108. *Steroids. Part VI.* The Reduction of Ergosteryl-D Acetate 22 : 23-Dibromide.*

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Catalytic hydrogenation of ergosteryl-D acetate 22 : 23-dibromide (I; R = $C_9H_{17}Br_2$) in neutral medium gives 22 : 23-dibromoergost-7-en-3β-yl acetate (II; R = $C_9H_{17}Br_2$, R′ = Ac) whereas in acetic acid the product is the $\Delta^{8(14)}$-compound (III; R = $C_9H_{17}Br_2$, R′ = Ac), also obtained by rearrangement of the Δ^7-isomer on a platinum catalyst saturated with hydrogen. Debromination of the $\Delta^{8(14)}$-compound, which is also obtained by hydrogenolysis of the 9α : 11α-epoxide (IV; R = $C_9H_{17}Br_2$) and of 3β-acetoxy-22 : 23-dibromoergost-8-en-11-one (V; R = $C_9H_{17}Br_2$), gives ergosta-8(14) : 22-dien-3β-yl acetate (III; R = C_9H_{17}, R′ = Ac). Treatment of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate with hydrogen chloride gives an inseparable mixture of 22 : 23-dibromoergost-14-en-3β-yl acetate and the $\Delta^{8(14)}$-isomer. Catalytic hydrogenation of this mixture followed by removal of unsaturated material gives 22 : 23-dibromoergostan-3β-yl acetate and thence ergost-22-en-3β-yl acetate.

In Part II of this series (*J.*, 1952, 2901) the preparation of 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate (ergosteryl-D acetate 22 : 23-dibromide) (I; R = $C_9H_{17}Br_2$, R′ = Ac) is described and in Parts III and V (*J.*, 1952, 3410, 4874) a preliminary account is given of its oxidation. Ergosteryl-D acetate 22 : 23-dibromide offers some advantage over ergosteryl-D acetate (I; R = C_9H_{17}, R′ = Ac) as a starting point for the synthesis of 11-keto-steroids since nuclear oxidation is more efficiently effected in the former than in the latter, presumably because of partial attack at the side-chain ethylenic linkage. The present paper describes the catalytic reduction of ergosteryl-D acetate 22 : 23-dibromide. The side-chain halogens proved to be a satisfactory protection of the 22 : 23-double linkage of

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* Part V, *J.*, 1952, 4874.

ergosteryl-D acetate under the hydrogenation conditions used, and, together with the easy regeneration of the ethylenic linkage by zinc dust, has led to efficient methods for the preparation of ergosta-8(14) : 22-dien-3β-ol and ergost-22-en-3β-ol. Of these compounds, the former has been described by Laubach and Brunings (*J. Amer. Chem. Soc.*, 1952, **74**, 705) since this work was completed; they prepared it by hydrogenation of ergosteryl-β_2 acetate [ergosta-6 : 8(14) : 22-trien-3β-yl acetate] in a neutral solvent over Raney nickel. Ergost-22-en-3β-ol has been obtained by Barton, Cox, and Holness (*J.*, 1949, 1771) by partial hydrogenation of *iso*ergosterone in neutral solution to ergost-22-en-3-one followed by reduction of the latter with sodium and propanol.

Hydrogenation of ergosteryl-D acetate 22 : 23-dibromide in ethyl acetate over platinum gives 22 : 23-dibromoergost-7-en-3β-yl acetate (II; $R = C_9H_{17}Br_2$, $R' = Ac$) which was characterised by hydrolysis to the alcohol and as the derived benzoate. The molecular-rotation data (Table 1) support the structure allocated to 22 : 23-dibromoergost-7-en-3β-ol. Furthermore the observed changes in molecular rotation accompanying saturation of the double bond (comparison with 22 : 23-dibromoergostan-3β-ol, its acetate and benzoate) are in good agreement with values for the saturation of comparable stenols (Barton, *J.*, 1946, 512; Barton and Cox, *J.*, 1948, 1354). The structure allocated to 22 : 23-dibromoergost-7-en-3β-yl acetate was confirmed by its conversion in high yield into ergosta-7 : 22-dien-3β-yl acetate (5-dihydroergosteryl acetate) (II; $R = C_9H_{17}$, $R' = Ac$) by treatment with zinc dust.

Hydrogenation of ergosteryl-D acetate 22 : 23-dibromide in acetic acid over platinum gives 22 : 23-dibromoergost-8(14)-en-3β-yl acetate (III; $R = C_9H_{17}Br_2$, $R' = Ac$) characterised as in the case of the Δ^7-isomer. Furthermore, shaking 22 : 23-dibromoergost-7-en-3β-yl acetate (II; $R = C_9H_{17}Br_2$, $R' = Ac$) in acetic acid solution with a platinum catalyst saturated with hydrogen isomerised it to 22 : 23-dibromoergost-8(14)-en-3β-yl acetate. The location of the double bond in these compounds follows from well-established considerations (see Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., 1949). Thus the molecular-rotation changes on acetylation (Δ_1) and benzoylation (Δ_2) of the alcohol are in good agreement with representative values for other 5α-st-8(14)-en-3β-ols and the ultra-violet absorption spectrum of the compound agrees with that expected for an 8(14)-stenol (Bladen, Henbest, and Woods, *Chem. and Ind.*, 1951, 866; Halsall, *ibid.*, p. 867). However, although the molecular-rotation changes on acetylation and benzoylation of 22 : 23-dibromoergost-8(14)-en-3β-ol are normal, the Δ-values for saturation of the double bond are only in fair agreement with standard values for 8(14)-stenols. This indicates some degree of vicinal effect of the side chain (cf. Mancera, Barton, Rosenkranz, and Djerassi, *J.*, 1952, 1021).

TABLE 1.

	$[M]_D$				
	Alcohol	Acetate	Benzoate	Δ_1	Δ_2
22 : 23-Dibromoergostan-3β-ol	+42°	+12°	+40°	−30° (−34°)	−2° (+2°)
22 : 23-Dibromoergost-7-en-3β-ol ...	−47	−42	−26	+5 (−6)	+21 (+30)
Δ (Saturation of ⊨)	+89 (+77)	+54 (+57)	+66 (+64)	—	—
22 : 23-Dibromoergost-8(14)-en-3β-ol	+73	+27	+20	−46 (−40)	−53 (−42)
Δ (Saturation of ⊨)	−31 (+9)	−15 (+14)	+20 (+53)	—	—

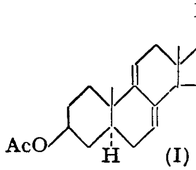
Standard values, from Barton, *J.*, 1945, 813; 1946, 512, are given in parentheses.

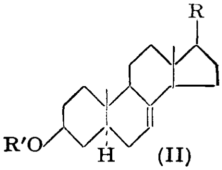
Debromination of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate with zinc gives ergosta-8(14) : 22-dien-3β-yl acetate (III; $R = C_9H_{17}$, $R' = Ac$), hydrolysed by alkali to the alcohol and hydrogenated in ethyl acetate or acetic acid over platinum to ergost-8(14)-en-3β-yl acetate (III; $R = C_9H_{19}$, $R' = Ac$) (α-ergostenyl acetate).

A study of the catalytic reduction of two oxidation products of ergosteryl-D acetate 22 : 23-dibromide, namely, 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (IV; $R = C_9H_{17}Br_2$) and 3β-acetoxy-22 : 23-dibromoergost-8-en-11-one (V; $R = C_9H_{17}Br_2$) (Part III, *loc. cit.*) was included in this investigation. In acetic acid solution over a platinum catalyst both compounds suffered hydrogenolysis with the formation of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate (III; $R = C_9H_{17}Br_2$, $R' = Ac$). 3β-Acetoxy-22 : 23-

dibromoergost-8-en-11-one was recovered unchanged after being shaken with hydrogen in ethyl acetate solution over platinum catalyst or in acetic acid solution over palladium black.

Treatment of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate or benzoate with dry hydrogen chloride gave mixed crystals which could not be resolved by crystallisation. Debromination of the acetate dibromide mixed crystal gave "β"-dihydroergosteryl acetate, characterised by the preparation of the corresponding alcohol and benzoate. "β"-Dihydroergosteryl acetate was shown by Barton, Cox, and Holness (*J.*, 1949, 1771) to be an inseparable equimolar mixture of ergosta-8(14) : 22-dien-3β-yl acetate and ergosta-14 : 22-dien-3β-yl acetate. The product obtained by isomerisation of 22 : 23-dibromoergost-8(14)-en-3-βyl acetate is therefore a mixture of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate and 22 : 23-dibromoergost-14-en-3β-yl acetate, and, since it gives "β"-dihydroergosteryl acetate in nearly quantitative yield, it is inferred that it likewise is an equimolar mixture. The molecular rotations of 22 : 23-dibromoergost-14-en-3β-ol and its derivatives, calculated from the values for 22 : 23-dibromoergost-8(14)-en-3β-ol and those of the mixed crystals (22 : 23-dibromoergost-8(14)-stenol and 22 : 23-dibromoergost-14-stenol) are shown in Table 2. Although the Δ values for acetylation and benzoylation of 22 : 23-dibromoergost-14-en-3β-ol are in reasonable agreement with standard values for Δ^{14}-stenols, the changes in molecular rotation accompanying saturation of the double bond of this compound and its derivatives (comparison with corresponding derivatives of 22 : 23-dibromoergostan-3β-ol) are anomalous, in this respect resembling 22*a*-*allo*spirost-8(14)-en-3β-ol in which a strong vicinal effect of the sapogenin side chain was also observed (Mancera, Barton, Rosenkranz, and Djerassi, *loc. cit.*). Summarising, the dibrominated side-chain exerts a profound vicinal effect upon the 14(15)-, a less pronounced effect upon the 8(14)-, and no effect upon a 7(8)-ethylenic linkage.


(I)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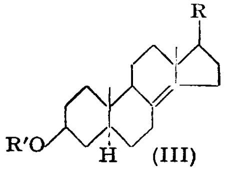
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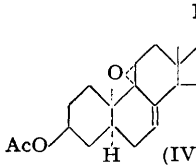
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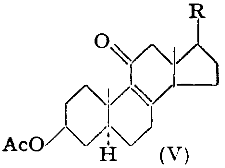
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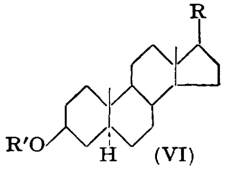
(VI)

A preparation of 22 : 23-dibromoergostan-3β-yl acetate (VI; $R = C_9H_{17}Br_2$, $R' = Ac$) was achieved by isomerisation of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate with dry hydrogen chloride, hydrogenation of the product, and removal of unsaturated material by Anderson and Nabenhauer's method (*J. Amer. Chem. Soc.*, 1924, **46**, 1951). Attempts to improve the preparation by reduction of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate in the presence of hydrochloric acid were not successful. Debromination of 22 : 23-dibromoergostanyl acetate gave ergost-22-en-3β-yl acetate (VI; $R = C_9H_{17}$, $R' = Ac$), characterised by hydrolysis to the alcohol.

TABLE 2.

	$[M]_D$				
	Alcohol	Acetate	Benzoate	Δ_1	Δ_2
22 : 23-Dibromoergost-8(14)-en-3β-ol	+73°	+27°	+20°	—	—
[22 : 23-Dibromoergost-8(14)-en-3β-ol + 22 : 23-Dibromoergost-14-en-3β-ol (1 : 1)]	+165	+126	+139	—	—
22 : 23-Dibromoergost-14-en-3β-ol	+257	+225	+258	−32° (−35°)	+1° (+30°)
22 : 23-Dibromoergostan-3β-ol	+42	+12	+40	—	—
Δ (Saturation of ⊨)	−215 (−24)	−213 (−20)	−218 (−59)	—	—

EXPERIMENTAL

M. p.s are corrected. Specific rotations were measured in chloroform solution in a 1-dm. tube at 18—20°. Ultra-violet absorption spectra were measured in absolute ethanol solution with a Unicam SP.500 spectrophotometer. " Working up in the usual way " means removal of catalyst, concentration under reduced pressure, addition of water, extraction with ether, washing of the extract with dilute sodium carbonate solution and water, drying (Na_2SO_4), and evaporation under reduced pressure.

22 : 23-*Dibromoergost*-8(14)-*en*-3β-*yl Acetate*.—(*a*) A solution of ergosteryl-D acetate 22 : 23-dibromide (500 mg.) in glacial acetic acid (250 c.c.) was added to a suspension of freshly reduced platinum (from 200 mg. of platinum oxide) in acetic acid (15 c.c.), and the mixture shaken with hydrogen for 20 hours at room temperature. Working up in the usual way gave 22 : 23-*dibromoergost*-8(14)-*en*-3β-*yl acetate* which separates from methanol–chloroform as elongated plates, m. p. 192—193° (400 mg.), $[\alpha]_D$ +5°, +4·5° (*c*, 2·0, 7·0). After chromatography of a specimen on alumina followed by crystallisation from methanol–chloroform it had $[\alpha]_D$ +4° (*c*, 2·5) (Found: C, 60·1; H, 8·3. $C_{30}H_{48}O_2Br_2$ requires C, 60·0; H, 8·0%). Light absorption: ε_{2100} 8000, ε_{2150} 7500, ε_{2200} 5600, ε_{2230} 1400. It gives a deep yellow colour with tetranitromethane in chloroform. The same product was obtained when chloroform–glacial acetic acid (1 : 9 parts) was used as solvent for the hydrogenation.

(*b*) A solution of 3β-acetoxy-22 : 23-dibromoergost-8-en-11-one (500 mg.) in glacial acetic acid (100 c.c.) was shaken with hydrogen over pre-reduced platinum oxide (200 mg.) for 10 hours. Working up in the usual way gave 22 : 23-dibromoergost-8(14)-en-3β-yl acetate as plates (from methanol–chloroform), m. p. 189—191° (250 mg.), $[\alpha]_D$ +3° (*c*, 1·0), undepressed in m. p. when mixed with the specimen described under (*a*) (Found: C, 60·2; H, 8·4%).

(*c*) A solution of 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (m. p. 216—218°; 500 mg.) in glacial acetic acid (80 c.c.) was shaken with hydrogen for 4 hours over platinum (from 100 mg. of PtO_2). Working up in the usual way gave 22 : 23-dibromoergost-8(14)-en-3β-yl acetate (450 mg.) as plates (from methanol–chloroform), m. p. 191—192°, $[\alpha]_D$ +3° (*c*, 1·1), undepressed in m. p. when mixed with the specimen described under (*a*) (Found: C, 60·0; H, 8·1%).

22 : 23-*Dibromoergost*-8(14)-*en*-3β-*ol*.—A solution of the acetate (250 mg.) in benzene (10 c.c.) and methanolic potassium hydroxide (40 c.c.; 1%) was refluxed for 1 hour. The solution was diluted with water and extracted with ether. Removal of ether gave a solid which crystallised from methanol–chloroform to give 22 : 23-*dibromoergost*-8(14)-*en*-3β-*ol* as plates, m. p. 213—214° (200 mg.), $[\alpha]_D$ +13 (*c*, 1·6) (Found: C, 60·3; H, 8·6. $C_{28}H_{46}OBr_2$ requires C, 60·2; H, 8·3%).

The alcohol in pyridine and benzoyl chloride was heated at 100° for 1 hour and kept at room temperature for 2 hours. Crystallisation of the product from chloroform–methanol gave the *benzoate* as plates, m. p. 242—243°, $[\alpha]_D$ +3° (*c*, 5·0, 4·5) (Found: C, 63·4; H, 7·8. $C_{35}H_{50}O_2Br_2$ requires C, 63·4; H, 7·6%).

22 : 23-*Dibromoergost*-7-*en*-3β-*yl Acetate*.—A solution of ergosteryl-D acetate 22 : 23-dibromide (0·5 g.) in ethyl acetate (100 c.c.) was shaken with hydrogen over pre-reduced platinum oxide (100 mg.) for 14 hours. Working up in the usual way gave 22 : 23-*dibromoergost*-7-*en*-3β-*yl acetate* (5-*dihydroergosteryl acetate* 22 : 23-*dibromide*) as needles (from methanol–ethyl acetate), m. p. 224° (decomp.) (0·4 g.), $[\alpha]_D$ −7° (*c*, 2·0, 1·4) (Found: C, 60·3; H, 8·2%). Light absorption: ε_{2100} 5000, ε_{2150} 3620, ε_{2200} 1700. It gives a yellow colour with tetranitromethane in chloroform.

22 : 23-*Dibromoergost*-7-*en*-3β-*ol*.—A solution of 22 : 23-dibromoergost-7-en-3β-yl acetate (200 gm.) in benzene (15 c.c.) and methanolic potassium hydroxide (25 c.c.; 2%) was refluxed for 1 hour, concentrated, and diluted with water. Isolation by means of ether, followed by crystallisation from methanol, gave 22 : 23-*dibromoergost*-7-*en*-3β-*ol* as plates, m. p. 222—223° (165 mg.), $[\alpha]_D$ −8° (*c*, 1·3) (Found: C, 59·1; H, 8·6. $C_{28}H_{46}OBr_2,CH_3{\cdot}OH$ requires C, 59·0; H, 8·5%). Reacetylation (acetic anhydride–pyridine) gave the parent acetate as needles (from methanol–chloroform), m. p. 224°, $[\alpha]_D$ −6° (*c*, 1·5). The *benzoate*, prepared in the usual way, separates from methanol–chloroform as needles, m. p. 205° (decomp.), $[\alpha]_D$ −4° (*c*, 4·0) (Found: C, 63·4; H, 7·8%).

Isomerisation of 22 : 23-*Dibromoergost*-7-*en*-3β-*yl Acetate*.—A solution of this acetate (500 mg.) in acetic acid (300 c.c.) was shaken with a platinum catalyst and hydrogen for 4 hours. Working up in the usual way gave 22 : 23-dibromoergost-8(14)-en-3β-yl acetate as plates (from methanol–chloroform), m. p. and mixed m. p. 190° (400 mg.), $[\alpha]_D$ +4° (*c*, 3·0).

Ergosta-7 : 22-*dien*-3β-*yl Acetate*.—A solution of 22 : 23-dibromoergost-7-en-3β-yl acetate (250 mg.) in ether–ethanol (60 c.c.; 1 : 1) was refluxed with zinc dust (1·5 g.) for 2 hours. The solution was filtered, concentrated, and diluted with water. Isolation by means of ether gave ergosta-7 : 22-dien-3β-yl acetate as plates (from methanol–chloroform), m. p. 182—183° (150 mg.), $[\alpha]_D$ −20° (*c*, 1·2), undepressed in m. p. when mixed with an authentic sample, m. p. 182°, $[\alpha]_D$ −20° (Found : C, 82·1; H, 11·1. Calc. for $C_{30}H_{48}O_2$: C, 81·8; H, 11·0%).

Ergosta-8(14) : 22-*dien*-3β-*yl Acetate*.—A solution of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate (m. p. 191—193°; 200 mg.) in ether–methanol (50 c.c.; 1 : 2) was refluxed with zinc dust (2 g.) added portionwise during 3 hours. The solution was filtered, concentrated, and diluted with water. Isolation by means of ether gave ergosta-8(14) : 22-dien-3β-yl acetate, as plates (from methanol), m. p. 122—123·5° (120 mg.), $[\alpha]_D$ −25° (*c*, 1·1) (Found : C, 81·5; H, 11·2. Calc. for $C_{30}H_{48}O_2$: C, 81·8; H, 11·0%). Light absorption : ε_{2120} 8000, ε_{2150} 7000, ε_{2200} 4900. It gives a deep yellow colour with tetranitromethane in chloroform. Laubach and Brunings (*loc. cit.*) give m. p. 122·6—124·0°, $[\alpha]_D$ −26·5°.

Ergosta-8(14) : 22-*dien*-3β-*yl Benzoate*.—A solution of 22 : 23-dibromoergost-8(14)-en-3β-yl benzoate (500 mg.) in pyridine (30 c.c.) containing water (3 drops) was heated with zinc dust (4 g.) for 3 hours on the steam-bath. The mixture was filtered, and the filtrate concentrated under reduced pressure and diluted with water. Working up using ether gave *ergosta*-8(14) : 22-*dien*-3β-*yl benzoate* (380 mg.) as flat needles (from methanol–chloroform), m. p. 126—127°, $[\alpha]_D$ −24°, −23° (*c*, 4·1, 4·0) (Found : C, 83·8; H, 10·2. $C_{35}H_{50}O_2$ requires C, 83·6; H 10·0%). It gives a deep yellow colour with tetranitromethane in chloroform.

Ergosta-8(14) : 22-*dien*-3β-*ol*.—A solution of ergosta-8(14) : 22-dien-3β-yl acetate (60 mg.) in methanolic potassium hydroxide (20 c.c.; 3%) was refluxed for 2 hours, then concentrated and diluted with water. Isolation by means of ether gave *ergosta*-8(14) : 22-*dien*-3β-*ol* which crystallised from methanol or acetone as elongated plates m. p. 126—127° (40 mg.), $[\alpha]_D$ −19°, −20° (*c*, 1·5, 1·0) (Found : C, 84·2; H, 11·8. $C_{28}H_{46}O$ requires C, 84·35; H, 11·6%).

Acetylation (acetic anhydride–pyridine) gave ergosta-8(14) : 22-dien-3β-yl acetate as plates (from methanol), m. p. 123—124° (25 mg.), $[\alpha]_D$ −27° (*c*, 1·3).

Ergost-8(14)-*en*-3β-*yl Acetate*.—A solution of ergosta-8(14) : 22-dien-3β-yl acetate (100 mg.) in ethyl acetate (60 c.c.) was shaken with hydrogen over freshly reduced platinum oxide catalyst for 5 hours. The filtered reaction mixture was concentrated, giving plates (80 mg.) which on recrystallisation from methanol gave ergost-8(14)-en-3β-yl acetate as plates, $[\alpha]_D$ +4° (*c*, 2·0), m. p. 109—110°, either alone or mixed with an authentic sample, m. p. 108—109°, $[\alpha]_D$ +3°, prepared by hydrogenation of ergosteryl-D acetate in glacial acetic acid (Found : C, 81·2; H, 11·4. Calc. for $C_{30}H_{50}O_2$: C, 81·4; H, 11·4%). Light absorption : ε_{2100} 7000, ε_{2150} 6400, ε_{2200} 4600. It gives a yellow colour with tetranitromethane in chloroform. The same product in similar yield was obtained by using chloroform or glacial acetic acid as solvent for the hydrogenation.

Treatment of 22 : 23-*Dibromoergost*-8(14)-*en*-3β-*yl Acetate with Hydrogen Chloride*.—Dry hydrogen chloride was passed into a solution of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate (1 g.) in dry chloroform (20 c.c.) for 90 minutes at 0°. The solvent was removed under reduced pressure and the solid crystallised from methanol–chloroform, to give plates, m. p. 225—226° (decomp.) (600 mg.), $[\alpha]_D$ +21° (*c*, 2·0) (Found : C, 60·1; H, 8·0. $C_{30}H_{48}O_2Br_2$ requires C, 60·0; H, 8·0%). Light absorption : ε_{2060} 4000, ε_{2100} 3000, ε_{2150} 1250, ε_{2200} 620. The *compound* gives a yellow colour with tetranitromethane in chloroform.

Hydrolysis of this acetate (300 mg.) in benzene (20 c.c.) by refluxing with methanolic potassium hydroxide (2%; 45 c.c.) for 2 hours gave the corresponding *alcohol* (240 mg.; m. p. 216—219°) which after three crystallisations from methanol separated as plates, m. p. 219—220°, $[\alpha]_D$ +29° (*c*, 1·9) (Found : C, 58·7; H, 8·7. $C_{28}H_{46}OBr_2,CH_3{\cdot}OH$ requires C, 59·0; H, 8·5%).

Acetylation of the alcohol (pyridine–acetic anhydride) gave the acetate which separated from methanol–chloroform as plates, $[\alpha]_D$ +22° (*c*, 1·3°), m. p. 223—225 (decomp.) alone or mixed with the acetate described above.

Refluxing the acetate (300 mg.) in ether–ethanol (40 c.c.; 1 : 1) with zinc dust (1 g.) gave " β "-dihydroergosteryl acetate which separated from methanol–chloroform as needles, m. p. 106—107° (200 mg.), $[\alpha]_D$ −18° (*c*, 1·6) (Found : C, 82·1; H, 11·4. Calc. for $C_{30}H_{48}O_2$: C, 81·8; H, 11·0%). Light absorption : ε_{2100} 2550, ε_{2150} 730. It gives a deep yellow colour with tetranitromethane in chloroform. Barton, Cox, and Holness (*loc. cit.*) give m. p. 104·5°, $[\alpha]_D$ −17°, for " β "-dihydroergosteryl acetate.

Hydrolysis of the acetate with methanolic potassium hydroxide (2%) followed by crystallisation of the product from methanol–chloroform gave " β "-dihydroergosterol as plates, m. p.

115—116°, $[\alpha]_D$ −11° (*c*, 1·2). Barton, Cox, and Holness (*loc. cit.*) give m. p. 116°, $[\alpha]_D$ −9°, for this compound.

Benzoylation of the alcohol by the usual procedure gave the benzoate (plates from methanol–chloroform), m. p. 118°, $[\alpha]_D$ −9·5° (*c*, 1·7) (lit., m. p. 116°, $[\alpha]_D$ −8°).

Treatment of 22 : 23-*Dibromoergost*-8(14)-*en*-3β-*yl Benzoate with Hydrogen Chloride*.—Dry hydrogen chloride was passed through a solution of 22 : 23-dibromoergost-8(14)-en-3β-yl benzoate (1 g.) in dry chloroform (30 c.c.) for 2 hours at 0°. Working up gave a product which separated from methanol–chloroform in plates (0·86 g.), m. p. 229—231°, $[\alpha]_D$ +21° (*c*, 2·0). Four further crystallisations from the same solvent gave mixed crystals, m. p. 232° (decomp.), $[\alpha]_D$ +21°, +20° (*c*, 2·4, 4·0) (Found : C, 63·3; H, 7·8. $C_{35}H_{50}O_2Br_2$ requires C, 63·4; H, 7·6%).

The benzoate (75 mg.) in refluxing benzene (25 c.c.) and methanolic potassium hydroxide (3%; 25 c.c.) (4 hours) gave the alcohol as plates (55 mg.) (from methanol), m. p. 219—220°, $[\alpha]_D$ +29° (*c*, 1·3). The alcohol was undepressed in m. p. when mixed with the alcohol obtained by isomerisation of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate followed by hydrolysis.

22 : 23-*Dibromoergostan*-3β-*yl Acetate*.—Dry hydrogen chloride was passed through a solution of 22 : 23-dibromoergost-8(14)-en-3β-yl acetate (0·8 g.) in chloroform (25 c.c.) for 2 hours at 0°. After the removal of the solvent under reduced pressure, a solution of the solid in ether (100 c.c.) and ethyl acetate (100 c.c.) was shaken with hydrogen over platinum (from 200 mg. of PtO_2) for 20 hours. Working up in the usual way gave a solid which was dissolved in carbon tetrachloride (30 c.c.). Acetic anhydride (10 c.c.) and concentrated sulphuric acid (10 c.c.) were added slowly with shaking and cooling, and the mixture shaken for 5 minutes. Water (10 c.c.) was added and the mixture extracted with carbon tetrachloride. The combined extracts were washed with water, sodium hydrogen carbonate, water, and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave a pale yellow solid (470 mg.) which crystallised from methanol–chloroform, to give 22 : 23-dibromoergostan-3β-yl acetate (250 mg.) as plates, m. p. 242—243° (decomp.), $[\alpha]_D$ +3°, +2·7° (*c*, 2·2, 3·0) (Found : C, 60·4; H, 8·6. Calc. for $C_{30}H_{50}O_2Br_2$: C, 59·9; H, 8·4%). It does not give a colour with tetranitromethane in chloroform and does not show absorption of high intensity above 2000 Å. Barton, Cox, and Holness (*loc. cit.*) give decomp. *ca.* 226° for this compound.

22 : 23-*Dibromoergostan*-3β-*ol*.—A solution of 22 : 23-dibromoergostan-3β-yl acetate (115 mg.) in benzene (20 c.c.) and methanolic potassium hydroxide (20 c.c.; 2%) was heated under reflux for 1 hour. Isolation by means of ether gave 22 : 23-*dibromoergostan*-3β-*ol* which crystallised from chloroform as plates, m. p. 239—240° (85 mg.), $[\alpha]_D$ +7° (*c*, 1·45) (Found : C, 58·4; H, 8·9. $C_{28}H_{48}OBr_2,CH_3{\cdot}OH$ requires C, 58·8; H, 8·9%).

22 : 23-*Dibromoergostan*-3β-*yl benzoate*, prepared in the usual way, crystallised from methanol–chloroform as plates, m. p. 218°, $[\alpha]_D$ +6° (*c*, 2·5) (Found: C, 63·6; H, 8·2. $C_{35}H_{52}O_2Br_2$ requires C, 63·3; H, 7·9%).

Ergost-22-*en*-3β-*yl Acetate*.—A solution of 22 : 23-dibromoergostan-3β-yl acetate (150 mg.) in ether–ethanol (75 c.c.; 1 : 1) was refluxed with zinc dust (1 g.) added portionwise during 2 hours. Working up in the usual way gave ergost-22-en-3β-yl acetate which crystallised from methanol–chloroform in plates (60 mg.), m. p. 157°, $[\alpha]_D$ −20°, −18° (*c*, 1·3, 1·4) (Found : C, 81·0; H, 11·4. Calc. for $C_{30}H_{50}O_2$: C, 81·4; H, 11·4%). Barton, Cox, and Holness (*loc. cit.*) give m. p. 155·5°, $[\alpha]_D$ −17°, for this compound.

Ergost-22-*en*-3β-*ol*.—A solution of ergost-22-en-3β-yl acetate (40 mg.) in benzene (2 c.c.) and methanolic potassium hydroxide (2 c.c.; 2%) was heated under reflux for 1 hour. Isolation by means of ether gave ergost-22-en-3β-ol which crystallised from methanol–chloroform as plates, m. p. 153—154° (25 mg.), $[\alpha]_D$ −10° (*c*, 1·3) (Found : C, 81·9; H, 12·2. Calc. for $C_{28}H_{48}O,\frac{1}{2}H_2O$: C, 82·1; H, 12·1%).

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