169. *Studies in the Sterol Group. Part XXXVII. The Structure of Lumisterol and its Stereoisomers.*

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A constitutional study of lumisterol has necessitated the preparation of the epimers of lumisterol, ergosterol, and dehydroergosterol.

Reduction of ergostatrienone (IV) gives a molecular complex of ergosterol and *epi*ergosterol, reduction of the carbonyl group being accompanied by migration of the Δ^4-ethylenic linkage. *epi*Ergosterol is extremely unstable, quickly isomerising to an ergostatrienol, m. p. 152°, which does not contain a system of conjugated ethylenic linkages. The compound was previously prepared by Marker, Kamm, Laucius, and Oakwood and, as shown by Windaus and Buchholz, was erroneously described by the American authors as "*epi*ergosterol." The view of Windaus and Buchholz that the trienol, m. p. 152°, is a *direct* reduction product of ergostatrienone is, however, incorrect.

Oxidation of lumisterol gives the αβ-unsaturated ketone lumistatrienone (IV), reduction of which gives a molecular complex of lumisterol and *epi*lumisterol, the Δ^4-ethenoid linkage migrating to the Δ^5-location during the course of reduction. Resolution of this complex by means of digitonin readily gives the two components; in contrast to *epi*ergosterol, *epi*lumisterol is relatively stable.

Oxidation of dehydroergosterol gives the αβ-unsaturated ketone ergostatetraenone (VII). Reduction of the latter yielded a molecular complex of dehydroergosterol and *epi*dehydroergosterol.

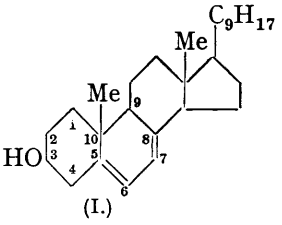
In view of the non-identity (a) of *epi*ergosterol with either lumisterol or pyrocalciferol and (b) of *epi*lumisterol with either ergosterol or *iso*pyrocalciferol, it is concluded that the four stereoisomers, ergosterol, lumisterol, pyrocalciferol, and *iso*pyrocalciferol,

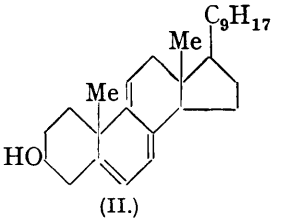
differ solely in the orientation around the two asymmetric centres C_9 and C_{10} and not around C_3.

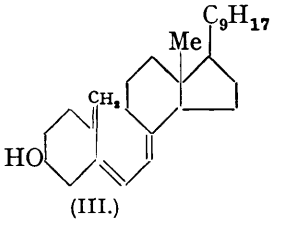
A preliminary study of the enol-acetates of polyunsaturated steroid ketones has been made; the enol-acetates of ergostatrienone, *iso*ergostatrienone, ergostatetraenone and lumistatrienone are described.

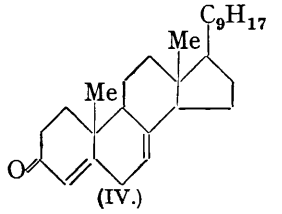
LUMISTEROL, a stereoisomer of ergosterol, has been shown to differ from the latter in the orientation of the groups attached to C_{10}, and possibly in the orientation around C_9. This decision was made by Windaus and Dimroth (*Ber.*, 1937, **70**, 376), who showed that, of the four stereoisomers known whose structure is represented by (I), ergosterol and *iso*pyrocalciferol both give dehydroergosterol (II) (Müller, *Z. physiol. Chem.*, 1935, **231**, 75) on treatment with mercuric acetate, whereas similar treatment of lumisterol and pyrocalciferol gives dehydrolumisterol (Heilbron, Spring, and Stewart, J., 1935, 1221). The conversion of calciferol (III) into the isomeric pyrocalciferols (I) clearly involves the appearance of two new centres of asymmetry within the molecule (C_9 and C_{10}) and the German authors considered that the four theoretically possible isomers differing in the relative orientation of these two asymmetric centres are represented by ergosterol, lumisterol, pyrocalciferol, and *iso*pyrocalciferol. The orientations of both C_9 and C_{10} in the case of ergosterol being indicated by +, the following is an expression of the relationships suggested :

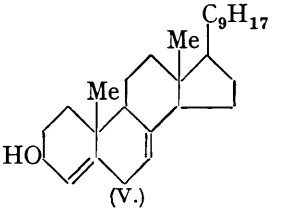
	C_9.	C_{10}.		C_{10}.
Ergosterol	+	+	→ Dehydroergosterol (II)	+
*iso*Pyrocalciferol	−	+		
Lumisterol	+(?)	−	→ Dehydrolumisterol (II)	−
Pyrocalciferol	−(?)	−		

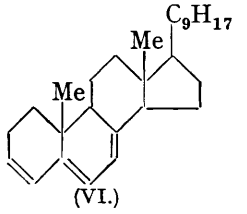












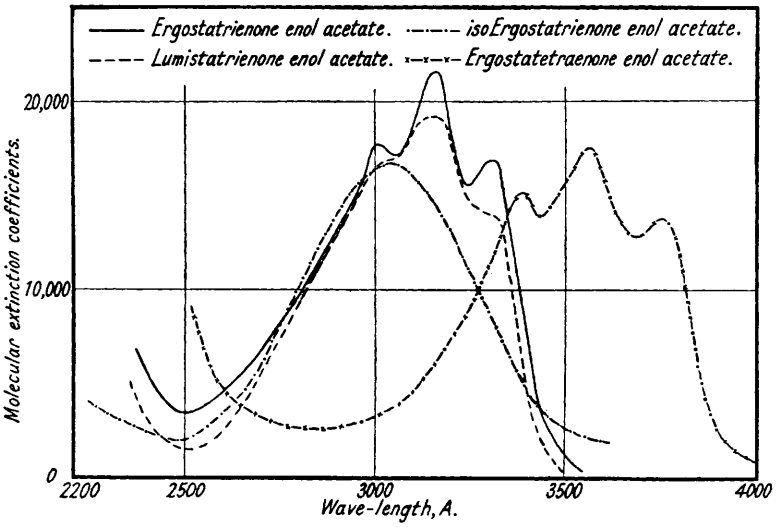
Theoretically, an equally valid interpretation of the reactions of the four isomers under discussion is obtained if it be assumed that they represent the possible stereoisomers obtained by varying the orientation around C_3 and C_9. According to this view we obtain the following representation :

	C_3.	C_9.		C_3.
Ergosterol	+	+	→ Dehydroergosterol	+
*iso*Pyrocalciferol	+	−		
Lumisterol	−	+(?)	→ Dehydrolumisterol	−
Pyrocalciferol	−	−(?)		

If this representation is correct, *epi*ergosterol must be identical with either lumisterol or pyrocalciferol (according to the orientation around C_9), and similarly *epi*lumisterol must be identical with either ergosterol or *iso*pyrocalciferol. Furthermore, dehydroergosterol and dehydrolumisterol according to this view are epimers. The preparation of *epi*ergosterol *epi*lumisterol, and *epi*dehydroergosterol has therefore been undertaken in order to effect the necessary comparisons.

The oxidation of ergosterol to an ergostatrienone was first described by Oppenauer (*Rec. Trav. chim.*, 1937, **56**, 137) and later, using a more tedious route, by Wetter and Dimroth (*Ber.*, 1937, **70**, 1665). Ergostatrienone shows the typical light absorption properties of an αβ-unsaturated ketone and is therefore formulated as (IV), migration of the Δ^5-ethenoid linkage of ergosterol (I) having occurred during the oxidation.

FIG. 1.

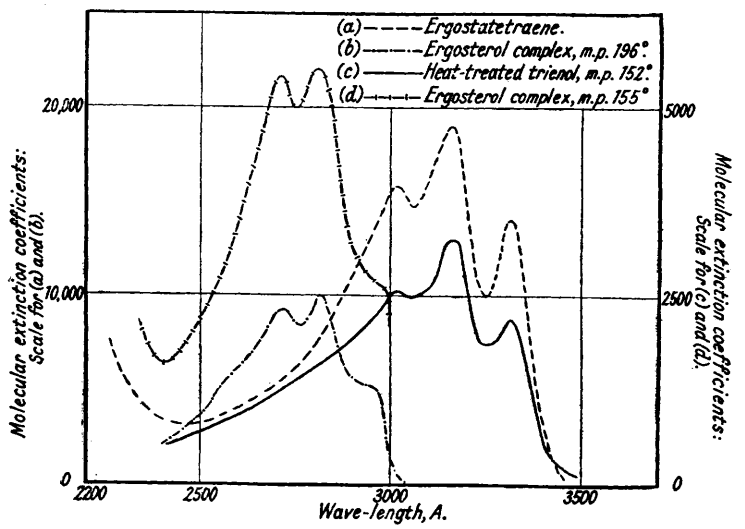


The reduction of ergostatrienone by the Ponndorf–Meerwein method was described by Marker, Kamm, Laucius, and Oakwood (*J. Amer. Chem. Soc.*, 1937, **59**, 1840); they reported that resolution of the crude reduction product by means of digitonin gave ergosterol and an isomeric ergostatrienol, m. p. 152°, which, unlike the former, does not give an insoluble digitonide and consequently was designated "*epi*ergosterol." More recently, Windaus and Buchholz (*Ber.*, 1938, **71**, 576) have shown that the ergostatrienol, m. p. 152°, does not exhibit selective absorption between 2400 and 3000 A., and therefore cannot contain the conjugated system of ethylenic linkages present in ergosterol. They therefore conclude that the reduction of ergostatrienone occurs without migration of an ethylenic linkage, that the trienol, m. p. 152°, has the structure (V), and that the ergosterol isolated by Marker *et al.* is not a true reaction product but is present as a contaminant in the ergostatrienone employed.

Before the appearance of the paper of Windaus and Buchholz, we had completed a detailed study of the reduction of ergostatrienone, using the method employed by Marker *et al.*, and whilst we agree with the former authors that the ergostatrienol, m. p. 152°, of Marker is not *epi*ergosterol, our results show that certain of the views of the German authors require modification. Reduction of ergostatrienone, m. p. 132°, $[\alpha]_D^{20°}$ — 0·8°, with aluminium *iso*propoxide gives a molecular complex which after three crystallisations has the constant melting point 196°. This complex is spectroscopically identical (Fig. 2) with ergosterol, but on standing its melting point rapidly decreases to a minimum value of approximately 155° and this change is accompanied by a marked decrease in the intensity of the light absorption, which finally reaches a value approximately half that of ergosterol. Resolution of either the complex, m. p. 196°, or that of m. p. 155° by means of digitonin gives in each case an insoluble digitonide in approximately 50% yield, which on decomposition by the pyridine method readily gives ergosterol. Thus there can be no possible doubt that ergosterol is obtained as one of the products of reduction of ergostatrienone. The digitonin non-precipitable fraction from each complex readily gave the ergostatrienol, m. p. 152°, described by Marker *et al.*; this compound is spectroscopically transparent and therefore cannot contain a conjugated system of ethenoid linkages.

A consideration of the foregoing facts establishes that reduction of ergostatrienone gives in the first place a mixture of ergosterol and *epi*ergosterol, or, in other words, the reduction of the carbonyl group is accompanied by a facile and complete migration of the C_4–C_5 linkage to the C_5–C_6 position. Furthermore, *epi*ergosterol is very unstable, readily isomerising to the trienol, m. p. 152°. It is not possible to decide between the several possible structures for this compound from the available evidence.

FIG. 2.

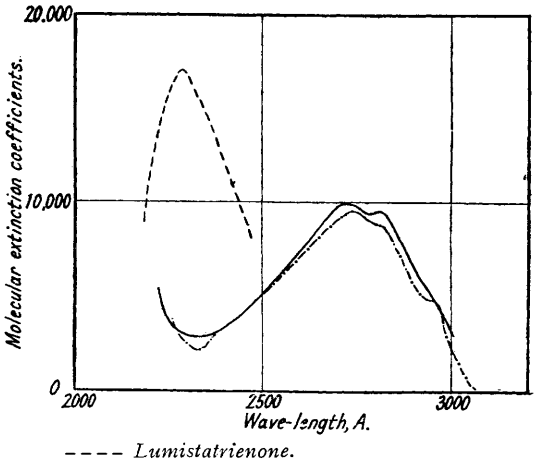


Although it has not been possible to isolate *epi*ergosterol other than in the form of its complex with ergosterol, its instability shows that it cannot be identical with either lumisterol or pyrocalciferol. The latter has been shown to isomerise on irradiation with ultra-violet light to photopyrocalciferol, which resembles the trienol, m. p. 152°, in its spectroscopic transparency (Dimroth, *Ber.*, 1937, **70**, 1621). Thus the change pyrocalciferol ⟶ photopyrocalciferol resembles that of *epi*ergosterol ⟶ trienol, m. p. 152°, in that a migration of one or both of the C_5–C_6 and C_7–C_8 ethylenic linkages has occurred with the production of a non-conjugated system. As photopyrocalciferol is reconverted into pyrocalciferol by heat treatment, it appeared possible that similar treatment of the trienol, m. p. 152°, would yield *epi*ergosterol. We find, however, that the trienol, m. p. 152°, gives a product which exhibits absorption in the ultra-violet with a maximum at 3165 A. (Fig. 2). Prolonged treatment of the trienol, m. p. 152°, with acetic anhydride gives an *ergostatetraene*, m. p. 104°, differing from the isomeric hydrocarbons described by Rygh (*Z. physiol. Chem.*, 1929, **185**, 99) and Stoll (*ibid.*, 1931, **202**, 233) and showing the same characteristic absorption as the product from the trienol, but in approximately ten-fold intensity (Fig. 2). In view of the similarity in the absorption spectrum of this ergostatetraene with that of both dehydroergosterol and the enol-acetate of the ergostatrienone described below, we conclude that it has the structure (VI).

Oxidation of lumisterol with aluminium *tert.*-butoxide in the presence of acetone gives *lumistatrienone*, m. p. 139—140°, characterised by its *semicarbazone*, m. p. 247°. Lumistatrienone shows the typical light absorption properties of an αβ-unsaturated ketone (Fig. 3) and is therefore a stereoisomer of ergostatrienone (IV). Reduction of lumistatrienone by the Ponndorf–Meerwein method gives a molecular complex, m. p. 159·5°, which is spectroscopically identical with lumisterol. Resolution of the complex by means of digitonin gives an insoluble digitonide which on decomposition with pyridine yields *epi-lumisterol*, m. p. 109—110° (*acetate*, m. p. 114—115°), showing the same absorption spectrum as lumisterol. Although the melting points of *epi*lumisterol and its acetate are very close to those of *iso*pyrocalciferol (112—115°) and its acetate (113—115°), the optical rot-

ations differ greatly. Furthermore, a strong depression in melting point was observed on mixing the acetates of *epi*lumisterol and *iso*pyrocalciferol. After removal of the digitonide of *epi*lumisterol the mother-liquors readily gave lumisterol. Thus once again it is established that reduction of the carbonyl group of a steroid ketone of type (IV) is accompanied by migration of the Δ^4-ethenoid linkage into the conjugated Δ^5-location.

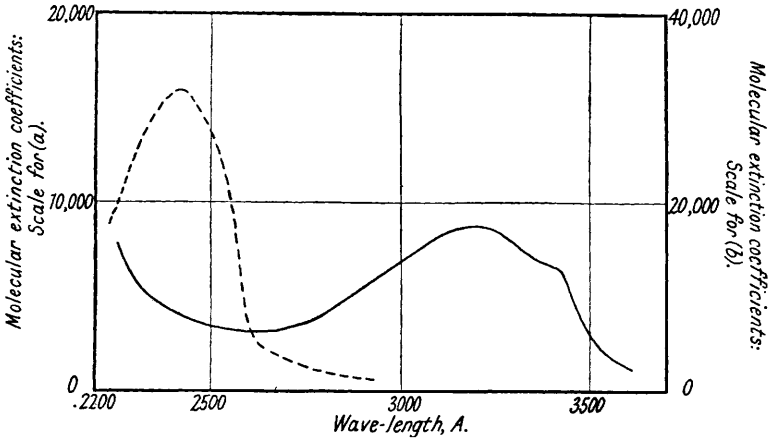
FIG. 3.



---- *Lumistatrienone.*
-·-·- epi*Lumisterol.*
—— *Lumisterol*–epi*lumisterol complex.*

Oxidation of dehydroergosterol by the Oppenauer method gives *ergostatetraenone* (VII), m. p. 140—142°, which also exhibits the characteristic absorption spectrum of an αβ-unsaturated ketone (Fig. 4). Reduction of this ketone with aluminium *iso*propoxide gives a molecular complex of dehydroergosterol and *epi*dehydroergosterol which, when freshly prepared, exhibits an absorption spectrum similar to that of dehydroergosterol

FIG. 4.



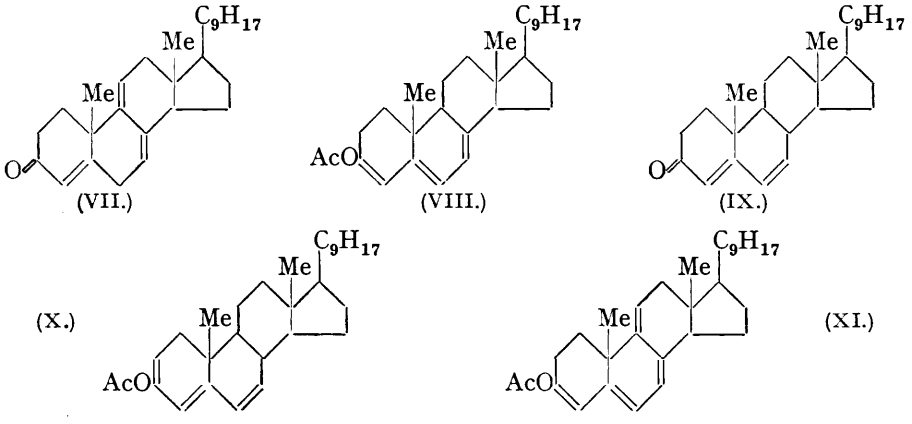
(*a*)—— *Dehydroergosterol*–epi*dehydroergosterol complex.*
(*b*)---- *Ergostatetraenone.*

(Fig. 4). Resolution by means of digitonin readily gives dehydroergosterol, but *epi*-dehydroergosterol, like *epi*ergosterol, is apparently unstable, since the product obtained from the non-digitonide forming fraction of the reduction product exhibits a light absorption of approximately one-fifth of that of dehydroergosterol. The amount of material at our disposal was too small to permit of a complete examination of this

product. It is clear, however, that reduction of the carbonyl group of ergostatetraenone is again accompanied by a migration of the Δ^4-ethenoid linkage to the Δ^5-location.

Since *epi*ergosterol is not identical with either lumisterol or pyrocalciferol, and *epi*-lumisterol is not identical with either ergosterol or *iso*pyrocalciferol, the structures assumed by Windaus and Dimroth (*loc. cit.*) for lumisterol, ergosterol, and the pyrocalciferols are substantiated, the stereovariants being C_9 and C_{10} and not C_3.

Enol-Acetates of Steroid Ketones.—Acetylation of ergostatrienone yields an *enol-acetate*, m. p. 146°, which exhibits an intense light absorption maximum at 3165 A. (Fig. 1) and to which is consequently allocated the structure (VIII). Hydrolysis of this enol-acetate gives *iso*ergostatrienone (IX), previously prepared by Wetter and Dimroth (*loc. cit.*) by the action of methyl-alcoholic hydrogen chloride on ergostatrienone. *iso*Ergostatrienone gives an *enol-acetate*, m. p. 137°, which exhibits an absorption maximum at 3040 A. (Fig. 1), and to which we ascribe the structure (X). We have also examined the acetylation of lumistatrienone, from which an *enol-acetate* has been obtained, m. p. 98°, spectroscopically identical with the enol-acetate of ergostatrienone, and which may therefore be represented by the structure (VIII). The *enol-acetate* of ergostatetraenone, m. p. 161°, exhibits an absorption maximum at 3560 A. (Fig. 1), in consequence of which we favour the structure (XI) for this compound.



(VII.) (VIII.) (IX.)

(X.) (XI.)

Experimental.

Reduction of Ergostatrienone.—The ketone prepared by the method of Oppenauer, after three crystallisations from light petroleum (b. p. 40—60°)–acetone (5 : 1), had m. p. 132°, $[\alpha]_D^{20°}$ − 0·8° (l = 1, c = 3·2 in chloroform). *Light absorption in alcohol :* maxima, (a) 2300 A., log ε = 4·30; (b) 3200 A., log ε = 1·61. The ketone (10 g.) in *iso*propyl alcohol (60 c.c.) was treated with aluminium *iso*propoxide (4·5 g.), and the mixture heated under reflux for 4 hours. The reaction mixture was treated as described by Marker *et al.* (*loc. cit.*), and the product (10 g.) crystallised from dioxan–methyl alcohol, from which the ergosterol–*epi*ergosterol complex separated in needles, m. p. 196°. *Light absorption in alcohol* (Fig. 2) : maxima, (a) 2815 A., log ε = 4·00; (b) 2720 A., log ε = 3·96. On standing for 2 days the complex had m. p. 155°, $[\alpha]_D^{20°}$ − 53·2° (l = 1, c = 0·6 in chloroform). A solution of the complex of either m. p. 196° or 155° (5 g.) in alcohol (90%; 200 c.c.) was treated with a solution of digitonin (20 g.) in alcohol (90%; 800 c.c.); and the mixture set aside overnight. The separated digitonide (10 g.) was taken up in hot pyridine (100 c.c.), and the solution treated with ether. The digitonin was removed by filtration, and the mother-liquor evaporated to dryness. Crystallisation of the residue from alcohol gave ergosterol (1·1 g.), m. p. 160°, $[\alpha]_D^{20°}$ − 127° (l = 1, c = 0·96 in chloroform), showing the characteristic absorption spectrum of ergosterol; the acetate, prepared in the usual manner, had m. p. 170°, $[\alpha]_D^{20°}$ − 90·1° (l = 1, c = 0·7 in chloroform). Neither the sterol nor its acetate depressed the m. p. of authentic ergosterol and its acetate respectively. The filtrate obtained after removal of ergosterol digitonide was worked up as described by Marker *et al.*, the trienol being obtained, after three crystallisations from acetone, in needles, m. p. 152°, $[\alpha]_D^{20°}$ + 41·3° (l = 1, c = 0·92 in chloroform). The acetate separated

from alcohol in plates, m. p. 126° (Marker *et al.* give m. p. 152°, $[\alpha]_D^{20°}$ + 50·0° for "*epi*ergosterol" and m. p. 126° for its acetate).

Ergostatetraene (VI).—The trienol (200 mg.), m. p. 152°, was heated under reflux with acetic anhydride (5 c.c.) and anhydrous sodium acetate (200 mg.) for 3 hours. On cooling, the ***hydrocarbon*** separated in plates, which after a single crystallisation from alcohol had m.p. 104°, $[\alpha]_D^{20°}$ − 40·5° (l = 1, c = 1·24 in chloroform) (Found: C, 88·6; H, 11·1. $C_{28}H_{42}$ requires C, 88·8; H, 11·2%). *Light absorption in alcohol* (Fig. 2): maxima, (a) 3015 A.; (b) 3160 A., log ε = 4·28; (c) 3315 A.

Lumistatrienone (IV).—Lumisterol was oxidised by the method of Oppenauer (*loc. cit.*). After two crystallisations from light petroleum (b. p. 40—60°)–acetone (1 : 1) *lumistatrienone* separated in hard needles, m. p. 139—140°, $[\alpha]_D^{20°}$ + 48·7° (l = 1, c = 1·05 in chloroform) (Found: C, 85·1; H, 10·7. $C_{28}H_{42}O$ requires C, 85·2; H, 10·8%). *Light absorption in alcohol* (Fig. 3): maximum, 2290 A., log ε = 4·23. The *semicarbazone* separated from methyl alcohol–chloroform in needles, m. p. 247° (decomp.) (Found: C, 77·2; H, 9·8; N, 9·05. $C_{29}H_{45}ON_3$ requires C, 77·05; H, 10·05; N, 9·3%).

Reduction of Lumistatrienone: epi*Lumisterol*.—The reduction of lumistatrienone (10 g.) was effected by the method employed for ergostatrienone. After three crystallisations from acetone the lumisterol–*epi*lumisterol complex separated in needles, m. p. 159·5°, $[\alpha]_D^{20°}$ + 196·7° (l = 1, c = 0·6 in chloroform). Treatment of the complex (2 g.) with excess of digitonin in 90% alcohol gave *epi*lumisterol digitonide (4 g.), which on decomposition with pyridine gave epi*lumisterol* (0·9 g.); this separated from methyl alcohol in needles, m. p. 109—110°, $[\alpha]_D^{20°}$ + 224·6° (l = 1, c = 0·6 in chloroform) (Found: C, 84·9; H, 11·1. $C_{28}H_{44}O$ requires C, 84·8; H, 11·2%). *Light absorption in alcohol* (Fig. 3): maximum, 2740 A., log ε = 3·98. The *acetate* separated from methyl alcohol in needles, m. p. 114—115°, $[\alpha]_D^{20°}$ + 175·0° (l = 1, c = 0·8 in chloroform) (Found: C, 82·2; H, 10·5. $C_{30}H_{46}O_2$ requires C, 82·1; H, 10·6%).

The filtrate obtained after removal of the digitonide was worked up as in the reduction of ergostatrienone, lumisterol being obtained, after two crystallisations from methyl alcohol, in needles, m. p. 116—117°, $[\alpha]_D^{20°}$ + 177·7° (l = 1, c = 1·1 in chloroform), showing the characteristic absorption spectrum of lumisterol; the acetate, prepared in the usual manner, had m. p. 99°, $[\alpha]_D^{20°}$ + 126·9° (l = 1, c = 0·4 in chloroform), and showed no depression in admixture with authentic lumisteryl acetate.

Ergostatetraenone (VII).—Dehydroergosterol was oxidised by the method of Oppenauer (*loc. cit.*). After five crystallisations from acetone *ergostatetraenone* separated in plates, m. p. 140—142°, $[\alpha]_D^{20°}$ + 190·0° (l = 1, c = 3·2 in chloroform) (Found: C, 85·75; H, 10·15. $C_{28}H_{40}O$ requires C, 85·65; H, 10·3%). *Light absorption in alcohol* (Fig. 4): maximum, 2420 A., log ε = 4·50. The *semicarbazone* separated from methyl alcohol–chloroform in needles, m. p. 244° (decomp.) (Found: C, 77·6; H, 9·45; N, 9·0. $C_{29}H_{43}ON_3$ requires C, 77·45; H, 9·65; N, 9·35%).

Reduction of Ergostatetraenone.—The reduction of ergostatetraenone (1·1 g.) was effected by the method employed for ergostatrienone. After one crystallisation from dioxan–water the dehydroergosterol–*epi*dehydroergosterol complex crystallised in plates (0·8 g.), m. p. indefinite about 145°. *Light absorption in alcohol* (Fig. 4): maxima, (a) 3200 A., log ε = 3·94; (b) 3400 A. Treatment of the complex with excess of digitonin in 90% alcohol gave dehydroergosterol digitonide (1·7 g.), which on decomposition with pyridine gave dehydroergosterol (0·35 g.); this separated from methyl alcohol in plates, m. p. 146°, $[\alpha]_D^{20°}$ + 148·3° (l = 1, c = 0·7 in chloroform). *Light absorption in alcohol:* maxima, (a) 3250 A., log ε = 4·045; (b) 3400 A.

Ergostatrienone Enol-acetate (VIII).—A solution of ergostatrienone (4 g.) in pyridine (10 c.c.) and acetic anhydride (10 c.c.) was heated under reflux for 3 hours. The solid separating on cooling was recrystallised from ethyl acetate–methyl alcohol (1 : 1), from which *ergostatrienone enol-acetate* separated in colourless plates (3·45 g.), m. p. 146°, $[\alpha]_D^{20°}$ − 143·5° (l = 1, c = 1·4 in chloroform) (Found: C, 82·8; H, 10·3. $C_{30}H_{44}O_2$ requires C, 82·6; H, 10·1%). *Light absorption in alcohol* (Fig. 1): maxima, (a) 3010 A.; (b) 3165 A., log ε = 4·33; (c) 3310 A.

iso*Ergostatrienone* (IX).—Ergostatrienone enol-acetate (0·5 g.) was heated under reflux for 3 hours with a solution of potassium hydroxide (0·5 g.) in methyl alcohol (20 c.c.). The solid obtained by precipitation with water was recrystallised twice from methyl alcohol; *iso*ergostatrienone was thus obtained in colourless needles (0·4 g.), m. p. 108° alone and on admixture with a specimen prepared by the method of Wetter and Dimroth (*loc. cit.*), $[\alpha]_D^{20°}$ − 30·0° (l = 1, c = 1·2 in chloroform) (Found: C, 85·0; H, 10·8. Calc. for $C_{28}H_{42}O$: C, 85·3; H, 10·7%). *Light absorption in alcohol:* maxima, (a) 2800 A., log ε = 4·52; (b) 3350 A. The semicarbazone

separated from methyl alcohol–chloroform in needles, m. p. 245—246° (decomp.) (Found: N, 9·45. Calc. for $C_{29}H_{45}ON_3$: N, 9·3%). *Light absorption in alcohol:* maximum, 3035 A., log $\varepsilon = 4{\cdot}67$.

iso*Ergostatrienone Enol-acetate* (X).—*iso*Ergostatrienone (0·5 g.) in acetic anhydride (4 c.c.) and acetyl chloride (4 c.c.) was heated under reflux for 6 hours, the excess of acetyl chloride removed, and the solution allowed to cool. Recrystallisation of the separated solid from ethyl alcohol gave iso*ergostatrienone enol-acetate* in colourless needles (0·35 g.), m. p. 137°, $[\alpha]_D^{20°} - 84{\cdot}6°$ ($l = 1$, $c = 0{\cdot}63$ in chloroform) (Found: C, 82·5; H, 9·8. $C_{30}H_{44}O_2$ requires C, 82·9; H, 10·1%). *Light absorption in alcohol* (Fig. 1): maximum, 3040 A., log $\varepsilon = 4{\cdot}22$.

Ergostatetraenone Enol-acetate (XI).—Ergostatetraenone (0·5 g.) was acetylated by the method employed for the preparation of the enol-acetate of ergostatrienone. *Ergostatetraenone enol-acetate* separated from ethyl acetate–methyl alcohol in flat needles (0·45 g.), m. p. 161°, $[\alpha]_D^{20°} - 232{\cdot}5°$ ($l = 1$, $c = 1{\cdot}2$ in chloroform) (Found: C, 82·8; H, 9·5. $C_{30}H_{42}O_2$ requires C, 82·95; H, 9·7%). *Light absorption in alcohol* (Fig. 1): maxima, (a) 3390 A.; (b) 3560 A., log $\varepsilon = 4{\cdot}24$; (c) 3750 A.

Lumistatrienone Enol-acetate (VIII).—Lumistatrienone (5·4 g.) was acetylated by the method employed for the preparation of the enol-acetate of ergostatrienone. *Lumistatrienone enol-acetate* separated from ethyl acetate–methyl alcohol in colourless needles (4·3 g.), m. p. 98°, $[\alpha]_D^{20°} + 293{\cdot}7°$ ($l = 1$, $c = 1{\cdot}2$ in chloroform) (Found: C, 82·4; H, 9·8. $C_{30}H_{44}O_2$ requires C, 82·6; H, 10·1%). *Light absorption in alcohol* (Fig. 1): maximum, 3150 A., log $\varepsilon = 4{\cdot}28$.

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