8°; λ_{max} 221, 227, 234.5 and 272 mμ (ϵ 19,600, 19,700, 13,400 and 9,800), infl. 304 mμ (ϵ 520).

In the catalytic hydrogenation of this oily compound (310 mg.) in 16 ml. of ethyl acetate and 2 ml. of glacial acetic acid with PtO₂ (75 mg.) one mole equivalent of hydrogen was absorbed in 5 minutes, when the hydrogenation came to a standstill. The oily triene Ir isolated resisted all efforts of crystallization even after extensive chromatography on alumina (neutral, Grade I). The apparently homogeneous compound showed $[\alpha]$D +84°; $\lambda_{max}^{isooctane}$ 273, 278 and 283 mμ (ϵ 684, 571 and 752, respectively); $\lambda_{max}^{CS_2}$ 11.54 μ.

14α-Δ⁵,⁷,⁹-Anthracholestatrien-x-ol p-Chlorobenzoate (IIo).—The oily residue (1.6 g.) obtained by evaporation of chromatographic fraction g (see above) was dissolved in 40 ml. of pyridine, 4 ml. of p-chlorobenzoyl chloride was added, and the mixture allowed to stand at room temperature overnight. The p-chlorobenzanhydride formed was removed by passing a solution of the reaction product in n-hexane–benzene (10:1) through a column of 50 g. of Florisil. The ester was recrystallized twice from acetone and melted at 125–126°, $[\alpha]$D +6.8°. Another recrystallization raised the m.p. to 126–127°, $[\alpha]$D +7.7°; $\lambda_{max}^{CS_2}$ 5.79 μ.

Anal. Calcd. for $C_{34}H_{45}O_2Cl$: C, 78.35; H, 8.70. Found: C, 78.43; H, 8.87.

Chromatographic fraction f (see above) apparently contained a mixture of both alcohols Im and IIm. Since the p-chlorobenzoate IIo is less soluble in acetone at room temperature then p-chlorobenzoate Io, a separation of the alcohol mixture could be effected by treatment with p-chlorobenzoyl chloride and fractional crystallization of the ester mixture from acetone. Thus the oily residue (2.2 g.) from fraction f yielded 450 mg. of homogeneous IIo.

14α-Δ⁵,⁷,⁹-**Anthracholestatrien-x-ol (IIm)**.—The crystalline alcohol was obtained by boiling the *p*-chlorobenzoate IIo in 5% ethanolic potassium hydroxide solution for 50 minutes. After two crystallizations from methanol the compound melted constantly at 62–64°, [α]D −9.5°.

Anal. Calcd. for C₂₇H₄₂O·1/2CH₃OH: C, 82.87; H, 11.13. Found: C, 83.26; H, 11.42.

After drying *in vacuo* at 60° for 3 hours, the m.p. rose to 82–82°, [α]D −9.7°; λmax 272.5, 277 and 282 mμ (ε 682, 575 and 708, respectively); λmax^CS2 2.77 and 11.47 μ; λmax^Nujol 3.02, 6.2 2, 6.35 and 11.43 μ.

Anal. Calcd. for C₂₇H₄₂O: C, 84.75; H, 11.07. Found: C, 84.61; H, 10.94.

The mixture of this alcohol IIm and its isomer Im melts unsharply at about 80°.

14α-Δ⁵,⁷,⁹-**Anthracholestatrien-x-ol Hexahydrobenzoate (IIn)**.—A mixture of 20 mg. of the above alcohol IIm, 1.2 ml. of hexahydrobenzoyl chloride and 26 ml. of pyridine was allowed to stand at room temperature overnight. The first crystallization of the reaction product gave 200 mg. of an ester melting at 113–114°, [α]D −4.3°. By a second crystallization from ethanol the m.p. rose to 114–115°, [α]D −4.7°; λmax 272, 277 and 281.5 mμ (ε 690, 580 and 710, respectively); λmax^CS2 5.77 and 11.45 μ; λmax^Nujol 5.99, 6.21, 6.35 and 11.54 μ.

Anal. Calcd. for C₃₄H₅₂O₂: C, 82.87; H, 10.64. Found: C, 83.03; H, 10.90.

A mixture of this ester and its isomer In melted at 112–114°.

14α-Δ⁵,⁷,⁹-**Anthracholestatrien-x-ol o-Chlorobenzoate (IIp)**.—A mixture of 150 mg. of alcohol IIa, 0.7 ml. of *o*-chlorobenzoyl chloride and 10 ml. of pyridine was allowed to stand at room temperature overnight. The *o*-chlorobenzanhydride formed in the reaction was removed by passing a benzene–petroleum ether solution (1:1) of the reaction product through an alumina column (Grade I, almost neutral). By crystallization from acetone 130 mg. of crystalline material melting at 141–142° was obtained, [α]D −1.4°. After a second crystallization, the derivative melted at 142°, [α]D −1.8°, λmax^CS2 5.76 μ.

Anal. Calcd. for C₃₄H₄₅O₂Cl: C, 78.35; H, 8.70. Found: C, 78.57; H, 8.96.

14α-Δ⁵,⁷,⁹-**Anthracholestatriene (IIr) from Trienol IIm via 14α-Δ¹⁽ᵒʳ ³⁾,⁵,⁷,⁹-Anthracholestatetraene (IIq)**.—Alcohol IIm (300 mg.) was tosylated, and the crude tosylate was added to a boiling xylene–collidine mixture (10:1) as described in the analogous experiment in the 14β-series. By chromatography, 190 mg. of a colorless and apparently homogeneous oil was obtained, [α]D +6.5°; λmax^isooctane 221.5, 227, 234, and 273 mμ (ε 25400, 28400, 19300 and 11400, respectively), infl. 306 mμ (ε 650). In the catalytic hydrogenation one mole equivalent of hydrogen was consumed rapidly. By crystallization from acetone–methanol 150 mg. of crystalline material melting at 78–79.5° was obtained. Additional crystallizations from the same solvent raised the m.p. to 80.82°,¹² [α]D +28.7°; λmax^isooctane 273, 278 and 283 mμ (ε 655, 553 and 701, respectively).

(12) Reference 8 reports]α]D +30°, and m.p. 71–73°. The latter value is

Anal. Calcd. for C₂₇H₄₂: C, 88.45; H, 11.55. Found: C, 88.40; H, 11.86.

The compound proved to be identical, by direct comparison, with an authentic sample⁸,¹² obtained in the catalytic hydrogenation of Δ⁵,⁷,⁹,¹⁴-anthracholestatetraene.

Rearrangement of Dehydroergosteryl Acetate with Acetic Acid.—A solution of 2.5 g. of dehydroergosteryl acetate in 60 ml. of acetic acid (reagent grade, minimum content 99.7%) was boiled under reflux for 4 hours. The resulting yellowish solution was evaporated to dryness *in vacuo* and the oily residue subjected to hydrolysis in 5% ethanolic potassium hydroxide. The oily hydrolysate dissolved in petroleum ether–benzene was absorbed on 85 g. of Florisil and the following eluates were collected: (a) 350 ml. of petroleum ether; (b) 350 ml. of petroleum ether–benzene, 10:1; (c) 350 ml. of benzene–petroleum ether, 1:1; (d) six 100-ml. portions of benzene; (f) 500 ml. of benzene–chloroform, 10:1; (g) 400 ml. of benzene–chloroform, 1:1.

The presence of minimal amounts of Δ⁵,⁷,⁹,¹⁴,²²-anthraergostapentaene in fraction a became evident in the ultraviolet spectrum. The oily residue (800 mg.) obtained from the combined fractions e, f and g was treated with *p*-chlorobenzoyl chloride as described previously. The crude acylation product was recrystallized twice from acetone–ethanol and yielded 600 mg. of crystalline 14α-Δ⁵,⁷,⁹,²²-**ergostatetraen-x-ol** *p*-**chlorobenzoate (IIc)**, m.p. 121–123°, [α]D −13.9°. Its identity was demonstrated by direct comparison with an authentic sample (m.p. of the mixture, ultraviolet and infrared spectra). 14α-Δ⁵,⁷,⁹,²²-**Ergostatetraen-x-ol (IIa)**, the crude alcohol obtained by hydrolysis of the above ester, was crystallized from methanol and then from ethanol. It melted at 126–127°, [α]D −28.2°; λmax^EtOH 273, 277 and 282 mμ (ε 687, 684 and 714, respectively). The compound was identical in every respect with an authentic sample. Fractions d₅ and d₆ gave 900 mg. of oily material which yielded on acylation 250 mg. of pure 14α-Δ⁵,⁷,⁹,²²-ergostatetraen-x-ol *p*-chlorobenzoate. Fraction d₄ and the hydrolyzed mother liquors of the above *p*-chlorobenzoate were combined and rechromatographed on Florisil and yielded 50 mg. of the 14α-*p*-chlorobenzoate and 100 mg. of a mixture of 14α- and 14β-Δ⁵,⁷,⁹,²²-ergostatetraen-x-ol hexahydrobenzoates, m.p. 106–108°, [α]D +0.7°.

Rearrangement of Δ⁵,⁷,⁹⁽¹¹⁾-Cholestatrien-3β-ol Acetate with Acetic Acid.—A solution of 300 mg. of the above trienol acetate in 10 ml. of acetic acid was boiled under reflux for 4.5 hr. The yellow oily residue obtained by evaporation *in vacuo* was hydrolyzed with 5% ethanolic potassium hydroxide and the reaction product subjected to treatment with *o*-chlorobenzoyl chloride in pyridine in the manner described above. Thus, 120 mg. of an *o*-chlorobenzoate, twice recrystallized from acetone and melting at 130–133°, was obtained. This ester was hydrolyzed and the resulting alcohol treated with *p*-chlorobenzoyl chloride in pyridine. Two recrystallizations from acetone of the reaction product yielded 85 mg. of 14α-Δ⁵,⁷,⁹-**anthracholestatrien-x-ol** *p*-**chlorobenzoate (IIo)** melting at 126–127°, [α]D +8.0°. Direct comparison, ultraviolet and infrared spectra and melting points of the appropriate mixture demonstrated the identity with an authentic sample.

obviously an error, since the original laboratory notes and the samples indicate the m.p. as 77–79°.

The Anthrasteroid Rearrangement. IX. The Acid-catalyzed Rearrangement of Δ⁵,⁷,⁹⁽¹¹⁾,²²-Ergostatetraene and Δ⁵,⁸⁽¹⁴⁾,⁹⁽¹¹⁾-Ergostatrien-3β-ol

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The acid-catalyzed rearrangement of Δ⁵,⁷,⁹⁽¹¹⁾,²²-ergostatetraene (VII) leads to 14α-Δ⁵,⁷,⁹,²²-anthraergostatetraene (VIII) in a yield of about 30% when *p*-toluenesulfonic acid monohydrate is used as catalyst and to the 14β-isomer IX in a yield of 8–10%, when hydrogen chloride is employed. When Δ⁶,⁸⁽¹⁴⁾,⁹⁽¹¹⁾,²²-ergostatetraene-3β-ol acetate was subjected to the customary conditions of the anthrasteroid rearrangement with either catalyst, the compound underwent rapid changes, but no anthrasteroid type product could be detected in the reaction mixture.

Mechanisms that have been proposed for the anthrasteroid rearrangement²,³ leading, with loss of the oxygen function, from steroid Δ⁵,⁷,⁹⁽¹¹⁾-trien-3β-ols or their

(1) Visiting Scientist, National Institutes of Health. (b) Deceased, May 31, 1962.

(2) A. W. Burgstahler, *J. Am. Chem. Soc.*, **79**, 6047 (1957).

(3) (a) W. R. Nes, *ibid.*, **78**, 193 (1956); (b) W. R. Nes and J. A. Steele, *J. Org. Chem.*, **22**, 1457 (1957); (c) W. R. Nes, J. A. Steele and E. Mosettig, *J. Am. Chem. Soc.*, **80**, 5230 (1958).

esters to anthrasteroid Δ⁵,⁷,⁹,¹⁴-tetraenes indicate a pathway through A, B, C and D (see Fig. 1). Of these suggested intermediates only type C has been isolated and characterized.³ᵃ We have demonstrated in the preceding paper⁴ that under certain conditions the rearrangement can be conducted so as to lead to anthra-

(4) K. Tsuda, R. Hayatsu, J. A. Steele, O. Tanaka and E. Mosettig, *ibid.*, **85**, 1126 (1963).