563. *Steroids of Unnatural Configuration. Part III.*[1] *Dihydro- and Tetrahydro-derivatives of Lumisterol.*

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The structures of three partial reduction products of lumisterol have been elucidated. Lumistenol, formed (as acetate) in hydrogenation of lumisteryl acetate (I; R = Ac), is the *cis*-A/B-Δ^7-tetrahydro-compound (IX; R = H). Reduction of lumisterol with sodium or lithium and ethanol in liquid ammonia affords 5,6-dihydrolumisterol (II; R = H), which on acetylation and partial hydrogenation is converted into the acetate of tetrahydrolumisterol, the *trans*-A/B-tetrahydro-compound (V; R = H).

The corresponding 3α-alcohols (XI, IV, and VII; R = H) were prepared in order to examine the conformations of this group of compounds.

During investigations into the stereochemistry of the hexahydro-derivatives of lumisterol [1] three partially reduced compounds were encountered. Of these, two were previously known [dihydrolumisterol [2] was prepared by reduction of lumisterol with sodium–alcohol, and lumistenol [3] (as acetate) by catalytic hydrogenation of lumisteryl acetate], but neither of them had been examined in detail. The main results of the present study of these compounds are summarised in the accompanying chart, which shows the trivial names used, the structures established for the partial reduction products, and their relations to the hexahydro-derivatives.

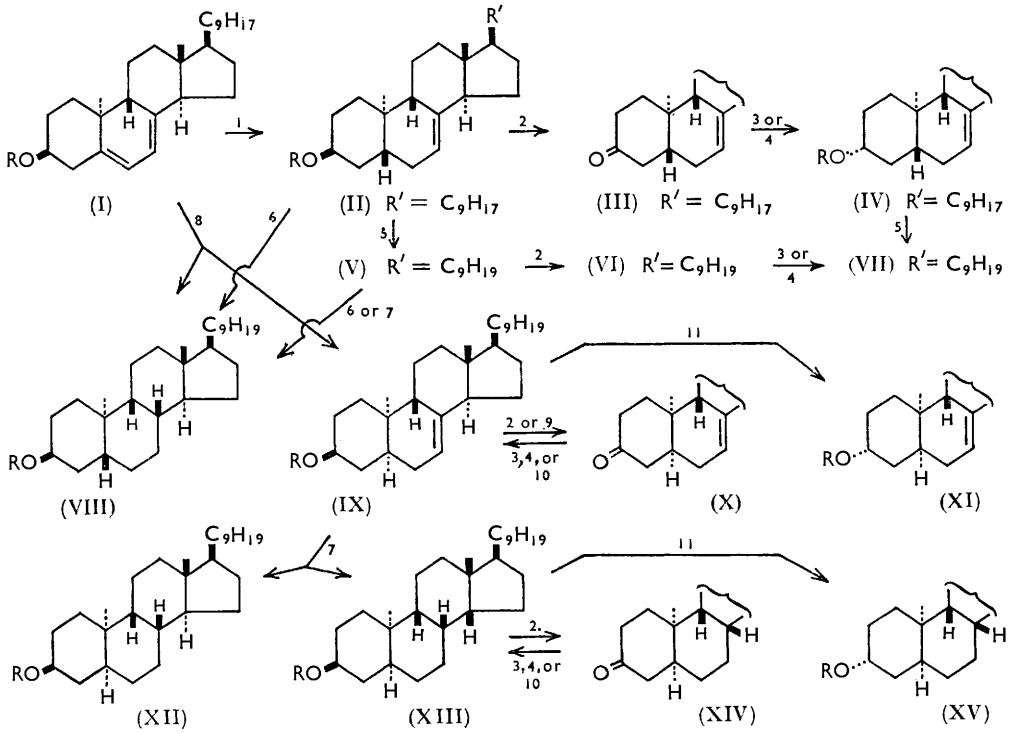
Catalytic hydrogenation of lumisteryl acetate (I; R = Ac) under a variety of conditions gave a mixture of 5β-lumistan-3β-yl (VIII; R = Ac) and lumistenyl acetate (IX; R = Ac) which was extremely difficult to resolve. Lumistenyl acetate was best obtained by partially reducing lumisteryl acetate as a saturated solution in acetic acid, the lumistenyl acetate formed being precipitated from solution (53% yield). Further hydrogenation of lumistenyl acetate afforded 5α,8β-lumistan-3β-yl acetate (XII; R = Ac) together with some 5α,14β-lumistan-3β-yl acetate (XIII; R = Ac).

Preparation of dihydrolumisterol (II; R = H) by reduction of lumisterol (I; R = H) with sodium and alcohol was unsatisfactory, more than five applications of the reducing agent being required to afford a product containing less than 10% of starting material. In liquid ammonia solution reduction was much quicker and the product consisted of dihydrolumisterol (II; R = H) and a small amount (~10%) of the 3α-epimer (IV; R = H). Partial hydrogenation of dihydrolumisteryl acetate (II; R = Ac) in ethyl acetate afforded a new compound, tetrahydrolumisterol [as acetate (V; R = Ac)]: complete hydrogenation of dihydrolumisterol and tetrahydrolumisteryl acetate gave 5β,8β-lumistan-3β-ol (VIII; R = H) and its acetate respectively.[1]

Structures (II), (V), and (IX) for the partial reduction products were established as follows. In dihydrolumisterol and tetrahydrolumisterol the degree of unsaturation was shown by their positions in the sequence between lumisterol and 5β-lumistan-3β-ol: the presence of only one double bond in lumistenol was confirmed by titration of the benzyl ether (IX; R = CH_2Ph) with perbenzoic acid. The infrared spectra of dihydrolumisterol and its derivatives [(II) and (IV), R = H and Ac; and (III)] closely resembled those of the tetrahydrolumisterol compounds [(V) and (VII), R = H and Ac; and (VI)] except that each compound of the first group showed a strong absorption near 970 cm.$^{-1}$ (1,2-di-substituted *trans*-olefinic bond) which was absent in the spectra of the corresponding tetrahydro-compounds. Thus conversion of dihydro- into tetrahydro-lumisterol involves saturation of the 22,23-bond. All these compounds and those derived from lumistenol

[1] Part II, Castells, Fletcher, Jones, Meakins, and Swindells, *J.*, 1960, 2627.
[2] Windaus, Dithmar, and Fernholz, *Annalen*, 1932, **493**, 259; Ahrens, Fernholz, and Stoll, *ibid.*, 1933, **500**, 109.
[3] Heilbron, Moffet, and Spring, *J.*, 1937, 411.

[(IX) and (XI), R = H and Ac; and (X)] had bands near 820 cm.$^{-1}$ indicative of a trisubstituted olefinic grouping. (The presence of such a grouping in lumistenol and tetrahydrolumisterol was confirmed by applying the osmium tetroxide–lead tetra-acetate sequence.[4]) This unsaturation was shown to be at the 7,8- rather than the 5,6-position by the properties of the derived 3-oxo-compounds [(III), (VI), and (X)] which neither exhibited the light absorption characteristic of conjugated ketones nor isomerised on treatment with alkali. (Recently it has been found possible to distinguish between Δ^5- and Δ^7-steroids by their ultraviolet absorption between 1900 and 2300 Å: tetrahydrolumisterol shows the exceptionally broad band characteristic of Δ^7-steroids.[5])



(I; R = H) Lumisterol.
(II; R = H) Dihydrolumisterol (5β-lumista-7,22-dien-3β-ol).
(V; R = H) Tetrahydrolumisterol (5β-lumist-7-en-3β-ol).
(VIII; R = H) 5β-Lumistan-3β-ol.
(IX; R = H) Lumistenol (5α-lumist-7-en-3β-ol).
(XIII; R = H) 5α,14β-Lumistan-3β-ol.
(XII; R = H) Lumistan-3β-ol.

Reagents: 1, Na or Li–NH_3–EtOH. 2, CrO_3 in $COMe_2$. 3, $LiAlH_4$. 4, Na–Pr^iOH. 5, H_2–Pt in EtOAc. 6, H_2–Pt in EtOAc + little $HClO_4$. 7, H_2–Pt in AcOH. 8, H_2–Pt in AcOH + little $HClO_4$. 9, $COMe_2$–$Al(O{\cdot}CMe_3)_3$. 10, Pr^iOH–$Al(O{\cdot}CHMe_2)_3$. 11, Toluene-*p*-sulphonate + KOH–Al_2O_3.

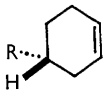
The remaining features, the 5β-configuration in dihydro- and tetra-hydrolumisterol and the 5α-configuration in lumistenol, follow from the further reduction of these compounds to lumistanols of established stereochemistry. Consideration of molecular-rotation values leads to the same conclusions, comparison between the partial reduction products being based on Mills's generalisation [6] that, in cyclohexenes with asymmetry at the β-position, compounds of type (A) (cf. Table 1) have more positive rotations than their enantiomers (B). The validity of this relation with Δ^7-steroids is demonstrated by the data for the three pairs of 10β-methyl-steroids of established constitution shown in the upper part of Table 1. With these compounds and with the six pairs of lumisterol derivatives shown in the lower part of the Table the ΔM_D (5β — 5α) values are positive

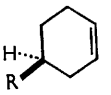
[4] Castells and Meakins, *Chem. and Ind.*, 1956, 248.
[5] Ellington and Meakins, *J.*, 1960, 697.
[6] Mills, *J.*, 1952, 4976.

and of the order of 200 units, thus confirming the nature of the orientations at position 5.

Conformational analysis revealed an interesting difference between the two types of reduction product. In compounds with the *trans*-A/B-ring fusion (*i.e.*, dihydro- and tetra-hydrolumisterol and their derivatives) only one all-chair form is possible (see diagram in Table 2). In this relatively rigid form 3β- and 3α-substituents are respectively axial and equatorial in conformation. However, more flexible *cis*-A/B-fused compounds (lumistenol and its derivatives) can adopt two all-chair arrangements, forms (*x*) and (*y*) in the diagram, which are interconvertible by rotational movements in rings A and B. [The presence of a 7,8-double bond removes the constraint on flexibility which normally occurs when the *cis*-fused system is incorporated into a steroid nucleus.[7] *cis*-A/B-Δ⁷-Steroids are thus comparable with *cis*-decalin (two all-chair forms) rather than with a saturated steroid such as coprostanone (one all-chair form).] A 3β-substituent is

TABLE 1. *Molecular rotations of* 5β- *and* 5α-Δ⁷-*steroids.*

Type (A)  5β-Compounds

Type (B)  5α-Compounds

	$[M]_D$		$[M]_D$	ΔM_D (5β − 5α)
		10β-Methyl steroids		
5β-Ergosta-7,22-dien-3α-ol [a]	+171°	Ergosta-7,22-dien-3α-ol [b]	−18°	+189°
3β-Hydroxypregn-7-en-20-one [c]	+366	3β-Hydroxyallopregn-7-en-20-one [d]	+128	+238
22a-Spirost-7-en-3β-ol [c]	−112	22a-Allospirost-7-en-3β-ol [e]	−313	+201
		10α-Methyl steroids		
5β-Lumist-7-en-3β-ol (V; R = H)	+198	5α-Lumist-7-en-3β-ol (IX; R = H)	−24	+222
3β-Acetoxy-5β-lumist-7-ene (V; R = Ac)	+128	3β-Acetoxy-5α-lumist-7-ene (IX; R = Ac)	−141	+269
5β-Lumist-7-en-3β-yl 3,5-dinitrobenzoate	+15	5α-Lumist-7-en-3β-yl 3,5-dinitrobenzoate	−220	+235
5β-Lumist-7-en-3-one (VI)	+147	5α-Lumist-7-en-3-one (X)	−20	+167
5β-Lumist-7-en-3α-ol (VII; R = H)	+250	5α-Lumist-7-en-3α-ol (XI; R = H)	−58	+308
3α-Acetoxy-5β-lumist-7-ene (VII; R = Ac)	+239	3α-Acetoxy-5α-lumist-7-ene (XI; R = Ac)	−53	+292

[a] Barton and Miller, *J.*, 1952, 4967. [b] Windaus, Dithmar, Murke, and Suckfüll, *Annalen*, 1931, **488**, 91. [c] Deduced from 3α-OH-compound (Velasco, Rivera, Rosenkranz, Sondheimer, and Djerassi, *J. Org. Chem.*, 1953, **18**, 92) by applying the standard correction (Barton and Klyne, *Chem. and Ind.*, 1948, 755). [d] Djerassi, Romo, and Rosenkranz, *J. Org. Chem.*, 1951, **16**, 754. [e] Rosenkranz, Romo, Batres, and Djerassi, *ibid.*, 1951, **16**, 298.

equatorial in form (*x*) but axial in form (*y*): a 3α-substituent occupies the converse positions.

To investigate this difference more fully it was necessary to prepare the 3α-alcohols in the two series. The 3α-hydroxy-5β-compounds [(IV) and (VII); R = H)] were easily obtained *via* the 3-oxo-derivatives [(III) and (VI)] which were reduced with sodium–propan-2-ol, all stages giving good yields. With the 5α-compound, lumistenol (IX; R = H), oxidation with chromic acid or by the Oppenauer method gave material which required purification through the semicarbazone before lumistenone (X) (30% yield) could be obtained. Reduction by lithium aluminium hydride or sodium–propan-2-ol or by the Meerwein–Ponndorf method converted lumistenone into lumistenol (IX; R = H) in high yield. Similar results had previously been obtained in attempts to prepare 5α,14β-lumistan-3α-ol (XV; R = H) from the corresponding 3-ketone (XIV), only the 3β-alcohol (XIII; R = H) being formed by the usual chemical reducing agents. After a general investigation of methods for converting 3β(equatorial)-alcohols into the 3α-epimers [8] it was

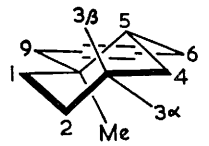
[7] Dreiding, *Chem. and Ind.*, 1954, 1419.
[8] Douglas, Ellington, Meakins, and Swindells, *J.*, 1959, 1720.

found that the 3α-alcohols [(XI) and (XV); R = H] could be prepared by treating the 3β-toluene-*p*-sulphonates [(IX) and (XIII); R = *p*-$C_6H_4Me{\cdot}SO_2$] with alumina which had been previously impregnated with potassium hydroxide and dried at 250°. [The expectation that this method would not be satisfactory for obtaining equatorial alcohols was verified by the decomposition of the axial toluene-*p*-sulphonyl ester (II; R = *p*-$C_6H_4Me{\cdot}SO_2$) which gave largely olefinic material and only 10% of the 3α-alcohol (IV; R = H).]

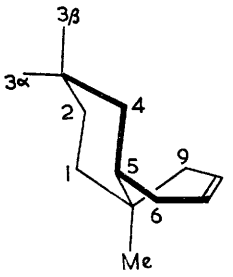
Infrared data for the partial reduction products and their 3α-epimers are shown in Table 2. With the *trans*-A/B-compounds derived from dihydro- and tetrahydro-lumisterol the spectral properties support the 3β-axial and 3α-equatorial conformations indicated by the preparative work. Inverse relations (3β-equatorial and 3α-axial) are suggested for the *cis*-A/B-compounds, lumistenol and its derivatives, by the form of the 1240 cm.$^{-1}$ bands

TABLE 2. *Conformations and infrared absorption of* 5β- *and* 5α-Δ^7-*compounds.*

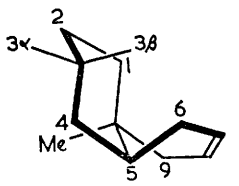
trans-A/B system



cis-A/B system



form (*x*)



form (*y*)

Parent compound	C–O stretching (cm.$^{-1}$) [a] 3β-Alcohol	3α-Alcohol	1240 cm.$^{-1}$ Acetate band [b] 3β-Acetate	3α-Acetate	Conformation 3β-Group	3α-Group
Dihydrolumisterol	(II; R = H) 1019	(IV; R = H) 1043	(II; R = Ac) complex	(IV; R = Ac) simple	Axial	Equat.
Tetrahydrolumisterol	(V; R = H) 1017	(VII; R = H) 1044	(V; R = Ac) complex	(VII; R = Ac) simple	Axial	Equat.
Lumistenol	(IX; R = H) 1037	(XI; R = H) 1035	(IX; R = Ac) simple	(XI; R = Ac) complex	Equat.	Axial

[a] Cole, R. N. Jones, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 5571. [b] R. N. Jones, Humphries, Herling, and Dobriner, *ibid.*, 1951, **73**, 3215.

in the acetates [(IX) and (XI); R = Ac]. While the C–O stretching frequency (1037 cm.$^{-1}$) of the 3β-alcohol (IX; R = H) is reasonable for an equatorial conformation, the value (1035 cm.$^{-1}$) of the 3α-epimer (XI; R = H) is unusually high for the axial type. However, coprostan-3β- and -3α-ol behave similarly (bands at 1038 and 1035 cm.$^{-1}$ respectively [9]) and other examples of epimeric 3-alcohols with *cis*-A/B-rings giving very close C–O frequencies have been encountered.[10] These results, combined with the chemical evidence, suggest that both 3β- and 3α-*cis*-A/B-compounds adopt form (*x*), and that this form even with a 3α-axial substituent is more stable than the alternative form (*y*) with a 3α-equatorial group. The situation is to be contrasted with that found in neoergosterol where the 3-epimers are thought to take up different conformations such that the 3β- and the 3α-hydroxyl group are both equatorial.[11]

EXPERIMENTAL

For general directions see *J.*, 1958, 2156. Acetates and 3,5-dinitrobenzoates are described in the sections headed by the name of the parent alcohol.

5α-Lumist-7-en-3β-ol (*Lumistenol*) (IX; R = H).—A saturated solution of lumisteryl acetate (20 g.) in glacial acetic acid (375 c.c.) and perchloric acid [3 c.c. of a solution made from

[9] Cole, R. N. Jones, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 5571.
[10] Unpublished work in this series.
[11] Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21.

60% aqueous perchloric acid (10 c.c.) and ethyl acetate (900 c.c.)] was shaken in hydrogen with freshly prepared Adams catalyst (1·2 g.). When *ca.* 2·1 mol. of hydrogen had been absorbed (30—90 min. depending on the catalyst's activity) the insoluble material was collected, washed with N-sodium hydrogen carbonate solution (100 c.c.), and dissolved in ether. Evaporation of the filtered solution and crystallisation of the residue from ethyl acetate gave 5α-lumist-7-en-3β-yl acetate (IX; R = Ac) (9·36 g.) as plates, m. p. 176—178°, $[\alpha]_D$ −32° (*c* 0·8) (Found: C, 81·45; H, 11·2. Calc. for $C_{30}H_{50}O_2$: C, 81·4; H, 11·4%), $\nu_{max.}$ 1736 and 1236 (simple band) (acetate), 1673 and 825 (Δ^7-bond) cm.$^{-1}$. (Heilbron *et al.*[3] record m. p. 178—179°, $[\alpha]_D$ −33·1°.) The material precipitated by mixing the acetic acid filtrate and the carbonate washings obtained above was collected, dried, and crystallised, to give 5α-lumist-7-en-3β-yl acetate (1·05 g.), m. p. 174—177°, $[\alpha]_D$ −29° (*c* 1·0).

Saponification of the acetate with 5% ethanolic potassium hydroxide and treatment of the product with 3,5-dinitrobenzoyl chloride–pyridine at 20° afforded *5α-lumist-7-en-3β-yl 3,5-dinitrobenzoate* which crystallised from ethyl acetate–ethanol as plates, m. p. 198—199°, $[\alpha]_D$ −37° (*c* 1·3) (Found: C, 70·5; H, 8·25; N, 4·75. $C_{35}H_{50}O_6N_2$ requires C, 70·7; H, 8·5; N, 4·7%). Hydrolysis of this ester on alkaline alumina [12] yielded 5α-lumist-7-en-3β-ol (IX; R = H), double m. p. 115—118° and 124—126° after crystallisation from methanol, $[\alpha]_D$ −6° (*c* 1·2) (Found: C, 84·1; H, 12·2. Calc. for $C_{28}H_{48}O$: C, 83·9; H, 12·1%), $\nu_{max.}$ 3628 and 1037 (OH) 1673 and 822 (Δ^7-bond) cm.$^{-1}$. Heilbron *et al.*[3] record m. p. 114—116°, $[\alpha]_D$ −0·5°.

3β-Benzyloxy-5α-lumist-7-ene (IX; R = CH_2Ph).—A solution of 5α-lumist-7-en-3β-ol (400 mg.) and benzyl chloride (2 c.c.) in dioxan (10 c.c.) was heated with powdered potassium hydroxide (4 g.) at 100° for 1 hr. After filtration and evaporation at 15 mm. the residue was extracted with light petroleum. The solution so obtained was washed with water and filtered through anhydrous sodium sulphate on to alumina (50 g.; Grade 0). Elution with light petroleum–benzene (4 : 1, 150 c.c.) afforded the *benzyl ether* (400 mg.), m. p. 109—111° (from methanol), $[\alpha]_D$ −20° (*c* 0·8) (Found: C, 85·9; H, 11·1. $C_{35}H_{54}O$ requires C, 85·65; H, 11·1%).

5β-Lumista-7,22-dien-3β-ol (Dihydrolumisterol) (II; R = H).—Sodium (1 g.) was added to a stirred solution of lumisterol (1 g.) in ether (50 c.c.) and liquid ammonia (60 c.c.). After 30 min. ethanol (~10 c.c.) was added slowly until the blue colour disappeared. The ammonia was allowed to evaporate, water was added, and the material isolated with ether (containing 10% of chloroform) was chromatographed on deactivated alumina (70 g.). Elution with light petroleum–benzene (3 : 1; 400 c.c.) afforded 5β-lumista-7,22-dien-3β-ol (0·85 g.), m. p. 141—144° (needles from methanol). Further elution with light petroleum–benzene (1 : 1; 250 c.c.) gave 5β-lumista-7,22-dien-3α-ol (IV; R = H) (see below) (0·1 g.), m. p. 134—138°.

In preparative work lithium (10 g.) and then absolute ethanol were added to lumisterol (40 g.) dissolved in dry ether (1500 c.c.) and liquid ammonia (1500 c.c.). Crystallisation of the product from chloroform–methanol (without chromatography) yielded 5β-lumista-7,22-dien-3β-ol (II; R = H) (35 g.), m. p. 140—144°. A part of this material was purified through the 3,5-dinitrobenzoate (see below), and then had m. p. 141—143°, $[\alpha]_D$ +33° (*c* 1·2) (Found: C, 84·4; H, 11·6. Calc. for $C_{28}H_{46}O$: C, 84·35; H, 11·6%), $\nu_{max.}$ 3620 and 1019 (OH), 1667 and 820 (Δ^7-bond), and 970 (Δ^{22}-bond) cm.$^{-1}$. Windaus *et al.*[2] give m. p. 138—139°, $[\alpha]_D$ +50·4°.

The acetate (II; R = Ac), prepared from the 3β-alcohol with acetic anhydride–pyridine at 20°, crystallised from ethanol as needles, m. p. 141—142°, $[\alpha]_D$ +22° (*c* 1·3) (Found: C, 81·5; H, 10·9. Calc. for $C_{30}H_{48}O_2$: C, 81·8; H, 11·0%), $\nu_{max.}$ 1737, 1254, and 1240 (complex band) (OAc), 1667, 970, and 823 cm.$^{-1}$ (Windaus *et al.*[2] record m. p. 142°, $[\alpha]$ +25·2°). The *3,5-dinitrobenzoate* had m. p. 166·5—167·5° (from ethyl acetate–ethanol), $[\alpha]_D$ +3° (*c* 1·1) (Found: C, 70·95; H, 8·3; N, 4·45. $C_{35}H_{48}O_6N_2$ requires C, 70·9; H, 8·2; N, 4·7%).

5β-Lumist-7-en-3β-ol (Tetrahydrolumisterol) (V; R = H).—A solution of 5β-lumista-7,22-dien-3α-yl acetate (10 g.) in ethyl acetate (300 c.c.) was shaken in hydrogen with Adams catalyst (1 g.). When *ca.* 1·1 mol. of hydrogen had been absorbed (~ 40 min.) the solution was filtered and concentrated to a small volume, whereupon 5β-lumist-7-en-3β-yl acetate (V; R = Ac) (8 g.) crystallised as needles, m. p. 108—111°. Part of this material was saponified with 5% ethanolic potassium hydroxide and the product treated with 3,5-dinitrobenzoyl chloride–pyridine at 20°. The *3,5-dinitrobenzoate* so obtained had m. p. 157·5—159° after crystallisation from ethyl acetate–alcohol, $[\alpha]_D$ +2·5° (*c* 1·8) (Found: C, 70·95; H, 8·6; N, 4·6. $C_{35}H_{50}O_6N_2$ requires C, 70·7; H, 8·5; N, 4·7%), and on hydrolysis [12] afforded *5β-lumist-7-en-3β-ol* (V; R = H), m. p. 128—131° (from ethanol), $[\alpha]_D$ +49·5° (*c* 1·9) (Found: C, 83·9; H, 12·0. $C_{28}H_{48}O$

[12] Castells and Fletcher, *J.*, 1956, 3245.

requires C, 83·9; H, 12·1%), $\nu_{max.}$ 3606 and 1017 (OH), 1663 and 820 (Δ^7-bond) cm.$^{-1}$. Acetylation with acetic anhydride–pyridine at 20° gave 5β-*lumist*-7-*ene*-3β-*yl acetate* (V; R = Ac), m. p. 111—112·5° (from ethanol), $[\alpha]_D$ +29° (*c* 1·3) (Found: C, 81·2; H, 11·35. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%), $\nu_{max.}$ 1729, 1253, and 1238 (complex band) (OAc), 1668 and 825 cm.$^{-1}$.

5β-*Lumista*-7,22-*dien*-3-*one* (III).—8N-Chromic acid (~1·3 c.c.) was added dropwise to a solution of 5β-lumista-7,22-dien-3β-ol (II; R = H) (2 g.) in acetone (30 c.c.) until the supernatant liquid remained yellow. After 2 min. the mixture was poured into water and extracted with ether. The material so obtained crystallised from methanol, to give the *ketone* (III) (1·2 g.), m. p. 168—172°, $[\alpha]_D$ +34° (*c* 0·5) (Found: C, 85·0; H, 11·4. $C_{28}H_{44}O$ requires C, 84·8; H, 11·2%), $\nu_{max.}$ 1718 (C=O), 975 (Δ^{22}-bond), and 826 (Δ^7-bond) cm.$^{-1}$. The ketone did not show selective ultraviolet absorption in the 2100—2600 Å range, neither did the solution obtained by heating the ketone (10 mg.) with potassium hydroxide (100 mg.) in ethanol (100 mg.).

5β-*Lumista*-7,22-*dien*-3α-*ol* (IV; R = H).—Sodium (5 g.) was added during 3 hr. to a refluxing solution of 5β-lumista-7,22-dien-3-one (500 mg.) in propan-2-ol (100 c.c.). Dilution with water and extraction with ether gave material which was adsorbed on deactivated alumina (40 g.). Light petroleum–benzene (2 : 1; 150 c.c.) eluted 5β-lumista-7,22-dien-3β-ol (II; R = H) (50 mg.), m. p. 139—143°, identified by mixed m. p. and comparison of infrared spectra with authentic material. Light petroleum–benzene (1 : 1; 400 c.c.) eluted the 3α-alcohol (420 mg.), m. p. 131—134°, which was converted into 5β-*lumista*-7,22-*dien*-3α-*yl* 3,5-*dinitrobenzoate*, m. p. 168—169° (from ethyl acetate–ethanol), $[\alpha]_D$ +29° (*c* 1·0) (Found: C, 70·7; H, 8·2; N, 4·8. $C_{35}H_{48}O_6N_2$ requires C, 70·9; H, 8·1; N, 4·7%). Hydrolysis [12] gave 5β-*lumista*-7,22-*dien*-3α-*ol* (IV; R = H), m. p. 135—138° (plates from ethanol), $[\alpha]_D$ +45° (*c* 0·7) (Found: C, 84·7; H, 11·7. $C_{28}H_{46}O$ requires C, 84·45; H, 11·6%), $\nu_{max.}$ 3620 and 1043 (OH), 981 (Δ^{22}-bond), and 825 (Δ^7-bond) cm.$^{-1}$. Acetylation with acetic anhydride–pyridine at 20° yielded 5α-*lumista*-7,22-*dien*-3α-*yl acetate* (IV; R = Ac), m. p. 125—128° (from methanol), $[\alpha]$ +54° (*c* 0·6) (Found: C, 81·9; H, 11·2. $C_{30}H_{48}O_2$ requires C, 81·8; H, 11·0%), $\nu_{max.}$ 1736 and 1243 (simple band) (OAc), 980, and 823 cm.$^{-1}$.

On reduction of 5β-lumista-7,22-dien-3-one (500 mg.) with lithium aluminium hydride the 3β-alcohol (II; R = H) (60 mg.) and the 3α-alcohol (IV; R = H) (410 mg.) were isolated.

5β-*Lumist*-7-*en*-3-*one* (VI).—Oxidation of 5β-lumist-7-en-3β-ol (V; R = H) (1 g.) in acetone (20 c.c.) with 8N-chromic acid (~0·6 c.c.) gave the *ketone* (VI) (0·77 g.), m. p. 161—164° (from methanol), $[\alpha]_D$ +37° (*c* 1·2) (Found: C, 84·65; H, 11·75. $C_{28}H_{46}O$ requires C, 84·35; H, 11·6%), $\nu_{max.}$ 1718 (C=O), 1680 and 825 (Δ^7-bond) cm.$^{-1}$, with no selective ultraviolet absorption between 2100 and 2600 Å before or after treatment with alkali.

5β-*Lumist*-7-*en*-3α-*ol* (VII; R = H).—Reduction of the preceding ketone (500 mg.) with sodium–propan-2-ol as described above, and chromatographic separation of the products, gave 5β-lumist-7-en-3β-ol (V; R = H) [60 mg.; m. p. 128—131°, eluted with light petroleum–benzene (2 : 1)] and 5β-*lumist*-7-*en*-3α-*ol* (VII; R = H) [405 mg.; eluted with light petroleum–benzene (1 : 1)], m. p. 139—142° (from methanol), $[\alpha]_D$ +63° (*c* 1·1) (Found: C, 84·2; H, 12·1. $C_{28}H_{48}O$ requires C, 84·0; H, 12·0%), $\nu_{max.}$ 3610 and 1045 (OH), and 829 (Δ^7-bond) cm.$^{-1}$.

With lithium aluminium hydride the ketone (500 mg.) gave the 3β-alcohol (V; R = H) (95 mg.) and the 3α-alcohol (VII; R = H) (390 mg.).

5β-Lumist-7-en-3α-yl acetate (VII; R = Ac) was obtained by treating the 3α-alcohol (VII; R = H) with acetic anhydride–pyridine at 20°, and also by hydrogenating 5β-lumista-7,22-dien-3α-yl acetate (IV; R = Ac) (0·2 g.) in ethyl acetate (10 c.c.) in the presence of Adams catalyst (0·1 g.). After crystallisation from acetone–methanol this *acetate* (VII; R = Ac) had m. p. 117—119°, $[\alpha]_D$ +54° (*c* 0·8) (Found: C, 81·7; H, 11·6. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%), $\nu_{max.}$ 1734 and 1243 (simple band) (OAc), and 826 (Δ^7-bond) cm.$^{-1}$.

5α-*Lumist*-7-*en*-3-*one* (X).—5α-Lumist-7-en-3β-ol (IX; R = H) (1 g.) in acetone (20 c.c.) was oxidised with 8N-chromic acid in the usual way. After two crystallisations from acetone–methanol the product (0·7 g.), m. p. 125—140°, was chromatographed on alumina (70 g.; Grade 0). Light petroleum–benzene (1 : 1; 250 c.c.) eluted impure 5α-lumist-7-en-3-one (0·6 g.) with m. p. 127—141°, not appreciably changed by repeated crystallisation.

A similar product (0·6 g.; m. p. 123—139°) was obtained by refluxing 5α-lumist-7-en-3β-ol (0·8 g.) and aluminium t-butoxide (2·5 g.) in dry benzene–acetone (2 : 1; 65 c.c.) for 20 hr., diluting the mixture with water, and extracting it with ether.

Samples (3 g.) of impure 5β-lumist-7-en-3-one prepared by the two methods yielded the

same semicarbazone (1·6 g.; m. p. 205—210° after three crystallisations from ethanol). A suspension of the derivative (1·6 g.) in ether (100 c.c.) and 2N-hydrochloric acid (100 c.c.) was shaken until no insoluble material remained. The product (0·9 g.) obtained from the ether layer crystallised from acetone–methanol to give 5α-*lumist*-7-*en*-3-*one*, m. p. 139—143°, $[\alpha]$ −5° (*c* 0·9) (Found: C, 84·25; H, 11·3. $C_{28}H_{46}O$ requires C, 84·4; H, 11·55%), $\nu_{max.}$ 1714 (C=O) and 825 (Δ^7-bond) cm.$^{-1}$, there being no selective ultraviolet absorption between 2100 and 2600 Å before or after treatment with alkali.

Reduction of 5α-*Lumist*-7-*en*-3-*one* (X).—(a) *With sodium in propan*-2-*ol.* Sodium (10 g.) was added during 3 hr. to a refluxing solution of the ketone (1·0 g.) in propan-2-ol (150 c.c.). The product obtained by dilution with water and extraction with ether was adsorbed on deactivated alumina (70 g.). Elution with light petroleum–benzene (3 : 1; 400 c.c.) gave material (0·95 g.) which was dissolved in pyridine and treated with 3,5-dinitrobenzoyl chloride. The product so obtained crystallised from ethyl acetate–ethanol, to give 5α-lumist-7-en-3β-yl 3,5-dinitrobenzoate (1·4 g.), m. p. and mixed m. p. 196—199°, $[\alpha]_D$ −36° (*c* 0·8). Saponification on alkaline alumina [12] gave the alcohol (IX; R = H), m. p. 121—126° (without crystallisation), identified by its infrared spectrum.

(b) *With lithium aluminium hydride.* Reduction of 5α-lumist-7-en-3-one (500 mg.) with an excess of lithium aluminium hydride followed by the procedure described above gave 5α-lumist-7-en-3β-yl 3,5-dinitrobenzoate (690 mg.), m. p. 197—199°.

(c) *Meerwein–Ponndorf method.* The ketone (800 mg.) was reduced with aluminium isopropoxide (1·5 g.) in propan-2-ol (60 c.c.) in the usual way, and the product chromatographed on deactivated alumina (60 g.). Elution with light petroleum–benzene (19 : 1; 250 c.c.) gave impure 5α-lumist-7-en-3-one (250 mg.), m. p. 130—141°, identified by its infrared spectrum. Light petroleum–benzene (3 : 1; 400 c.c.) eluted 5α-lumist-7-en-3β-ol (IX; R = H) (500 mg.) which was converted into its 3,5-dinitrobenzoate (710 mg.), m. p. 196—199°.

Reduction of 5α,14β-*Lumistan*-3-*one* (XIV).—Samples (500 mg.) of the ketone [1] were reduced by each of the three methods described under the Δ^7-ketone (X) above. In each case only 5α,14β-lumistan-3β-ol [1] (XIII; R = H) was isolated: the yields of this product after crystallisation were 82, 80, and 81% in methods (a), (b), and (c) respectively.

Epimerisation of Hydroxyl Groups via *Toluene*-p-*sulphonates.*—(a) *With* 5α-*lumista*-7,22-*dien*-3β-*ol* (II; R = H). Treatment of the alcohol (1 mol.) with toluene-*p*-sulphonyl chloride (2 mol.) in an excess of pyridine at 0° for 24 hr. gave the *toluene*-p-*sulphonate* (II; R = *p*-$C_6H_4Me{\cdot}SO_2$), m. p. 131—133° (from ethanol) (Found: C, 76·3; H, 9·3. $C_{35}H_{52}O_3S$ requires C, 76·1; H, 9·4%), $\nu_{max.}$ 1189 and 1180 cm.$^{-1}$. This ester (1 g.) was decomposed on alumina impregnated with potassium hydroxide in the usual way.[8] After 66 hr. elution with benzene (100 c.c.) gave a *compound* (probably 5β-lumista-2,7,22-triene) (0·6 g.), m. p. 111—113° (Found: C, 88·5; H, 11·8. $C_{28}H_{44}$ requires C, 88·4; H, 11·6%). Elution with ether–methanol (20 : 1; 200 c.c.) gave 5β-lumista-7,22-dien-3α-ol (IV; R = H) (0·15 g.), m. p. 134—138°, $[\alpha]_D$ +44° (*c* 0·7), identified by mixed m. p. and comparison of infrared spectra with an authentic sample.

(b) *With* 5α-*lumist*-7-*en*-3β-*ol* (IX; R = H). The alcohol with toluene-*p*-sulphonyl chloride–pyridine at 0° afforded the *toluene*-p-*sulphonate* (IX; R = *p*-$C_6H_4Me{\cdot}SO_2$), m. p. 165—170° (variable) (Found: C, 75·8; H, 9·8. $C_{35}H_{56}O_3S$ requires C, 75·6; H, 10·0%), $\nu_{max.}$ 1191 and 1178 cm.$^{-1}$. After decomposition of the ester (1 g.) on alkaline alumina, elution with benzene gave a *compound* (probably 5α-lumista-2,7-diene) (0·27 g.), m. p. 89—91° after crystallisation from methanol (Found: C, 88·0; H, 11·9. $C_{28}H_{46}$ requires C, 87·9; H, 12·05%). Ether–methanol (50 : 1; 250 c.c.) eluted 5α-lumist-7-en-3α-ol (0·37 g.), m. p. 120—125°. This material was converted into the corresponding 3,5-*dinitrobenzoate*, m. p. 177—179° (plates from ethyl acetate–alcohol), $[\alpha]_D$ −33° (*c* 0·5) (Found: C, 70·4; H, 8·5; N, 4·9. $C_{35}H_{50}O_6N_2$ requires C, 70·7; H, 8·6; N, 4·7%). Hydrolysis of the ester afforded 5α-*lumist*-7-*en*-3α-*ol* (XI; R = H), m. p. 124—125° (from ethanol), $[\alpha]_D$ −14° (*c* 0·5) (Found: C, 83·7; H, 12·1. $C_{28}H_{48}O$ requires C, 84·0; H, 12·0%), $\nu_{max.}$ 3613 and 1035 (OH), and 823 (Δ^7-bond) cm.$^{-1}$. Acetylation with acetic anhydride–pyridine at 20° yielded 5α-*lumist*-7-*en*-3α-*yl acetate* (XI; R = Ac), m. p. 71—74° (needles from methanol), $[\alpha]_D$ −12° (*c* 0·7) (Found: C, 81·6; H, 11·2. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%), $\nu_{max.}$ 1735, 1252, and 1236 (complex band) (OAc), and 820 (Δ^7-bond) cm.$^{-1}$.

In another experiment 5α-*lumist*-7-*en*-3β-*yl* p-*bromobenzenesulphonate* (IX; R = *p*-$C_6H_4Br{\cdot}SO_2$) [1 g.; m. p. 144—148° (Found: C, 66·0; H, 8·1. $C_{34}H_{51}BrO_3S$ requires C, 65·9; H, 8·2%), $\nu_{max.}$ 1188 and 1178 cm.$^{-1}$] was decomposed on alkaline alumina, to give 5α-lumist-7-en-3α-ol (0·31 g.), m. p. and mixed m. p. 121—125°, further identified by its infrared spectrum.

(c) *With* 5α,14β-*lumistan*-3β-*ol* [1] (XIII; R = H). The 3β-toluene-*p*-sulphonate (XIII; R = *p*-$C_6H_4Me{\cdot}SO_2$) (0·7 g.; m. p. 154—158°; $\nu_{max.}$ 1190 and 1180 cm.$^{-1}$; not analysed) was decomposed on a column of alkaline alumina. Olefinic material (0·2 g.) eluted with benzene was discarded. Ether–methanol (50 : 1; 250 c.c.) eluted 5α,14β-*lumistan*-3α-*ol* (XV; R = H) (0·25 g.), m. p. 122—124° (after purification through the 3,5-dinitrobenzoate and crystallisation from methanol), $[\alpha]_D$ +40° (*c* 0·6) (Found: C, 83·3; H, 12·5. $C_{28}H_{50}O$ requires C, 83·6; H, 12·4%), $\nu_{max.}$ 3660 and 1036 (OH) cm.$^{-1}$. The 3,5-*dinitrobenzoate* had m. p. 184—186° (from ethyl acetate–ethanol), [α] +38° (*c* 0·3) (Found: C, 70·5; H, 8·75; N, 4·7. $C_{35}H_{52}O_6N_2$ requires C, 70·4; H, 8·8; N, 4·7%). The *acetate* (XV; R = Ac) was an oil, $[\alpha]_D$ +23° (*c* 1·0) (Found: C, 81·2; H, 11·6. $C_{30}H_{52}O_2$ requires C, 81·1; H, 11·7%), $\nu_{max.}$ 1737, 1254, and 1236 (complex band) (OAc) cm.$^{-1}$.

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