655. *Steroids. Part III.** 11-*Oxygenated Steroids from* 22 : 23-*Dibromoergosta*-7 : 9(11)-*dien*-3β-*yl Acetate* (*Ergosteryl-D Acetate* 22 : 23-*Dibromide*).

By Richard Budziarek, Francis Johnson, and F. S. Spring.

Oxidation of ergosteryl-D acetate 22 : 23-dibromide (I) with perbenzoic acid gives 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (II; R = $C_9H_{17}Br_2$), treatment of which with sulphuric acid gives 22 : 23-dibromo-7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate (III; R = $C_9H_{17}Br_2$, R′ = H). Oxidation of the last compound yields 22 : 23-dibromo-7 : 11-diketoergost-8-en-3β-yl acetate (IV; R = $C_9H_{17}Br_2$) and 22 : 23-dibromo-8α : 9α-epoxy-7 : 11-diketoergostan-3β-yl acetate (V; R = $C_9H_{17}Br_2$), treatment of which with zinc gives in each case 7 : 11-diketoergost-22-en-3β-yl acetate (VI; R = C_9H_{17}). 22 : 23-Dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (II; R = $C_9H_{17}Br_2$) has been rearranged to 3β-acetoxy-22 : 23-dibromoergost-8-en-7-one (VII; R = $C_9H_{17}Br_2$) by treatment with dilute hydrochloric acid and to 3β-acetoxy-22 : 23-dibromoergost-8-en-11-one (VIII; R = $C_9H_{17}Br_2$) by treatment with boron trifluoride.

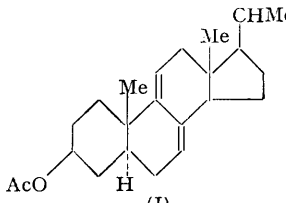
Recent communications from this Laboratory (Anderson, Budziarek, Newbold, Stevenson, and Spring, *Chem. and Ind.*, 1951, 1035; Anderson, Stevenson, and Spring, *J.*, 1952, 2901) described 22 : 23-dibromoergosta-7 : 9(11)-dien-3β-yl acetate (ergosteryl-D acetate 22 : 23-dibromide) (I), its conversion into 7 : 11-diketoergost-22-en-3β-yl acetate (VI; R = C_9H_{17}), and preparation of the last compound directly from ergosteryl-D acetate (Budziarek, Newbold, Stevenson, and Spring, *J.*, 1952, 2892). This paper describes alternative routes to 7 : 11-diketoergost-22-en-3β-yl acetate (VI; R = C_9H_{17}) starting from ergosteryl-D acetate 22 : 23-dibromide (I).

Oxidation of ergosteryl-D acetate 22 : 23-dibromide (I) with one molecular proportion of perbenzoic acid gives a monoepoxide in 70% yield. The reactions of this compound, which are described below, show that it is the 22 : 23-dibromide of ergosteryl-D acetate epoxide, itself obtained by similar oxidation of ergosteryl-D acetate (Chamberlin, Ruyle, Erickson, Chemerda, Aliminosa, Erickson, Sita, and Tishler, *J. Amer. Chem. Soc.*, 1951, **73**, 2396) to which the structure 9α : 11α-epoxyergosta-7 : 22-dien-3β-yl acetate (II; R = C_9H_{17}) was ascribed by Heusser, Eichenberger, Kurath, Dällenbach, and Jeger (*Helv. Chim. Acta*, 1951, **34**, 2106; cf. Budziarek, Newbold, Stevenson, and Spring, *loc. cit.*). An unpublished observation made in this laboratory is that catalytic hydrogenation of ergosteryl-D acetate 22 : 23-dibromide leads to initial saturation of the 9 : 11-ethylenic linkage with formation of 22 : 23-dibromoergost-7-en-3β-yl acetate, which leads us to the view that the monoepoxide of ergosteryl-D acetate 22 : 23-dibromide is likewise formed by saturation of the 9 : 11-ethylenic linkage and is therefore 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (II; R = $C_9H_{17}Br_2$).

Controlled treatment of 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate with sulphuric acid in dioxan gives 22 : 23-dibromo-7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate (III; R = $C_9H_{17}Br_2$, R′ = H) in excellent yield. The latter compound is also obtained by treatment of 9α : 11α-epoxyergosta-7 : 22-dien-3β-yl acetate (II; R = C_9H_{17}) in chloroform with bromine. It is readily acetylated to give 3β : 7ξ : 11α-triacetoxy-22 : 23-dibromoergost-8-ene (III; R = $C_9H_{17}Br_2$, R′ = Ac), debromination of which with zinc dust yields 3β : 7ξ : 11α-triacetoxyergosta-8 : 22-diene (III; R = C_9H_{17}, R′ = Ac) identical with a specimen prepared by acetylation of 7ξ : 11α-dihydroxyergosta-8 : 22-dien-3β-yl acetate (III; R = C_9H_{17}, R′ = H) obtained from 9α : 11α-epoxyergosta-7 : 22-dien-3β-yl acetate (II; R = C_9H_{17}) (Chamberlin *et al.*, *loc. cit.*). The triacetate (III; R = C_9H_{17}, R′ = Ac) has recently been obtained by the last route by Heusser, Anliker, Eichenberger, and Jeger (*Helv. Chim. Acta*, 1952, **35**, 936). Debromination of 22 : 23-dibromo-7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate (III; R = $C_9H_{17}Br_2$, R′ = H) with zinc gives 7ξ : 11α-dihydroxyergosta-8 : 22-dien-3β-yl acetate (III; R = C_9H_{17}, R′ = H) in excellent yield.

* Part II, *J.*, 1952, 2901.

Oxidation of 22 : 23-dibromo-7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate (III; R = $C_9H_{17}Br_2$, R′ = H) with chromic acid gives a mixture of 22 : 23-dibromo-7 : 11-diketoergost-8-en-3β-yl acetate (IV; R = $C_9H_{17}Br_2$) and 22 : 23-dibromo-8α : 9α-epoxy-7 : 11-diketoergostan-3β-yl acetate (V; R = $C_9H_{17}Br_2$). This parallels the similar oxidation of 7ξ : 11α-dihydroxyergosta-8 : 22-dien-3β-yl acetate (III; R = C_9H_{17}, R′ = H)



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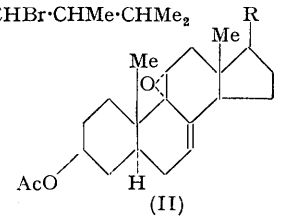

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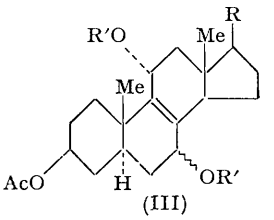

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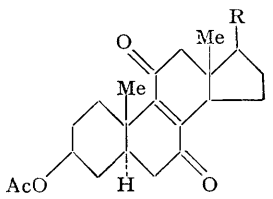

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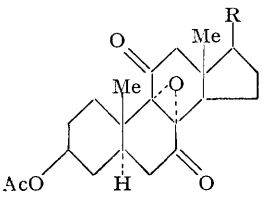

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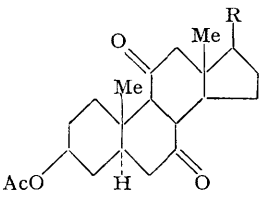
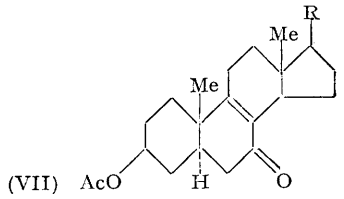


(VI)

(Heusser *et. al.*, *loc. cit.*, 1951) to 7 : 11-diketoergosta-8 : 22-dien-3β-yl acetate (IV; R = C_9H_{17}) and 8α : 9α-epoxy-7 : 11-diketoergost-22-en-3β-yl acetate (V; R = C_9H_{17}). Treatment of (IV; R = $C_9H_{17}Br_2$) or (V; R = $C_9H_{17}Br_2$) with zinc dust in acetic acid gives 7 : 11-diketoergost-22-en-3β-yl acetate (VI; R = C_9H_{17}). 22 : 23-Dibromo-7 : 11-diketoergost-8-en-3β-yl acetate (IV; R = $C_9H_{17}Br_2$) was also obtained in poor yield by oxidation of 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (II; R = $C_9H_{17}Br_2$) with chromic acid.

Treatment of 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (II; R = $C_9H_{17}Br_2$) with aqueous hydrochloric acid, followed by acetylation of the product, gives 3β-acetoxy-22 : 23-dibromoergost-8-en-7-one (VII; R = $C_9H_{17}Br_2$), debromination of which with zinc gives the known 3β-acetoxyergosta-8 : 22-dien-7-one (VII; R = C_9H_{17}) (Stavely and Bollenback, *J. Amer. Chem. Soc.*, 1943, **65**, 1290; Heusser, Eichenberger,



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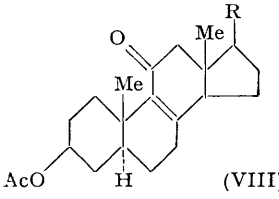

(VIII)

Kurath, Dällenbach, and Jeger, *loc. cit.*; Budziarek, Newbold, Stevenson, and Spring, *loc. cit.*). 3β-Acetoxy-22 : 23-dibromoergost-8-en-11-one (VIII; R = $C_9H_{17}Br_2$) was obtained by treatment of 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (II; R = $C_9H_{17}Br_2$) with boron trifluoride, using the method described by Heusser *et al.* (*loc. cit.*) for the preparation of 3β-acetoxyergosta-8 : 22-dien-11-one (VIII; R = C_9H_{17}). The compound (VIII; R = C_9H_{17}) was obtained in excellent yield by debromination of (VIII; R = $C_9H_{17}Br_2$) with zinc.

Experimental

M. p.s are corrected. Specific rotations were determined on chloroform solutions (unless otherwise stated) in a 1-dm. tube at approx. 15°. Ultra-violet absorption spectra were measured on ethanol solutions, with a Unicam SP.500 spectrophotometer. For chromatography, activated alumina, Grade II, standardised according to Brockmann, was employed.

22 : 23-*Dibromo*-9α : 11α-*epoxyergost*-7-*en*-3β-*yl Acetate*.—Ergosteryl-D acetate 22 : 23-di-

bromide (2 g.) in chloroform (50 c.c.) was treated dropwise with perbenzoic acid (1·2 mols.) in chloroform (10 c.c.), added with stirring during 3 hours at 0°. The mixture was kept at 0° for a further 2 hours. The solution was concentrated under reduced pressure until solid separated, whereafter the mixture was diluted with ether (50 c.c.). The solution was shaken successively with 5% sodium carbonate solution and water and dried ($MgSO_4$). The solid (2 g.), obtained by removal of the solvents at 30—40° under reduced pressure, crystallised from pure acetone or from light petroleum (b. p. 40—60°), to give 22 : 23-*dibromo*-9α : 11α-*epoxyergost*-7-*en*-3β-*yl acetate* as flat needles, m. p. 218°, $[\alpha]_D$ −24°, −26° (*c*, 1·5, 1·7) (Found: C, 58·5; H, 7·6. $C_{30}H_{46}O_3Br_2$ requires C 58·6; H, 7·55%). It gives a yellow colour with tetranitromethane in chloroform and does not show selective absorption of high intensity above 2200 Å. Attempted crystallisation of the epoxide from technical acetone or methanol caused rearrangement.

22 : 23-*Dibromo*-9α : 11α-*epoxyergost*-7-*en*-3β-*ol*.—A solution of 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-ylacetate (300 mg.) in benzene (50 c.c.) and methanolic potassium hydroxide (50 c.c.; 2%) was refluxed for 2 hours. Precipitation with water and isolation by means of ether gave a product which after three crystallisations from methanol gave 22 : 23-*dibromo*-9α : 11α-*epoxyergost*-7-*en*-3β-*ol* as plates, m. p. 200—202° (260 mg.), $[\alpha]_D$ −27° (*c*, 0·7) (Found: C, 58·0; H, 8·0. $C_{28}H_{44}O_2Br_2,CH_3{\cdot}OH$ requires C, 57·6; H, 8·0%). It gives a yellow colour with tetranitromethane in chloroform and does not show selective absorption of high intensity above 2200 Å.

22 : 23-*Dibromo*-7ξ : 11α-*dihydroxyergost*-8-*en*-3β-*yl Acetate*.—(*a*) Powdered 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (600 mg.) was shaken vigorously in dioxan (50 c.c.) containing aqueous sulphuric acid 2N; 10 c.c.). After a few seconds solution was complete and almost immediately solid separated. After 15 minutes the crystalline solid was filtered off and washed successively with methanol, water, methanol, and ether (small prisms, m. p. 204°; 420 mg.). Two crystallisations from pyridine gave 22 : 23-*dibromo*-7ξ : 11α-*dihydroxyergost*-8-*en*-3β-*yl acetate* as needles, m. p. 216—217°, $[\alpha]_D$ +93° (*c*, 0·3 in pyridine) (Found: C, 56·8; H, 7·8. $C_{30}H_{48}O_4Br_2$ requires C, 57·0; H, 7·65%). It does not show selective absorption of high intensity above 2200 Å; it is very sparingly soluble in most organic solvents including chloroform.

Attempted crystallisation of the dibromo-epoxide from technical acetone led to the separation of a microcrystalline solid, m. p. 200°, which is very insoluble in most organic solvents, including chloroform, and is undepressed in m. p. when mixed with 22 : 23-dibromo-7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate, m. p. 204° (Found: C, 56·6; H, 8·0.

(*b*) 9α : 11α-Epoxyergosta-7 : 22-dien-3β-yl acetate (200 mg.) in chloroform (10 c.c.) was treated dropwise with a solution of bromine (1 mol.) in chloroform during 20 minutes at −4°. The solution was kept overnight at −5°. Chloroform was removed under reduced pressure at room temperature. The residue separated from acetone as a microcrystalline powder (100 mg.), very insoluble in most organic solvents including chloroform, and has m. p. 200°, undepressed when mixed with 22 : 23-dibromo-7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate, m. p. 204°.

3β : 7ξ : 11α-*Triacetoxy*-22 : 23-*dibromoergost*-8-*ene*.—A suspension of 22 : 23-dibromo-7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate (400 mg.) in pyridine (15 c.c.) and acetic anhydride (15 c.c.) was heated on the steam-bath for 30 minutes, after which solution was complete; the solution was kept overnight at room temperature. Most of the solvents were removed under reduced pressure at 60—80°, the residue was diluted with water, and the product isolated by means of ether. Crystallisation from methanol gave 3β : 7ξ : 11α-*triacetoxy*-22 : 23-*dibromoergost*-8-*ene* as prisms, m. p. 171—172° (350 mg.), $[\alpha]_D$ +77° (*c*, 1·9) (Found: C, 56·8; H, 7·5. $C_{34}H_{52}O_6Br_2$ requires C, 57·0; H, 7·3%). It gives a pale yellow colour with tetranitromethane in chloroform and does not show selective absorption of high intensity above 2200 Å.

3β : 7ξ : 11α-*Triacetoxyergosta*-8 : 22-*diene*.—(*a*) A solution of 3β : 7ξ : 11α-triacetoxy-22 : 23-dibromoergost-8-ene (100 mg.) in ether–methanol (30 c.c.; 1 : 1) was refluxed for 3 hours with zinc dust (2 g.) added portionwise. After filtration, water was added and the product isolated by means of ether. Crystallisation from methanol gave 3β : 7ξ : 11α-triacetoxyergosta-8 : 22-diene as prismatic needles, m. p. 172° (90 mg.), $[\alpha]_D$ +88° (*c*, 1·2) (Found: C, 73·5; H, 9·6. Calc. for $C_{34}H_{52}O_6$: C, 73·3; H, 9·4%). Heusser, Anliker, Eichenberger, and Jeger (*loc. cit.*) give m. p. 170—171°, $[\alpha]_D$ +92°. It gives a pale yellow colour with tetranitromethane in chloroform and does not exhibit selective absorption of high intensity above 2200 Å.

(*b*) Acetylation of 7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate on the steam-bath for 1 hour with acetic anhydride and pyridine gave 3β : 7ξ : 11α-triacetoxyergosta-8 : 22-diene which separated from methanol as prismatic needles, $[\alpha]_D$ +90° (*c*, 2·0), m. p. 172—173°, undepressed in m. p. when mixed with a specimen prepared as described above (Found: C, 72·9; H, 9·4%).

7ξ : 11α-*Dihydroxyergosta*-8 : 22-*dien*-3β-*yl Acetate*.—A solution of 22 : 23-dibromo-7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate (m. p. 204°; 200 mg.) in pyridine (30 c.c.) containing water (3 drops) was heated with zinc dust (2 g.) for 3 hours on the steam-bath. The mixture was filtered and the filtrate evaporated to dryness under reduced pressure. The residue separated from acetone in felted needles, m. p. 231—234° (150 mg.), which on recrystallisation from methanol separated as prismatic needles, m. p. 251—253°, $[\alpha]_D$ +85° (*c*, 0·4), identical with a specimen obtained by the treatment of ergosteryl-D acetate epoxide with sulphuric acid in dioxan (m. p. 230—232°, $[\alpha]_D$ +83° from acetone; m. p. 248—250° from methanol). It gives a pale yellow colour with tetranitromethane in chloroform and does not exhibit selective absorption of high intensity above 2200 Å (Found: C, 76·6; H, 10·5. Calc. for $C_{30}H_{48}O_4$: C, 76·2; H, 10·2%). Chamberlin, Ruyle, Erickson, Chemerda, Aliminosa, Erickson, Sita, and Tishler (*loc. cit.*) give m. p. 248—252°, $[\alpha]_D$ +85°, and Heusser, Eichenberger, Kurath, Dällenbach, and Jeger (*loc. cit.*) give m. p. 270—272°, $[\alpha]_D$ +82°.

22 : 23-*Dibromo*-8α : 9α-*epoxy*-7 : 11-*diketoergostan*-3β-*yl Acetate*.—A suspension of 22 : 23-dibromo-7ξ : 11α-dihydroxyergost-8-en-3β-yl acetate (m. p. 204°; 3·6 g.) in acetic acid (400 c.c.) was treated portionwise with a solution of chromic anhydride in acetic acid (1·05N; 2·5 g.-atoms of oxygen), and the mixture stirred for 2 hours at room temperature and then kept overnight. After addition of a little methanol, the solution was concentrated under reduced pressure and diluted with water. The product, isolated by means of ether, separated from methanol–chloroform as plates (1·7 g.), m. p. 240°. A solution of this solid in benzene (100 c.c.) was chromatographed on activated alumina (2 × 8 cm.). Evaporation of the first benzene fraction (300 c.c.) gave a solid (200 mg.) which after crystallisation from methanol gave 22 : 23-*dibromo*-8α : 9α-*epoxy*-7 : 11-*diketoergostan*-3β-*yl acetate* as flat needles, m. p. 210—212°, $[\alpha]_D$ −44° (*c*, 1·8) (Found: C, 56·2; H, 7·2. $C_{30}H_{44}O_5Br_2$ requires C, 55·9; H, 6·9%). It gives no colour with tetranitromethane in chloroform and does not show selective absorption of high intensity above 2000 Å.

22 : 23-*Dibromo*-7 : 11-*diketoergost*-8-*en*-3β-*yl Acetate*.—(*a*) Evaporation of the second benzene fraction (500 c.c.) from the above chromatogram gave 22 : 23-*dibromo*-7 : 11-*diketoergost*-8-*en*-3β-*yl acetate* (600 mg.), separating from methanol–chloroform as hexagonal plates, m. p. 250—251°, $[\alpha]_D$ +27°, +24° (*c*, 1·9, 0·9) (Found: C, 57·2; H, 7·25. $C_{30}H_{44}O_4Br_2$ requires C, 57·3; H, 7·05%). Light absorption: Maximum at 2690 Å (ε = 8200). It does not give a colour with tetranitromethane in chloroform.

(*b*) A solution of 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (2 g.) in acetic acid (170 c.c.) was treated dropwise with a solution of chromic anhydride in acetic acid (1·05N; 4 atomic equivs. of oxygen) during 1 hour at 50° with stirring. The mixture was stirred for an additional hour at 50°, cooled to room temperature, and diluted with water. Isolation by means of ether gave a yellow solid, a solution of which in light petroleum (b. p. 60—80°)–benzene (10 : 1; 100 c.c.) was chromatographed on activated alumina (2 × 12 cm.). Elution with light petroleum–benzene (4 : 1; 400 c.c.) gave a solid *substance* (450 mg.) which crystallised from methanol in blades, m. p. 218—219°, $[\alpha]_D$ +100°, +101° (*c*, 1·4, 1·0). Light absorption: Maximum at 2460 Å (ε = 9000) (Found: C, 57·1; H, 7·3. $C_{30}H_{46}O_4Br_2$ requires C, 57·1; H, 7·35. $C_{30}H_{44}O_4Br_2$ requires C, 57·3; H, 7·05%). Evaporation of the next light petroleum–benzene (3 : 2; 400 c.c.) fraction gave a solid (100 mg.) which on crystallisation from methanol gave 22 : 23-dibromo-7 : 11-diketoergost-8-en-3β-yl acetate as plates, m. p. 248°, $[\alpha]_D$ +20° (*c*, 0·5) (Found: C, 57·0; H, 7·2%). Light absorption: Maximum at 2680 Å (ε = 8000); it showed no depression of the m. p. when mixed with the specimen described above.

7 : 11-*Diketoergost*-22-*en*-3β-*yl Acetate*.—(*a*) A solution of 22 : 23-dibromo-7 : 11-diketoergost-8-en-3β-yl acetate (50 mg.) in glacial acetic acid (25 c.c.) was heated on the steam bath for 3 hours with zinc dust (1 g.) and then boiled under reflux for 15 minutes. Isolation of the product with ether gave 7 : 11-diketoergost-22-en-3β-yl acetate (30 mg.) as needles (from methanol), m. p. 195—196°, $[\alpha]_D$ −26° (*c*, 0·4) (Found: C, 76·4; H, 10·0. Calc. for $C_{30}H_{46}O_4$: C, 76·55; H, 9·85%); It is undepressed in m. p. when mixed with an authentic specimen prepared as described by Budziarek *et al.* (*loc. cit.*). It gives a faint yellow colour with tetranitromethane in chloroform and does not show high intensity light absorption above 2200 Å.

(*b*) Similar reduction of 22 : 23-dibromo-8α : 9α-epoxy-7 : 11-diketoergostan-3β-yl acetate (100 mg.) with zinc dust and acetic acid gave a product isolated by means of ether. A solution of this product in benzene (20 c.c.) was filtered through a column of alumina (5 × 1 cm.), and the column washed with benzene (250 c.c.). Evaporation of the benzene filtrate gave 7 : 11-diketoergost-22-en-3β-yl acetate (60 mg.), m. p. 197—198°, $[\alpha]_D$ −28° (*c*, 1·2); it is undepressed in m. p. when mixed with the specimen described under (*a*).

3β-*Acetoxy*-22 : 23-*dibromoergost*-8-*en*-7-*one*.—A solution of 22 : 23-dibromo-9α : 11α-epoxyer-

gost-7-en-3β-yl acetate (700 mg.) in benzene (7 c.c.) was refluxed with aqueous methanolic hydrochloric acid (100 c.c.; 1%) for 1½ hours. A solution of the product, isolated in the usual manner, in pyridine (15 c.c.) was heated with acetic anhydride (10 c.c.) for 4 hours at 100°. The acetylated product (m. p. 233°; 120 mg.), isolated by means of ether, was purified by filtration of its solution in benzene (10 c.c.) through a short column of activated alumina. Elution with the same solvent gave 3β-*acetoxy*-22 : 23-*dibromoergost*-8-*en*-7-*one* which crystallised from methanol in plates, m. p. 241—242°, $[\alpha]_D$ −29° (*c*, 1·5) (Found : C, 58·6; H, 7·6. $C_{30}H_{46}O_3Br_2$ requires C, 58·6; H, 7·55%). Light absorption : Maximum at 2520 Å (ε = 10,000). It does not give a colour with tetranitromethane in chloroform.

3β-*Acetoxyergosta*-8 : 22-*dien*-7-*one*.—A solution of 3β-acetoxy-22 : 23-dibromoergost-8-en-7-one (50 mg.) in ether–ethanol (40 c.c.; 1 : 1) was refluxed for 2 hours with zinc dust (1 g.), added portionwise. After filtration, the solution was concentrated and poured into water. Isolation by means of ether gave a solid which crystallised from methanol to yield 3β-acetoxyergosta-8 : 22-dien-7-one as plates, m. p. 209—211°, $[\alpha]_D$ −56° (*c*, 0·5) (Found : C, 79·3; H, 10·3. Calc. for $C_{30}H_{46}O_3$: C, 79·2; H, 10·2%); it is undepressed in m. p. when mixed with an authentic specimen. Light absorption : Maximum at 2520 Å (ε = 10,000). It gives a yellow colour with tetranitromethane in chloroform.

3β-*Acetoxy*-22 : 23-*dibromoergost*-8-*en*-11-*one*.—(*a*) A solution of 22 : 23-dibromo-9α : 11α-epoxyergost-7-en-3β-yl acetate (1 g.) in dry benzene (50 c.c.) was treated with redistilled boron trifluoride–ether complex (15 drops) and the solution kept at room temperature for 3 days. The solution was diluted with ether (50 c.c.), washed successively with water, sodium hydrogen carbonate solution, and water, and dried (Na_2SO_4). The solvents were removed under reduced pressure; the residue separated from methanol–chloroform in elongated plates, m. p. 190° (0·73 g.). Light absorption : Maximum at 2530 Å (ε = 9100). A solution of the solid in benzene (25 c.c.) was filtered through a short column of activated alumina, and the column washed with the same solvent. Evaporation of the filtrate gave 3β-*acetoxy*-22 : 23-*dibromoergost*-8-*en*-11-*one* which separated from methanol–chloroform in blades, m. p. 201—202°, $[\alpha]_D$ +98° (*c*, 1·7) (Found : C, 58·7; H, 7·7. $C_{30}H_{46}O_3Br_2$ requires C, 58·6; H, 7·55%). Light absorption : Maximum at 2530 Å (ε = 9800 . It does not give a colour with tetranitromethane in chloroform.

(*b*) 3β Acetoxyergosta-8 : 22-dien-11-one (100 mg.) in chloroform (10 c.c.) was treated with a solution of bromine (1 mol.) in chloroform, added dropwise during 20 minutes with stirring at 0°. The colourless solution was kept overnight at −4°, diluted with chloroform (50 c.c.), washed with sodium hydrogen carbonate solution and water, and dried (Na_2SO_4). A solution of the solid obtained by removal of the ether, in light petroleum (b. p. 60—80°)–benzene (7 : 3; 50 c.c.), was filtered through a column of activated alumina (2 × 10 cm.). Elution of the column with the same solvent gave a fraction, m. p. 194—195° (50 mg.), which crystallised from methanol, to give 3β-acetoxy-22 : 23-dibromoergost-8-en-11-one as plates, m. p. 200—201°, $[\alpha]_D$ +99° (*c*, 1·0) (Found : C, 58·4; H, 7·6%). Light absorption : Maximum at 2530 Å (ε = 9000). A mixture with a specimen described under (*a*) had m. p. 200—201°.

3β-*Acetoxyergosta*-8 : 22-*dien*-11-*one*.—A solution of 3β-acetoxy-22 : 23-dibromoergost-8-en-11-one (300 mg.) in ether (60 c.c.) and methanol (60 c.c.) was refluxed for 2 hours with zinc dust (3 g.), added portionwise. The mixture was filtered, the filtrate concentrated under reduced pressure, and the crystalline solid (m. p. 120—130°; 200 mg.) separating collected and thrice crystallised from methanol, to give 3β-acetoxy-8 : 22-dien-11-one as elongated plates, m. p. 129—131°, $[\alpha]_D$ +105°, +102° (*c*, 1·6, 0·9) (Found : C, 79·2; H, 10·2. Calc. for $C_{30}H_{46}O_3$: C, 79·2; H, 10·2%); it is undepressed in m. p. when mixed with an authentic specimen, m. p. 129—130°, $[\alpha]_D$ +102°, prepared according to Heusser *et al.* (*loc. cit.*) who give m. p. 122—123°, $[\alpha]_D$ +92°. Light absorption : Maximum at 2540 Å (ε = 9600).

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