*Steroids. Part XV.** 22 : 23-*Dibromo*-11-*oxoergosta*-8 : 14-*dien*-3β-*yl Acetate and Related Compounds.*

By James Grigor, G. T. Newbold, and F. S. Spring.

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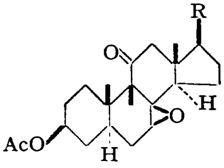
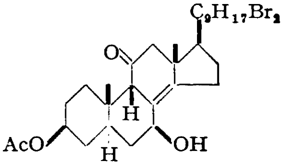
This paper describes the preparation of a 22 : 23-dibromo-11-oxo-9β-ergostadien-3β-yl acetate which contains a conjugated diene chromophore remote from the carbonyl group. It is readily isomerised by acid or alkali to 22 : 23-dibromo-11-oxoergosta-8 : 14-dien-3β-yl acetate (V*a*), and is probably the 8(14) : 15- or 7 : 14-diene.

In Part XIV * the preparation of 22 : 23-dibromo-7β : 8β-epoxy-11-oxo-9β-ergostan-3β-yl acetate (I*a*), and its behaviour with acid and alkali, were described. On treatment with dilute sulphuric acid in dioxan it gives 22 : 23-dibromo-7β-hydroxy-11-oxo-9β-ergost-8(14)-en-3β-yl acetate (II), whilst with a trace of aqueous hydrogen bromide in chloroform it gives 22 : 23-dibromo-7β-hydroxy-11-oxoergost-8-en-3β-yl acetate (III). Whereas the latter with aqueous hydrogen bromide in acetic acid–chloroform gives the saturated diketone (IV*a*), treatment of the former with the same reagent in chloroform leads to dehydration and the formation of an oxo-diene. This oxo-diene is also obtained by treatment of the oxo-epoxide (I*a*) with (i) concentrated sulphuric acid in dioxan, (ii) glacial acetic acid, or (iii) dry hydrogen chloride in chloroform. The oxo-diene exhibits an absorption maximum at 2640 Å (ε 8500) and when treated with zinc in a neutral solvent is converted into the related Δ^{22}-compound which likewise exhibits an absorption maximum at 2640 Å (ε 8300). The position of the ultra-violet absorption maximum shows that the oxo-diene cannot contain a fully conjugated dienone system.

Treatment of the oxo-diene (" non-conjugated " oxo-diene) with alkali or with aqueous hydrogen bromide in acetic acid–chloroform converts it into an isomer which shows a well-defined absorption maximum at 2940 Å (ε 14,000) ; this isomer is also obtained from the oxo-epoxide (I*a*) and from (II) by aqueous hydrogen bromide in acetic acid–chloroform ; in the former case, 22 : 23-dibromo-7 : 11-dioxoergostan-3β-yl acetate (IV*a*) was isolated as a second product. Debromination of the isomeric oxo-diene with zinc gives the corresponding Δ^{22}-compound which also has an absorption maximum at 2940 Å and was obtained, together with 7 : 11-dioxoergost-22-en-3β-yl acetate (IV*b*), by treatment of the oxo-epoxide (I*b*) with aqueous hydrogen bromide in acetic acid–chloroform. The location of



(I*a*) R = $C_9H_{17}Br_2$
(I*b*) R = C_9H_{17}



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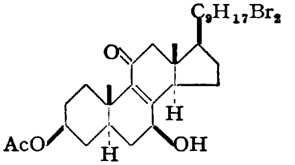

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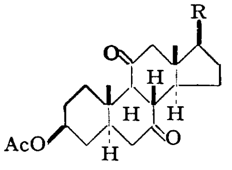
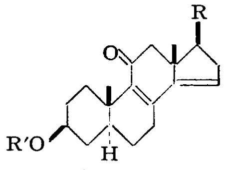
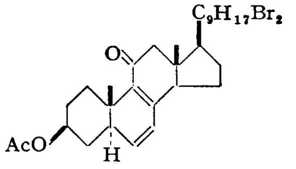


(IV*a*) R = $C_9H_{17}Br_2$
(IV*b*) R = C_9H_{17}



(V*a*) R = $C_9H_{17}Br_2$, R' = Ac
(V*b*) R = C_9H_{17} R' = Ac
(V*c*) R = $C_9H_{17}Br_2$ R' = H



(VI)

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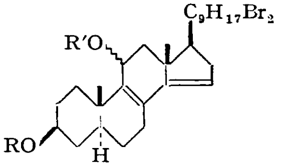
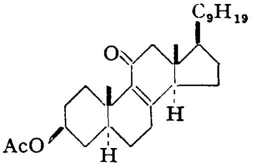
* Part XIV, *J.*, 1954, 2333.

the ultra-violet absorption maximum in the isomeric oxo-diene (conjugated oxo-diene) shows that it contains a fully conjugated dienone system, *i.e.*, that it is 22 : 23-dibromo-11-oxoergosta-8 : 14- (V*a*) or -6 : 8-dien-3β-yl acetate (VI). Reduction of the conjugated oxo-diene with lithium borohydride gives a compound considered to be 22 : 23-dibromo-ergosta-8 : 14-diene-3β : 11ξ-diol (VII*a*). Although the diol readily forms a diacetate (VII*b*) we do not on this evidence ascribe a configuration to the 11-hydroxyl group since the adjacent double bond may well affect the reactivity of this hydroxyl group. The position of the dienic chromophore in the diol is inferred from its ultra-violet absorption spectrum which shows a maximum at 2500 Å (ε 19,400) closely corresponding to that of ergosterol-B$_1$ (ergosta-8 : 14 : 22-trien-3β-ol, $\lambda_{\text{max.}}$ 2500 Å, ε 19,400; Fieser, Rosen, and Fieser, *J. Amer. Chem. Soc.*, 1952, **74**, 5397) and differing considerably from that expected for a steroid 6 : 8-diene (2750—2800 Å, ε *ca.* 10,000). It follows that the conjugated oxo-diene is (V*a*) and not (VI).

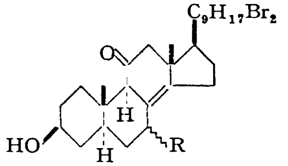
The debrominated product from the conjugated oxo-diene is consequently 11-oxo-ergosta-8 : 14 : 22-trien-3β-yl acetate (V*b*). The structure (V*b*) has been assigned by Laubach, Schreiber, Agnello, Lightfoot, and Brunings (*J. Amer. Chem. Soc.*, 1953, **75**, 1514) to a compound obtained by selective hydrogenation of 11-oxoergosta-6 : 8 : 14 : 22-tetraen-3β-yl acetate, the constants of which (m. p. 127—128·2°, $[\alpha]_D$ +20°; $\lambda_{\text{max.}}$ 2910 Å, log ε 4·06 in ether) differ considerably from those of our compound (m. p. 145—146°, $[\alpha]_D$ −2°; $\lambda_{\text{max.}}$ 2940 Å, ε 14,000). In view of this it was necessary rigidly to establish the structure of our compound. Hydrogenation of the conjugated oxo-diene over Raney nickel gave 11-oxoergost-8-en-3β-yl acetate (VIII), identical with a specimen prepared similarly from 22 : 23-dibromo-11-oxoergost-8-en-3β-yl acetate (Budziarek, Johnson, and Spring, *J.*, 1952, 3410). It follows that our compound is correctly represented by (V*b*). Dr. Laubach has since informed us that he and his colleagues have observed some variations in physical properties in subsequent preparations of 11-oxoergosta-8 : 14 : 22-trien-3β-yl acetate probably owing to the not entirely selective course of the hydrogenation; a later preparation had m. p. 140—141°, $[\alpha]_D$ +1°, in close agreement with our values, and we find that a mixture of this preparation with our sample was undepressed in m. p. We express our best thanks to Dr. Laubach for this information.



(VII*a*) R = R' = H
(VII*b*) R = R' = Ac

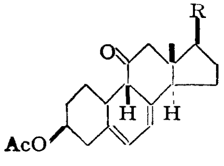


(VIII)

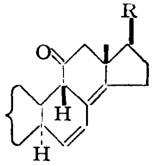


(XIII) R = 7β-OH
(XIV) R = 7α-OH

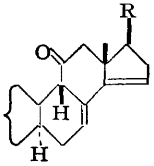
With the establishment of the structure of the conjugated oxo-diene it became possible to consider that of the " non-conjugated " oxo-diene. The fact that it gives a deep brown colour with tetranitromethane suggested that the chromophore in the " non-conjugated " oxo-diene consists of the isolated 11-carbonyl group and a conjugated diene system and not of an αβ-unsaturated carbonyl group together with an isolated double bond. The method of formation of the " non-conjugated " oxo-diene from (II) by an acid-induced dehydration also makes the latter view extremely unlikely and it was excluded by the following experiment. Treatment of the " non-conjugated " oxo-diene ($\lambda_{\text{max.}}$ 2640 Å) with lithium borohydride gave the related 11-alcohol, the ultra-violet absorption spectrum of which shows a maximum at 2610 Å (ε 11,000) thus proving that the carbonyl group is not a part of the major chromophore. As a consequence the formulæ (IX)—(XII) are to be considered for the " non-conjugated " oxo-diene. The exclusion of corresponding structures of 9α-configuration is based on the following consideration: The non-conjugated oxo-diene can only be obtained from parents with unnatural (β) configuration at C$_{(9)}$, *i.e.*, from (I*a*) or (II). Whereas treatment of 22 : 23-dibromo-7β-hydroxy-11-oxo-9β-ergost-8(14)-en-3β-yl acetate (II) with sulphuric acid gives the " non-conjugated " oxo-diene, the same treatment of 22 : 23-dibromo-11-oxoergost-8(14)-ene-3β : 7β-diol (XIII) yields the conjugated oxo-diene, 22 : 23-dibromo-11-oxoergosta-8 : 14-dien-3β-ol (V*c*). In the latter case the configuration of the 7-hydroxyl group does not influence the course of reaction, similar treatment of 22 : 23-dibromo-11-oxoergost-8(14)-ene-3β : 7α-diol (XIV) likewise giving the conjugated oxo-diene (V*c*). A number of attempts to convert the non-conjugated oxo-diene into its 9α-epimer (cf. similar conversions described by Bladon, Henbest, Jones, Lovell, Wood, Woods, Elks, Evans, Hathway, Oughton, and Thomas, *J.*, 1953, 2921, and by Grigor, Laird, MacLean, Newbold, and Spring, *J.*, 1954, 2333) were unsuccessful; either unchanged material was recovered or isomerisation to the conjugated oxo-diene occurred.



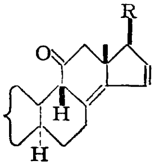
(IX)



(X)



(XI)



(XII)

(R = $C_9H_{17}Br_2$)

It is difficult accurately to assess the effect, if any, of unnatural configuration at $C_{(9)}$ on the ultra-violet absorption associated with well-known steroid dienic chromophores. In our view such an effect is unlikely to be profound; then the ultra-violet absorption spectrum of the " non-conjugated " 11-oxo-diene ($\lambda_{max.}$ 2640 Å, ε 8500) is not compatible with the view that this compound is the 5 : 7- (IX), the 6 : 8(14)- (X), or the 7 : 14-diene (XI). The relatively low intensity of absorption shown by the diene chromophore in the non-conjugated oxo-diene is consonant with the view that it contains a *cisoid*-diene system as in (XI). The position of this maximum however (2640 Å) is substantially different from that of ergosteryl-B_3 acetate (2420 Å) and, further, the non-conjugated oxo-diene fails to react with maleic anhydride under conditions whereby ergosteryl-B_3 acetate readily forms an adduct. Although this behaviour suggests that the " non-conjugated " oxo-diene is probably 22 : 23-dibromo-11-oxo-9β-ergosta-8(14) : 15-dien 3β-yl acetate (XII) (and, for convenience, the compound is so named in the experimental section), we do not believe that the available evidence allows a final decision to be made with confidence. So far as we are aware a steroid 8(14) : 15-diene has not been described hitherto (cf. Lemin, Rosenkranz, and Djerassi, *J. Amer. Chem. Soc.*, 1953, **75**, 1745; Fieser, Nakanishi, and Huang, *ibid.*, p. 4719).

EXPERIMENTAL

Specific rotations were determined in $CHCl_3$ in a 1-dm. tube at approx. 15°, and ultra-violet absorption spectra in EtOH with a Unicam S.P. 500 spectrophotometer. For chromatography, activated alumina Grade II, standardised according to Brockmann, and light petroleum, b. p. 60—80°, were used.

22 : 23-*Dibromo*-11-*oxo*-9β-*ergosta*-8(14) : 15-*dien*-3β-*yl Acetate* (XII).—(*a*) 22 : 23-Dibromo-7β : 8β-epoxy-11-oxo-9β-ergostan-3β-yl acetate (I*a*) (200 mg.) in dioxan (25 c.c.) at 15° was treated with sulphuric acid (1 c.c.; *d* 1·84) and kept for 40 min. Water (10 c.c.) was added and after 1 hr. the precipitate was collected and washed with methanol. Crystallisation from chloroform–methanol gave 22 : 23-*dibromo*-11-*oxo*-9β-*ergosta*-8(14) : 15-*dien*-3β-*yl acetate* (90 mg.) as plates, m. p. 216—217°, $[\alpha]_D$ +25° (*c*, 1·1) (Found: C, 59·15; H, 7·3. $C_{30}H_{44}O_3Br_2$ requires C, 58·8; H, 7·2%). Light absorption: Max. at 2640 Å (ε 8400). It gives a red-brown colour with tetranitromethane in chloroform rapidly fading to yellow.

(*b*) A solution of the same acetate (I*a*) (1·0 g.) in dry chloroform (20 c.c.) at −5° was treated with dry hydrogen chloride for 15 min. and the solution kept for 3½ hr. The product, isolated by using chloroform, was recrystallised from chloroform–methanol, to give the previous product (XII) (220 mg.), m. p. and mixed m. p. 216—217°, $[\alpha]_D$ and absorption as before (Found: C, 58·85; H, 7·4%).

(*c*) The acetate (I*a*) (500 mg.) was treated with boiling glacial acetic acid (25 c.c.) for 2—3 min., the solution cooled, and the product precipitated by addition of water and isolated by using ether. The solid crystallised from chloroform–methanol (mother-liquor A), to give 22 : 23-dibromo-11-oxo-9β-ergosta-8(14) : 15-dien-3β-yl acetate (XII) (200 mg.) as plates, m. p. and mixed m. p. 214—215°, $[\alpha]_D$ +24° (*c*, 1·2) (Found : C, 59·0; H, 7·35%) (absorption : as above).

(*d*) 22 : 23-Dibromo-7β-hydroxy-11-oxo-9β-ergost-8(14)-en-3β-yl acetate (II) (100 mg.) in dioxan (10 c.c.) was treated with sulphuric acid (10 drops; *d* 1·84) and kept at 15° for 40 min. Water (5 c.c.) was added and after 3 hr. the mixture gave 22 : 23-dibromo-11-oxo-9β-ergosta-8(14) : 15-dien-3β-yl acetate (XII) (40 mg.) crystallising from chloroform–methanol as plates, m. p. and mixed m. p. 217—218°, $[\alpha]_D$ +25° (*c*, 1·3) (Found : C, 58·75; H, 7·5%) (absorption : as before).

11-*Oxo*-9β-*ergosta*-8(14) : 15 : 22-*trien*-3β-*yl Acetate* (XII; but R = C_9H_{17}).—(*a*) 22 : 23-Dibromo-11-oxo-9β-ergosta-8(14) : 15-dien-3β-yl acetate (250 mg.), in a mixture of benzene (20 c.c.) ether (30 c.c.), and ethanol (30 c.c.), was refluxed with activated zinc (1·5 g.) for 4 hr. 11-*Oxo*-9β-*ergosta*-8(14) : 15 : 22-*trien*-3β-*yl acetate*, isolated in the usual manner, crystallised from chloroform–methanol as plates, m. p. 180—182°, $[\alpha]_D$ −28° (*c*, 1·1). Light absorption : Max. at 2660 (ε 8300) and 2140 Å (ε 3600) (Found: C, 79·3; H, 10·0. $C_{30}H_{44}O_3$ requires C, 79·6; H, 9·8%).

(*b*) A solution of 22 : 23-dibromo-7β : 8β-epoxy-11-oxo-9β-ergostan-3β-yl acetate (I*a*) (550 mg.) in glacial acetic acid (50 c.c.) was heated on the steam-bath with zinc (6 g.) and stirred vigorously for 2½ hr. Isolation from ether, followed by crystallisation from chloroform–methanol, gave the preceding product, m. p. and mixed m. p. 180—182°, $[\alpha]_D$ −29° (*c*, 1·8) (Found : C, 79·4; H, 9·9%). Light absorption : Max. at 2640 Å (ε 8200). A solution in chloroform gave a red-brown colour with tetranitromethane.

22 : 23-*Dibromo*-11-*oxoergosta*-8 : 14-*dien*-3β-*yl Acetate* (V*a*).—(*a*) A solution of 22 : 23-dibromo-7β : 8β-epoxy-11-oxo-9β-ergostan-3β-yl acetate (I*a*) (400 mg.) in chloroform (25 c.c.) was treated with glacial acetic acid (50 c.c.) containing aqueous 46% hydrobromic acid (10 drops) and kept overnight at room temperature. The product crystallised from chloroform–methanol, to give 22 : 23-dibromo-7 : 11-dioxoergostan-3β-yl acetate (IV*a*), m. p. and mixed m. p. 263° (decomp.). Evaporation of the mother-liquors gave a residue, m. p. *ca.* 210° (strong yellow colour with tetranitromethane in chloroform), which was dissolved in light petroleum–benzene (1 : 1; 40 c.c.) and adsorbed on a column of alumina (10 × 1·5 cm.). The column was washed with the same solvent mixture (250 c.c.) and then with benzene (400 c.c.) which eluted a solid (120 mg.), seven crystallisations of which from chloroform–methanol gave 22 : 23-*dibromo*-11-*oxoergosta*-8 : 14-*dien*-3β-*yl acetate* (50 mg.) as plates, m. p. 221—223°, $[\alpha]_D$ +35°, +34° (*c*, 2·1) (Found : C, 59·2; H, 7·4. $C_{30}H_{44}O_3Br_2$ requires C, 58·8; H, 7·2%). It gives a bright yellow colour with tetranitromethane in chloroform. Light absorption : Max. at 2140 (ε 11,700) and 2920 Å (ε 13,700).

(*b*) Treatment of the epoxy-acetate (I*a*) with acetic acid gave a mixture from which 22 : 23-dibromo-11-oxo-9β-ergosta-8(14) : 15-dien-3β-yl acetate was isolated in 40% yield as described above. Evaporation of the mother-liquor A from this compound gave a solid (300 mg.) which was chromatographed in benzene–light petroleum (1 : 3; 100 c.c.) on alumina (15 × 2 cm.). The column was washed with benzene–light petroleum (1 : 3, 320 c.c.; 1 : 2, 250 c.c.; 1 : 1, 100 c.c.) and then with benzene–ether (19 : 1; 220 c.c.) which eluted 22 : 23-dibromo-11-oxoergosta-8 : 14-dien-3β-yl acetate (50 mg.); crystallisation from methanol gave prisms, m. p. and mixed m. p. 221—223°, $[\alpha]_D$ +35° (*c*, 0·4). Light absorption : Max. at 2130 (ε 10,000) and 2940 Å (ε 13,000). Further elution with benzene–ether (19 : 1, 370 c.c.; 17 : 3, 100 c.c.; 4 : 1, 150 c.c.; 3 : 2, 150 c.c.; 1 : 2, 250 c.c.) and ether (200 c.c.) followed by evaporation of the combined eluates and crystallisation of the residue from methanol gave 22 : 23-dibromo-7 : 11-dioxoergostan-3β-yl acetate (40 mg.), m. p. and mixed m. p. 262° (decomp.), $[\alpha]_D$ −3° (*c*, 0·8).

(*c*) 22 : 23-Dibromo-11-oxo-9β-ergosta-8(14) : 15-dien-3β-yl acetate (100 mg.) in benzene (10 c.c.) and methanolic 10% potassium hydroxide (10 c.c.) was heated under reflux for 1 hr. The product was isolated by using ether and heated on the steam-bath with acetic anhydride and pyridine for 1 hr., to give 22 : 23-dibromo-11-oxoergosta-8 : 14-dien-3β-yl acetate (50 mg.), which crystallised from chloroform–methanol as plates, m. p. and mixed m. p. 222—223°, $[\alpha]_D$ +36° (*c*, 0·7) (Found : C, 59·1; H, 7·1%). Light absorption : Max. at 2090 (ε 8000) and 2920 Å (ε 13,000).

(*d*) 22 : 23-Dibromo-11-oxo-9β-ergosta-8(14) : 15-dien-3β-yl acetate (100 mg.) in chloroform (5 c.c.) and glacial acetic acid (10 c.c.) containing aqueous 46% hydrogen bromide (10 drops) was kept at room temperature for 24 hr. Isolation by means of chloroform gave 22 : 23-dibromo-11-oxoergosta-8 : 14-dien-3β-yl acetate (60 mg.) crystallising from chloroform–methanol as plates, m. p. and mixed m. p. 222—223°, $[\alpha]_D$ +35° (*c*, 0·4) (Found : C, 59·0; H, 7·5%). Light absorption : Max. at 2100 (ε 9000) and 2940 Å (ε 13,000).

(*e*) 22 : 23-Dibromo-7β-hydroxy-11-oxo-9β-ergost-8(14)-en-3β-yl acetate (250 mg.) in chloroform (20 c.c.) was treated with glacial acetic acid (40 c.c.) containing aqueous 46% hydrogen bromide (8 drops) and set aside at room temperature overnight. Isolation from chloroform and crystallisation from chloroform–methanol gave a solid (110 mg.), m. p. 208—211° showing absorption at 2100 (ε 9800) and 2940 Å (ε 11,100). Purification by chromatography followed by repeated crystallisation from chloroform–methanol yielded 22 : 23-dibromo-11-oxoergosta-8 : 14-dien-3β-yl acetate as plates, m. p. and mixed m. p. 219—220°, $[\alpha]_D$ +35° (*c*, 2·0). Light absorption : Max. at 2110 (ε 10,000) and 2920 Å (ε 12,500).

22 : 23-*Dibromo*-11-*oxoergosta*-8 : 14-*dien*-3β-*ol* (V*c*).—(*a*) A solution of 22 : 23-dibromo-11-oxoergost-8(14)-ene-3β : 7α-diol (XIV) (100 mg.) in dioxan (52 c.c.) and sulphuric acid (2 c.c.; *d* 1·84) was kept at room temperature for 40 min. Isolation of the product in the usual manner followed by crystallisation from chloroform–methanol gave 22 : 23-*dibromo*-11-*oxoergosta*-8 : 14-*dien*-3β-*ol* (25 mg.) as plates, m. p. 208—209°, $[\alpha]_D$ +45° (*c*, 1·5) (Found : C, 57·1; H, 7·9. $C_{28}H_{42}O_2Br_2$,2MeOH requires C, 56·8; H. 7·9%). Light absorption : Max. at 2100 (ε 10,000) and 2920 Å (ε 12,000). Acetylation gave the corresponding acetate which separated from chloroform–methanol as plates, m. p. and mixed m. p. 220—221° $[\alpha]_D$ +35° (*c*, 0·9).

(*b*) 22 : 23-Dibromo-11-oxoergost-8(14)-ene-3β : 7β-diol (XIII) (80 mg.) was dissolved in dioxan (10 c.c.) and sulphuric acid (0·4 c.c.; *d*, 1·84) and kept at room temperature for 40 min., to give 22 : 23-dibromo-11-oxoergosta-8 : 14-dien-3β-ol (35 mg.), m. p. and mixed m. p. 208—209°, $[\alpha]_D$ +47° (*c*, 0·7). Light absorption : Max. at 2100 (ε 9600) and 2910 Å (ε 11,800).

11-*Oxoergosta*-8 : 14 : 22-*trien*-3β-*yl Acetate* (V*b*).—(*a*) 22 : 23-Dibromo-11-oxoergosta-8 : 14-dien-3β-yl acetate (160 mg.) was debrominated by activated zinc (750 mg.) in ether–ethanol (50 c.c.). The product, 11-*oxoergosta*-8 : 14 : 22-*trien*-3β-*yl acetate* (90 mg.), separated from aqueous methanol as flat needles, m. p. 145—146°, $[\alpha]_D$ −2° (*c*, 1·6) (Found : C, 79·7; H, 9·8. $C_{30}H_{44}O_3$ requires C, 79·6; H, 9·8%). The compound gives a deep yellow colour with tetranitromethane in chloroform. Light absorption : Max. at 2120 (ε 8900) and 2940 Å (ε 12,500).

(*b*) 7β : 8β-Epoxy-11-oxo-9β-ergost-22-en-3β-yl acetate (I*b*) (800 mg.) in chloroform (30 c.c.) and glacial acetic acid (60 c.c.) containing aqueous 46% hydrobromic acid (12 drops) was kept overnight at room temperature. Isolation by means of chloroform and crystallisation from methanol gave a solid (500 mg.), m. p. *ca.* 130°, a solution of which in benzene–light petroleum (2 : 1, 100 c.c.) was adsorbed on a column (15 × 2 cm.) of alumina (grade II—III). Elution with benzene (50 c.c.) gave 11-oxoergosta-8 : 14 : 22-trien-3β-yl acetate (228 mg.), m. p. 143—144°, forming from aqueous methanol flat needles (180 mg.), m. p. and mixed m. p. 144—145°, $[\alpha]_D$ −3° (*c*, 3·0) (Found : C, 79·5; H, 9·8%). Light absorption : Max. at 2120 (ε 9000) and 2950 Å (ε 14,000).

Continued washing of the column with benzene (250 c.c.) and benzene–ether (200 c.c.; 19 : 1) gave a solid (130 mg.), m. p. 198°, crystallisation of which from aqueous methanol yielded 7 : 11-dioxoergost-22-en-3β-yl acetate (IV*b*) (100 mg.) as felted needles, m. p. and mixed m. p. 198—200°, $[\alpha]_D$ −30° (*c*, 1·7) (Found : C, 76·6; H, 9·85. Calc. for $C_{30}H_{46}O_4$: C, 76·55; H, 9·85%).

22 : 23-*Dibromoergosta*-8 : 14-*diene*-3β : 11ξ-*diol* (VII*a*).—22 : 23-Dibromo-11-oxoergosta-8 : 14-dien-3β-ol (V*c*) (150 mg.) in tetrahydrofuran (12 c.c.) was added dropwise wth stirring during 40 min. to lithium borohydride (150 mg.) in tetrahydrofuran (15 c.c.) at 20°. Stirring was continued for 7 hr., the solution kept overnight, and the product isolated in the usual manner. Crystallisation from chloroform–methanol gave 22 : 23-*dibromoergosta*-8 : 14-*diene*-3β : 11ξ-*diol* (120 mg.), m. p. 187—188° (decomp.), $[\alpha]_D$ −18° (*c*, 1·2), −17° (*c*, 1·0) (Found : C, 56·35; H, 8·2. $C_{28}H_{44}O_2Br_2$,2MeOH requires C, 56·6; H, 8·2%). Light absorption : Max. at 2500 Å (ε 19,400). Acetylation of the diol at room temperature gave the *diacetate* (VII*b*), needles (from chloroform–methanol), m. p. 178—179° (varies with rate of heating), $[\alpha]_D$ −35° (*c*, 1·3) (Found : C, 58·5; H, 7·4. $C_{32}H_{48}O_4Br_2$ requires C, 58·5; H, 7·4%). Light absorption : Max. at 2500 Å (ε 19,600). Infra-red absorption in Nujol suspension : Acetate peaks at 1730 and 1240 cm.$^{-1}$.

11-*Oxoergost*-8-*en*-3β-*yl Acetate* (VIII).—(*a*) A mixture of 22 : 23-dibromo-11-oxoergost-8-en-3β-yl acetate (Budziarek *et al.*, *loc. cit.*) (1 g.) in benzene (150 c.c.) and Raney nickel sludge in ethanol (W7; 1 c.c.) was shaken with hydrogen until absorption was complete. Crystallisation of the product from aqueous methanol gave 11-oxoergost-8-en-3β-yl acetate (420 mg.) as blades m. p. 137—139°, $[\alpha]_D$ +122° (*c*, 0·7) (Found : C, 79·2; H, 10·9. Calc. for $C_{30}H_{48}O_3$:

C, 78·9; H, 10·6%). Light absorption: Max. at 2540 Å (ε 8600). Bladon *et al.* (*loc. cit.*) give m. p. 138—140°, $[\alpha]_D$ +119°; Laubach *et al.* (*loc. cit.*) give m. p. 137·8—138·6°, $[\alpha]_D$ +125°.

(*b*) A solution of 22 : 23-dibromo-11-oxoergosta-8 : 14-dien-3β-yl acetate (1 g.) in dioxan (150 c.c.) was shaken with hydrogen over Raney nickel (W.7; 1 c.c.) to yield 11-oxoergost-8-en-3β-yl acetate (400 mg.) as blades m. p. 137—139°, $[\alpha]_D$ +119° (*c*, 1·7). A mixture with the specimen described above was undepressed in m. p. Light absorption: Max. at 2540 Å (ε 8500).

3β-*Acetoxy*-22 : 23-*dibromo*-9β-*ergosta*-8(14) : 15-*dien*-11ξ-*ol*.—22 : 23-Dibromo-11-oxo-9β-ergosta-8(14) : 15-dien-3β-yl acetate (300 mg.) in tetrahydrofuran (60 c.c.) was treated with a solution of lithium borohydride (320 mg.) in tetrahydrofuran (25 c.c.) during 5 min. The solution was kept at room temperature overnight and the product isolated in the usual manner. Crystallisation from benzene–light petroleum gave 3β-*acetoxy*-22 : 23-*dibromo*-9β-*ergosta*-8(14) : 15-*dien*-11ξ-*ol* (130 mg.) as needles, m. p. 232° (decomp.), $[\alpha]_D$ −51° (*c*, 1·1) (Found: C, 58·7; H, 7·8. $C_{30}H_{46}O_3Br_2$ requires C, 58·6; H, 7·55%). Light absorption: Max. at 2610 Å (ε 11,400).

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