548. *Steroids. Part II.** 22 : 23-*Dibromoergosta*-7 : 9(11)-*dien*-3β-*yl Acetate* (*Ergosteryl-D Acetate* 22 : 23-*Dibromide*).

By R. C. Anderson, Robert Stevenson, and F. S. Spring.

Treatment of 5-dihydroergosteryl acetate with bromine yields a tetrabromoergostenyl acetate, partial debromination of which by sodium iodide gives 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate (ergosteryl-D acetate 22 : 23-dibromide) (I; R = Ac). Debromination of ergosteryl-D acetate 22 : 23-dibromide with zinc dust gives ergosteryl-D acetate. Treatment of 5-dihydroergosteryl acetate with bromine, followed by debromination of the reaction mixture (without isolation of intermediates) gives ergosteryl-D acetate in excellent yield. Treatment of 5-dihydroergosteryl acetate with chlorine gives a mixture of two tetrachloroergostenyl acetates. Treatment of tetrachloroergostenyl acetate I with sodium iodide yields 22 : 23-dichloroergosta-7 : 9(11)-dien-3β-yl acetate. Oxidation of 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate with hydrogen peroxide in acetic acid gives 3β-acetoxy-22 : 23-dibromo-9α : 11α-epoxyergostan-7-one (II), debromination of which yields 3β-acetoxy-9α : 11α-epoxyergost-22-en-7-one (III) characterised by its conversion by relatively mild alkaline hydrolysis followed by acetylation into 3β : 11α-diacetoxyergosta-8 : 22-dien-7-one (IV).

The conversion of ergosteryl-D acetate into 11-hydroxy-steroids which, it is hoped, will serve as intermediates in a projected partial synthesis of cortisone from ergosterol, has been described in the preceding paper. At an early stage in this investigation, the efficiency of the methods available for the preparation of ergosteryl-D acetate became of importance. In the most practicable recorded method 5-dihydroergosteryl acetate is oxidised with mercuric acetate (Windaus and Auhagen, *Annalen*, 1929, **472**, 185; Heilbron, Johnstone, and Spring, *J.*, 1929, 2248). The most efficient method for the preparation of the dihydroacetate appeared to be the partial hydrogenation of ergosteryl esters (Heilbron and Sexton, *J.*, 1929, 921; Wieland and Benend, *Annalen*, 1943, **554**, 1; Barton and Cox, *J.*, 1948, 1354); using a platinum catalyst and chloroform as solvent, the last-named authors obtained a 30—35% yield, which we have improved to 92—95% by partially reducing ergosteryl acetate over Raney nickel in benzene. It has recently been reported by Heusser, Eichenberger, Kurath, Dällenbach, and Jeger (*Helv. Chim. Acta*, 1951, **34**, 2123, footnote) that Panizzon and Kägi have obtained a similar yield in ether over Rupe nickel. Although we improved the yield obtained in the oxidation of 5-dihydroergosteryl acetate to ergosteryl-D acetate by mercuric acetate, the method is still far from satisfactory: a crude reaction product is isolable in fair yield but its purification to constant optical rotation proved extremely wasteful, the yield of product with $[\alpha]_D \not< +28°$ not exceeding 30%.

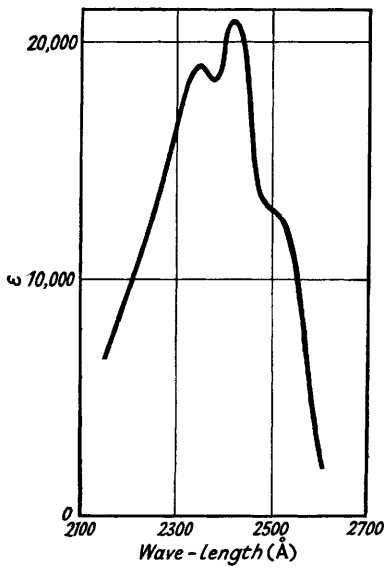
In a search for alternative methods for the preparation of ergosteryl-D acetate, a study of the action of bromine on 5-dihydroergosteryl acetate was commenced since, according to Eck and Hollingsworth (*J. Amer. Chem. Soc.*, 1942, **64**, 140) oxidation of cholest-7-ene in chloroform with bromine at −75° gives cholesta-7 : 9(11)-diene. Treatment of 5-dihydroergosteryl acetate in ether at −60° with bromine gives in good yield (48—53%) a tetrabromoergostenyl acetate which separates from the reaction mixture. This tetrabromide, which can also be obtained directly from ergosteryl-D acetate, is moderately stable in the solid state, as are solutions of the compound in dioxan and benzene. However, its solutions in alcohol and particularly in chloroform suffer profound decomposition after a short time at room temperature. Sodium iodide effects partial debromination, to 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate (ergosteryl-D acetate 22 : 23-dibromide) (I; R = Ac), the structure of which was established, first, by its conversion into ergosteryl-D acetate by zinc dust and, secondly, by its ultra-violet absorption spectrum (see Figure) which is identical in location with that of ergosteryl-D acetate. In contrast to tetrabromoergostenyl acetate, 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate is very

* Part I, preceding paper.

stable and can be hydrolysed by means of alkali to 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-ol (I; R = H).

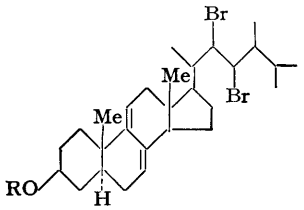
Ergosteryl-D Acetate.

Method of prepn.	M. p.	$[\alpha]_D$	ε at 2420 Å in EtOH
Bromine (this paper)	178—180°	+32°, +33°	19,000
Mercuric acetate (this paper)	176	+30	17,000
Perbenzoic acid (Windaus and Lüttringhaus, *Annalen*, 1930, **481**, 119)	171	+25·7	—
Mercuric acetate (Heusser *et al.*, *loc. cit.*)	169—170	+21	16,000

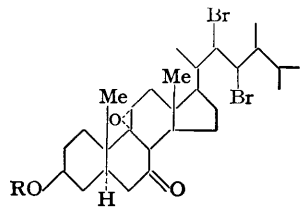


22 : 23-*Dibromoergosta*-7 : 9(11)-*dien*-3β-*yl acetate.*

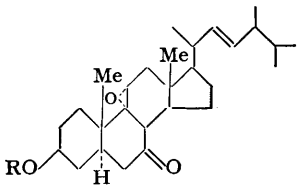
Conversion of tetrabromoergostenyl acetate into 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate is nearly quantitative, as is that of the latter into ergosteryl-D acetate. Ergosteryl-D acetate obtained by this method is of high purity and attains the physical constants shown in the Table after a single crystallisation. A specimen prepared by the



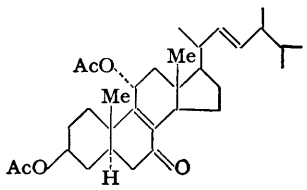
(I)



(II)



(III)



(IV)

mercuric acetate method required seven crystallisations before the constants shown in the Table were obtained. The bromine method can be used for the preparation of ergosteryl-D acetate from 5-dihydroergosteryl acetate, without the isolation of either tetrabromoergostenyl acetate or 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate. Treatment of

5-dihydroergosteryl acetate with bromine followed by debromination of the mixture with zinc dust gives ergosteryl-D acetate in 70% yield.

22 : 23-Dibromoergosta-7 : 9(11)-dien-3β-yl acetate and hydrogen peroxide give a compound $C_{30}H_{46}O_4Br_2$, identified as 3β-acetoxy-22 : 23-dibromo-9α : 11α-epoxyergostan-7-one (II) by its conversion into 3β-acetoxy-9α : 11α-epoxyergost-22-en-7-one (III) by zinc dust. The identity of (III) was in turn established by direct comparison with the specimen obtained by Budziarek, Newbold, Stevenson, and Spring (preceding paper) and by its conversion into 3β : 11α-diacetoxyergosta-8 : 22-dien-7-one (IV) by hydrolysis with dilute potassium hydroxide followed by acetylation.

A preliminary study of the action of chlorine on 5-dihydroergosteryl acetate has been made. The reaction product is a mixture from which tetrachloroergostenyl acetates I and II have been obtained. The isomer I with sodium iodide gives 22 : 23-dichloroergosta-7 : 9(11)-dien-3β-yl acetate.

Experimental

Specific rotations were determined in chloroform solution (unless otherwise stated) in a 1-dm. tube at approx. 15°. Ultra-violet absorption spectra were measured in ethanol solution with a Unicam S.P. 500 spectrophotometer.

5-Dihydroergosteryl Acetate.—A solution of ergosteryl acetate (35 g.; m. p. 173—175°, $[\alpha]_D$ −93°) in sulphur-free benzene (300 c.c.) was treated with a suspension of Raney nickel sludge (*Org. Synth.*, **29**, 25) (W6; 15—20 c.c.) in benzene (50 c.c.), and the mixture shaken at 17° with hydrogen under slight positive pressure until the total absorption was 2140 c.c. (calc., 1900 c.c.), of which, according to a blank experiment, approximately 150 c.c. were absorbed by the solvent. The time required for the gas absorption varied considerably; with a very active catalyst and pure benzene it was 15 minutes. The filtered reaction solutions from five such experiments were combined, and the solvent was removed under reduced pressure, to yield a crystalline residue, m. p. 172—174°, which gave a yellow colour with tetranitromethane in chloroform. Crystallisation from chloroform–methanol gave 5-dihydroergosteryl acetate (93 g.) as lustrous plates, m. p. 178—181°; $[\alpha]_D$ −19·5° (*c*, 2·0), showing no high-intensity absorption above 2200 Å. A further quantity (69 g.) (total yield, 92%), m. p. 177—179°, $[\alpha]_D$ −18° (*c*, 1·8), was obtained from the mother-liquor. In other experiments yields varying between 92% and 95% of material of similar m. p. and specific rotation were obtained. Recrystallisation of the product from chloroform–methanol gave plates, m. p. 180—182°; $[\alpha]_D$ −20·5° (*c*, 2·1).

Ergosteryl-D Acetate.—Application of a modified procedure used by Bergmann and Stevens (*J. Org. Chem.*, 1948, **13**, 10) for the preparation of dehydroergosteryl acetate from ergosteryl acetate to 5-dihydroergosteryl acetate gives an improved yield of ergosteryl-D acetate; this method has also been used by Heusser *et al.* (*loc. cit.*). By this method 5-dihydroergosteryl acetate (44 g.) was converted into ergosteryl-D acetate (18 g.), m. p. 168—172°, $[\alpha]_D$ +19° (*c*, 1·0). After six recrystallisations from chloroform–methanol the product (12 g.) was obtained as large blades, m. p. 176°, $[\alpha]_D$ +30°, +30° (*c*, 1·9, 1·4) (Found: C, 82·2; H, 10·4. Calc. for $C_{30}H_{46}O_2$: C, 82·1; H, 10·6%). Light absorption: Max. at 2350 (ε = 15,500) and 2420 Å (ε = 17,000), and an inflection at 2510 Å (ε = 12,500). Ergosteryl-D acetate gives a brown colour with tetranitromethane in chloroform.

Ergosterol-D was obtained by hydrolysis of the acetate with ethanolic potassium hydroxide. It separates from methanol–chloroform as felted needles, m. p. 165—167°, $[\alpha]_D$ +30°, +30° (*c*, 1·5, 1·4). Light absorption: Max. at 2350 (ε = 15,500) and 2420 Å (ε = 16,700). Confirmation of the homogeneity of the acetate and alcohol was obtained by reacetylation of the latter. The alcohol (1·6 g.; m. p. 167°) in pyridine (10 c.c.) and acetic anhydride (2 c.c.) was kept in nitrogen for 16 hours at room temperature. The product isolated in the usual manner was crystallised once from methanol–chloroform, to give ergosteryl-D acetate, m. p. 176°, as large blades, $[\alpha]_D$ +31° (*c*, 1·4). Light absorption: Max. at 2350 (ε = 15,300) and 2420 Å (ε = 17,000) with an inflection at 2510 Å (ε = 12,000).

Tetrabromoergostenyl Acetate.—A solution of 5-dihydroergosteryl acetate (10 g.; $[\alpha]_D$ −20·5°) in dry ether (1000 c.c.) was treated rapidly at 0° with a solution of dry bromine (5·1 c.c.) in glacial acetic acid (50 c.c.). The mixture was cooled to −60°, with shaking, and allowed to regain room temperature during 2 hours with frequent shaking. The solid (8·3—9·0 g.) was collected, washed with ether, and dried at room temperature under reduced pressure. Two crystallisations of a sample of the colourless amorphous solid from benzene–light petroleum (b. p. 60—80°) gave

tetrabromoergostenyl acetate as felted needles, m. p. 128° (decomp.) (Found: C, 47·7; H, 6·4; Br, 42·5. $C_{30}H_{46}O_2Br_4$ requires C, 47·5; H, 6·1; Br, 42·2%).

Treatment of ergosteryl-D acetate (1·0 g.) with bromine as described above for 5-dihydroergosteryl acetate gave tetrabromoergostenyl acetate (1·05 g.) as needles [from benzene–light petroleum (b. p. 60—80°)], m. p. 123—124° (decomp.) alone or mixed with the specimen described above. The tetrabromo-compound decomposes on storage and its solutions in chloroform, acetone, or acetic acid decompose with evolution of hydrogen bromide and considerable coloration; it is very sparingly soluble in cold ether and light petroleum, and has $[\alpha]_D$ +233°, +225° (*c*, 0·2, 0·2 in dioxan), $[\alpha]_D$ +260° (*c*, 1·2 in benzene). A freshly prepared solution of the tetrabromo-compound in chloroform (*c*, 1·1) had $[\alpha]_D$ +205°; after 90 minutes the value was +93°.

22 : 23-*Dibromoergosta*-7 : 9(11)-*dien*-3β-*yl Acetate* (I; R = Ac).—A solution of tetrabromoergostenyl acetate (9·0 g.) in warm benzene (500 c.c.) was treated with sodium iodide (25 g.) in ethanol (500 c.c.) added in one portion. Iodine was immediately liberated. After 20 hours at 15° the solution was diluted with water (500 c.c.), the benzene layer separated, and the aqueous phase extracted with benzene (300 c.c.). The combined extracts were washed with sodium hydroxide solution (2 × 200 c.c.; 1%), then with water, and dried (Na_2SO_4). Removal of the benzene and solution of the solid in the minimum volume of chloroform followed by addition of methanol and storage at 0° gave a solid. This was purified by percolation of its solution in benzene (approx. 100 c.c.) through a column of alumina (Grade II; 15 × 2·5 cm.), followed by washing with benzene (200 c.c.). Removal of the solvent from the filtrate gave a solid (6·5—6·9 g.) which on crystallisation from methanol–chloroform gave 22 : 23-*dibromoergosta*-7 : 9(11)-*dien*-3β-*yl acetate* as prismatic needles, m. p. 233—234° (decomp.), $[\alpha]_D$ +32°, +30° (*c*, 1·4, 1·7) (Found: C, 60·0; H, 7·8. $C_{30}H_{46}O_2Br_2$ requires C, 60·2; H, 7·75%). Light absorption: Max. at 2350 (ε = 19,000) and 2420 Å (ε = 21,000), and an inflection at 2500 Å (ε = 13,000). The dibromide gives a dark brown colour with tetranitromethane in chloroform.

Treatment of a specimen of tetrabromoergostenyl acetate obtained from ergosteryl-D acetate with sodium iodide as described above gave 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate as prismatic needles from methanol–chloroform, undepressed in m. p. when mixed with the specimen described above and having $[\alpha]_D$ +30° (*c*, 1·4). Treatment of 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate (600 mg.) with bromine as described above for 5-dihydroergosteryl acetate gave tetrabromoergostenyl acetate (510 mg.) which separated from benzene–light petroleum (b. p. 60—80°) as felted needles, m. p. 123—124° (decomp.).

22 : 23-*Dibromoergosta*-7 : 9(11)-*dien*-3β-*ol* (I; R = H).—A solution of the acetate (300 mg.) in benzene (5 c.c.) and aqueous methanolic potassium hydroxide (40 c.c.; 3%) was refluxed for 6 hours, and concentrated to 30 c.c. The crystals separating on cooling were recrystallised from methanol-chloroform, giving 22 : 23-*dibromoergosta*-7 : 9(11)-*dien*-3β-*ol* (270 mg.) as elongated plates, m. p. 230—231° (decomp.), $[\alpha]_D$ +26° (*c*, 2·0) (Found: C, 59·5, 59·0; H, 8·4, 8·3. $C_{28}H_{44}OBr_2,CH_3{\cdot}OH$ requires C, 59·2; H, 8·2%). The alcohol gives a brown colour with tetranitromethane in chloroform. Light absorption: Max. at 2350 (ε = 18,000) and 2420 Å (ε = 20,000), and an inflection at 2500 Å (ε = 13,500).

Ergosteryl-D Acetate.—(*a*) 22 : 23-Dibromoergosta-7 : 9(11)-dien-3β-yl acetate (2·0 g.) in a mixture of ether (200 c.c.) and ethanol (300 c.c.) was treated with zinc dust (10 g.) (activated by washing with ammonium chloride) added in one portion. The stirred reaction mixture was heated under reflux for 2 hours, filtered, and concentrated, and the residue treated with water and extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue (m. p. 178—180°; 1·4 g., 95%) from methanol–chloroform gave ergosteryl-D acetate, m. p. 178—180°, $[\alpha]_D$ +32°, +33° (*c*, 1·5, 1·6) (Found: C, 82·1; H, 10·7. Calc. for $C_{30}H_{46}O_2$: C, 82·1; H, 10·6%). Light absorption: Max. at 2350 (ε = 17,000) and 2420 Å (ε = 19,000), and an inflection at 2510 Å (ε = 12,000).

(*b*) A solution of 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate (500 mg.) in *cyclo*hexane (100 c.c.) was treated with Raney nickel sludge (5 c.c.) previously washed with *cyclo*hexane, and the mixture shaken with hydrogen for 18 hours. The mixture was filtered and the filtrate evaporated to dryness. The solid was crystallised from chloroform–methanol, to yield ergosteryl-D acetate as plates (250 mg.), m. p. 173—176°, $[\alpha]_D$ +27° (*c*, 1·25); the m. p. was undepressed when the material was mixed with a specimen, m. p. 175—177°, $[\alpha]_D$ +30°, obtained by oxidation of 5-dihydroergosteryl acetate with mercuric acetate.

(*c*) A solution of 5-dihydroergosteryl acetate (2·5 g.) in ether (250 c.c.) at 0° was treated with bromine (1·25 c.c.) in glacial acetic acid (5 c.c.). The temperature was immediately lowered to −60° and then allowed to rise to −5° during 1½ hours. Benzene (100 c.c.) and zinc dust (7 g.)

were then added, and the mixture stirred at 0° for 1 hour and kept overnight at 0°. After removal of the zinc, ethanol (250 c.c.) and zinc dust (25 g.) were added to the filtrate, the mixture was heated under reflux for 3 hours, and the product (2·3 g.; m. p. 160—167°) isolated in the usual manner. Filtration of a benzene solution of this product through a short column of alumina (Grade II), followed by crystallisation from chloroform–methanol, yielded ergosteryl-D acetate as plates (1·5—1·8 g.), m. p. 173—174°; $[\alpha]_D$ +28° (*c*, 2·1). Light absorption: Max. at 2360 (ε = 14,500) and 2420 Å (ε = 16,300), with an inflection at 2500 Å (ε = 10,900) (Found: C, 81·8; H, 10·6%).

Tetrachloroergostenyl Acetates.—A solution of 5-dihydroergosteryl acetate (10 g.) in dry ether (1 l.) at 0° was treated rapidly with a solution of dry chlorine (6·5 g.) in glacial acetic acid (100 c.c.) and immediately cooled to −50° and kept at this temperature for 75 minutes. The solution was allowed to attain room temperature, kept for 12 hours, and then concentrated to 150 c.c. under reduced pressure below 40°. The solid (2·2 g.), which separated was collected (liquor A), washed with a little glacial acetic acid, and thrice crystallised from benzene–light petroleum (b. p. 60—80°) from which *tetrachloroergostenyl acetate I* separated as felted needles, m. p. 167—169° (decomp.), $[\alpha]_D$ +190° (*c*, 1·2), +192° (*c*, 1·3) (Found: C, 62·1; H, 8·0; Cl, 24·8. $C_{30}H_{46}O_2Cl_4$ requires C, 62·1; H, 8·0; Cl, 24·4%).

A second crop of crystalline solid (660—750 mg.), which slowly separated from liquor A, was recrystallised from benzene–light petroleum (b. p. 60—80°), to give *tetrachloroergostenyl acetate II* as needles, m. p. 213—214° (decomp.), $[\alpha]_D$ −248° (*c*, 1·1), −257° (*c*, 2·0) (Found: C, 62·3; H, 8·1; Cl, 24·6%).

22 : 23-*Dichloroergosta*-7 : 9(11)-*dien*-3β-*yl Acetate*.—Tetrachloroergostenyl acetate I (400 mg.) in dry benzene (30 c.c.) was treated with a solution of sodium iodide (1·5 g.) in ethanol (30 c.c.), iodine being immediately liberated. After 16 hours at 15° the mixture was diluted with water, and the benzene solution washed with 5% sodium hydroxide solution, then water, dried (Na_2SO_4), and evaporated to dryness. The solid was thrice crystallised from methanol–chloroform, from which 22 : 23-*dichloroergosta*-7 : 9(11)-*dien*-3β-*yl acetate* separated as long prismatic needles, m. p. 235—237°, $[\alpha]_D$ +43° (*c*, 0·5), +44° (*c*, 1·3) (Found: C, 70·6; H, 9·1; Cl, 14·5. $C_{30}H_{46}O_2Cl_2$ requires C, 70·7; H, 9·1; Cl, 13·9%). The dichloride gives a brown colour with tetranitromethane in chloroform. Light absorption: Max. at 2360 (ε = 18,800) and 2420 Å (ε = 21,000), with an inflection at 2500 Å (ε = 14,000).

3β-*Acetoxy*-22 : 23-*dibromo*-9α : 11α-*epoxyergostan*-7-*one* (II).—A solution of 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate (4·5 g.) in carbon tetrachloride (100 c.c.) and glacial acetic acid (600 c.c.) (purified by refluxing over chromium trioxide) was treated with hydrogen peroxide solution (8 c.c.; 30%) added in one portion, and heated to 95° with stirring during 25 minutes. The mixture was kept at this temperature for 3 hours, then evaporated under reduced pressure. The partly crystalline residue was treated with methanol (30 c.c.) and kept at 0° overnight, and the solid (1·50 g.; m. p. 218—221°) collected. Recrystallisation from methanol–chloroform gave 3β-*acetoxy*-22 : 23-*dibromo*-9α : 11α-*epoxyergostan*-7-*one* as plates, m. p. 234—235°, $[\alpha]_D$ −47° (*c*, 1·7) (Found: C, 56·9; H, 7·4. $C_{30}H_{46}O_4Br_2$ requires C, 57·1; H, 7·35%). The compound does not give a colour with tetranitromethane in chloroform and shows no high-intensity absorption above 2200 Å.

3β-*Acetoxy*-9α : 11α-*epoxyergost*-22-*en*-7-*one* (III).—A stirred solution of 3β-acetoxy-22 : 23-dibromo-9α : 11α-epoxyergostan-7-one (1·35 g.; m. p. 218—221°) in stabilised glacial acetic acid (150 c.c.) was treated at 95° during 2 hours with zinc dust (11 g.), added portionwise. After a further 2 hours at 95° the mixture was filtered, concentrated under reduced pressure until solid separated, and diluted with water. The whole was extracted with ether (3 × 50 c.c.), and the extract washed successively with sodium hydrogen carbonate solution and water and dried (Na_2SO_4). Removal of the ether gave a solid residue (0·90 g.; m. p. 208—213°). The product was twice crystallised from methanol from which 3β-acetoxy-9α : 11α-epoxyergost-22-en-7-one was obtained as needles (which formed slowly from an initial gel), m. p. 223—224° alone or mixed with a specimen of the compound prepared as described in the preceding paper, $[\alpha]_D$ −79° (*c*, 0·8) (Found: C, 76·5; H, 9·95. Calc. for $C_{30}H_{46}O_4$: C, 76·55; H, 9·85%). The compound does not show high-intensity absorption above 2200 Å and gives a faint yellow colour with tetranitromethane in chloroform.

3β : 11α-*Diacetoxyergosta*-8 : 22-*dien*-7-*one* (IV).—A solution of 3β-acetoxy-9α : 11α-epoxyergost-22-en-7-one (150 mg.; m. p. 217—219°), prepared as described above, in benzene (2 c.c.) and methanol (25 c.c.) was treated with aqueous potassium hydroxide solution (20%; 4 c.c.), and the mixture refluxed for 1 hour. The cooled solution was diluted with water and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated under reduced

pressure. The solid was acetylated by heating it for 1 hour with pyridine (3 c.c.) and acetic anhydride (0·5 c.c.). The acetylated product, isolated by means of ether, separated as needles, m. p. 172—173°, from aqueous methanol. Recrystallisation from the same solvent gave 3β : 11α-diacetoxyergosta-8 : 22-dien-7-one, $[\alpha]_D$ +12° (*c*, 1·55), m. p. 173—174° undepressed on admixture with the specimen described in the preceding paper (Found : C, 75·2, 75·2; H, 9·6, 9·9. Calc. for $C_{32}H_{48}O_5$: C, 75·0; H, 9·4%). Light absorption : Max. at 2520 Å (ε = 9200). The compound gives a light yellow colour with tetranitromethane in chloroform.

We are grateful to Messrs. B. H. Thickett and Richard Budziarek, B.Sc., for help with some of the experiments described. The microanalyses were by Dr. A. C. Syme and Mr. Wm. McCorkindale, and the ultra-violet absorption spectra were measured by Miss Norma Caramando and Miss Elizabeth Davidson.

THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, March 3rd,* 1952.]