528. *Steroids of Unnatural Configuration. Part II.* Reduction Products of Lumisterol: Hexahydro-compounds.*

By J. Castells, G. A. Fletcher, E. R. H. Jones, G. D. Meakins, and R. Swindells.

Lumisterol (I; R = H) is reduced by sodium in liquid ammonia to a $\Delta^{7,22}$-dihydro-compound (II), hydrogenation of which gives successively a *trans*-A/B-Δ^{7}-tetrahydro-compound and the known fully saturated lumistanol A. Catalytic reduction of lumisterol gives lumistanol A and a *cis*-A/B-Δ^{7}-tetrahydro-compound (III) which can be hydrogenated to a new lumistanol B. A third saturated alcohol (lumistanol C) has been obtained by hydrogenating a $\Delta^{8(14)}$-tetrahydro-compound (IV).

Elucidation of the stereochemistry of these lumistanols has shown that they arise from the Δ^{7}- and $\Delta^{8(14)}$-compounds (III), (IV), and (V) by frontwise (β-face) addition of hydrogen.

Although the reduction products of ergosterol have been studied in detail, only preliminary work on the reduction of lumisterol (I; R = H) [1] is recorded. Three reduction products are known: dihydrolumisterol, obtained by treating lumisterol with sodium and alcohol, afforded a saturated hexahydrolumisterol on catalytic reduction [2] while hydrogenation of lumisteryl acetate produced the acetates of lumistanol (identical with hexahydrolumisterol) and lumistenol (a tetrahydro-compound).[3] Neither the structures nor the stereochemistry of dihydrolumisterol and lumistenol were studied, and only one proposal [4] (shown in the sequel to be incorrect) for the stereochemistry of lumistanol has appeared. In continuing the study of steroids with unnatural stereochemistry we have established the structures of these and several new reduction products. The results together with parallel investigations [5] on 9α-lumisterol (pyrocalciferol) and 9β-ergosterol (isopyrocalciferol) clarify the the course of catalytic and chemical reduction of steroid ring B diene systems.

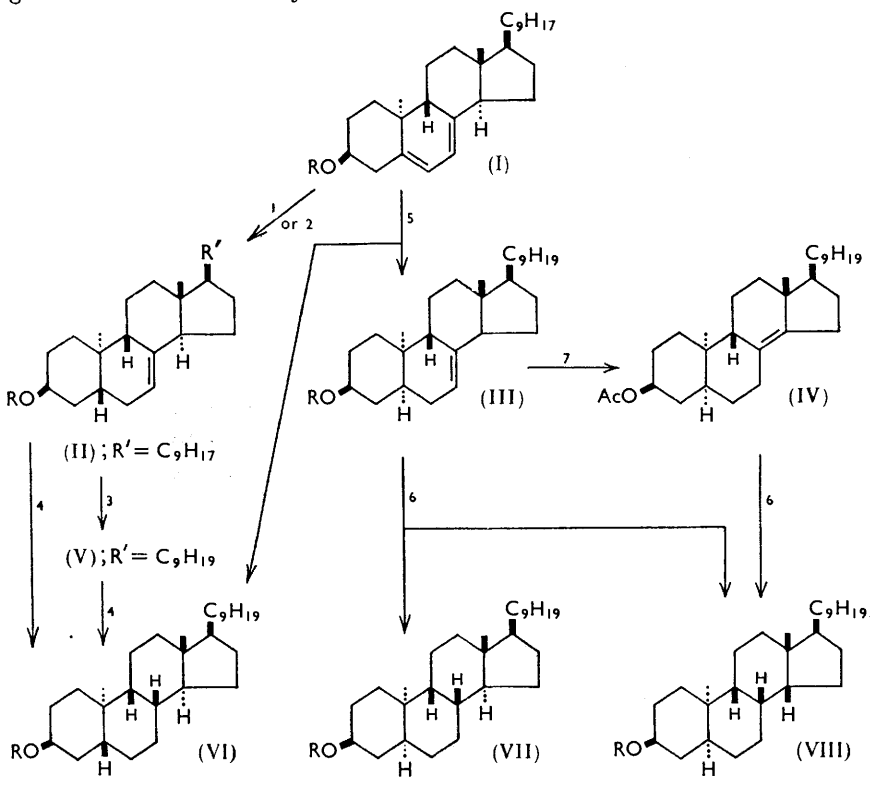
Nomenclature. At the Editor's suggestion systematic nomenclature is based on the name lumistane for the C_{28} hydrocarbon with the skeleton of ergosterol in which (i) the stereochemistry at positions 8, 13, 14, and 17 is as usual in steroids (8β-H, 18β-methyl, 14α-H, 17β-side chain), (ii) the stereochemistry at positions 9 and 10 is the opposite to that usual in steroids (*i.e.*, in lumistane, 19α-methyl and 9β-H), and (iii) the stereochemistry at position 5 must be stated in each individual name as 5α or 5β (as now obligatory in other steroid nomenclature also). Variations from this stereochemistry and the presence of double bonds or substituents are shown in the usual way; thus, lumisterol (I; R = H) is lumista-5,7,22-trien-3β-ol, lumistenol (III; R = H) is 5α-lumist-7-en-3β-ol, and lumistanols A, B, and C have the systematic names shown for formulæ (VI), (VII), and (VIII), respectively. The new trivial names tetrahydrolumisterol and lumistanols B and C are introduced to distinguish these compounds from previously known isomeric reduction products, *viz.*, lumistenol and lumistanol (to the latter of which the letter A is now added).

To simplify discussion and to avoid undue repetition of cumbrous systematic names the structures and trivial names of the reduction products are shown at the outset. The sodium–alcohol reduction of lumisterol (I; R = H) to dihydrolumisterol (II; R = H) was greatly improved by conducting the reaction in liquid ammonia. Reduction of the side chain in dihydrolumisterol was best achieved by hydrogenating the acetate (III; R = Ac) in ethyl acetate–acetic acid. Hydrolysis gave a new compound, tetrahydrolumisterol (V; R = H), the acetate of which was reduced in ethyl acetate containing a

* Part I, *J.*, 1959, 1159.

[1] Castells, Jones, Meakins, and Williams, *J.*, 1959, 1159.
[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.
[4] Cole, *J.*, 1952, 4969.

little perchloric acid to lumistanol A (as acetate, VI; R = Ac). Both double bonds in dihydrolumisterol could be hydrogenated in ethyl acetate containing a little perchloric acid to give lumistanol A directly.



lumistanol A
5β-lumistan-3β-ol

lumistanol B
5α-lumistan-3β-ol

lumistano C
5α,14β-lumistan-3β-ol

Reagents: 1, Na–EtOH. 2, Na or Li–NH_3–EtOH. 3, H_2–Pt in EtOAc. 4, H_2–Pt in EtOAc + little $HClO_4$. 5, H_2–Pt in AcOH + little $HClO_4$. 6, H_2–Pt in AcOH. 7, HBr–AcOH.

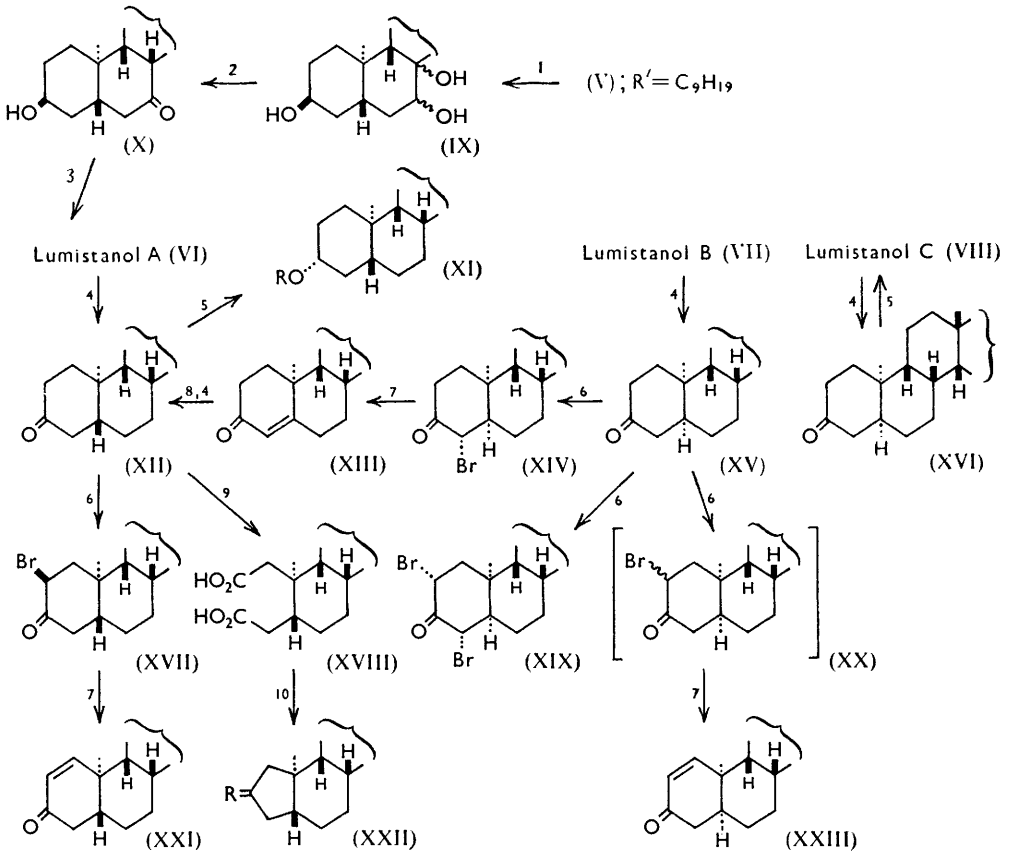
Catalytic reduction of lumisteryl acetate (I; R = Ac) under a variety of conditions gave a mixture of lumistanyl A and lumistenyl acetates (VI and III; R = Ac) which was extremely difficult to separate. Although lumistenyl acetate could be obtained by interrupting the hydrogenation, isolation of lumistanyl A acetate from the product of complete reduction was achieved in only very poor yield. A more effective method was to reduce lumisterol in ethyl acetate containing perchloric acid at increased temperature and pressure, and then to oxidise the mixture of products. This procedure gave lumistanone A (XII) [3] in 60% yield.

Saturation of the Δ^7-bond in lumistenyl acetate (III; R = Ac) was slow, and the product after hydrolysis consisted of two new lumistanols, the major one being lumistanol B (VII; R = H). The minor product, lumistanol C (VIII; R = H), was more conveniently obtained (as acetate) by reducing the $\Delta^{8(14)}$-tetrahydro-compound (IV; R = Ac), itself prepared by acidic isomerisation [5] of lumistenyl acetate (III; R = Ac).

The remainder of this communication deals with the stereochemistry of the lumistanols, proof of the structures shown here for the partial reduction products being deferred.[5] Although the arguments relating to the various centres are interdependent and cannot be entirely separated from each other a convenient starting point is a discussion of the $C_{(8)}$-configuration of lumistanol A.

[5] Forthcoming papers in this series.

Reaction of tetrahydrolumisterol (V; R = H) with osmium tetroxide and dehydration of the resulting triol (IX) with methanolic sulphuric acid [6] afforded a 7-oxo-compound (X). Since the reaction probably proceeds through the (Δ^7) enolic form, the ketone (X) should have the more stable configuration at position 8. Ketone (X) was unaffected by boiling ethanolic potassium hydroxide, and on Wolff–Kishner reduction afforded lumistanol A (VI; R = H).



Reagents: 1, OsO_4. 2, H_2SO_4–MeOH. 3, Wolff-Kishner reduction. 4, CrO_3 in Me_2CO at 20°. 5, Na–ROH. 6, Br_2 in AcOH. 7, Dehydrobromination *via* the 2,4-dinitrophenylhydrazone. 8, Li–NH_3–EtOH. 9, CrO_3 in AcOH at 60°. 10, Pyrolysis of barium salt.

TABLE 1. *Conformations of lumistanols arising from variations at positions* 5 *and* 8.
[*The configurations at other asymmetric centres are as shown in lumisterol* (I; R = H).]

Configuration at C_5	Configuration at C_8	Conformation	3β-Hydroxyl group
α	α	Ring c boat	Equatorial
β	α	Ring c boat	Axial
α	β	All-chair	Equatorial
β	β	All-chair	Axial

In the reduction of lumisterol, asymmetry is created at positions 5 and 8, and four structures are thus possible for lumistanol A. However only two of these (see Table 1), each with an 8β-configuration, allow all-chair forms. The second route to lumistanol A through an intermediate [the ketone (X)] allowing stabilisation at $C_{(8)}$ therefore establishes the β-configuration at this position.

[6] Meakins and Stephenson, *J.*, 1958, 526.

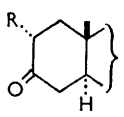
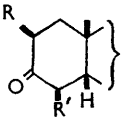
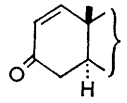
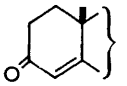
A similar conclusion (8β-configuration) for lumistanol B (VII; R = H) follows from conversion of this stanol into lumistanone A (XII) by a sequence in which only the $C_{(5)}$-centre can be inverted. Thus oxidation of lumistanol B [to (XV)], bromination [to (XIV)], dehydrobromination [to (XIII)], and reduction with lithium in ammonia gave lumistanone A (XII). (The structures of the intermediates are discussed below.) Lumistanols A and B are therefore 8β-compounds, epimeric at position 5.

TABLE 2. *Spectroscopic data for compounds derived from 5β- and 5α-lumistan-3-ones.*

[*Infrared frequencies* (cm.$^{-1}$) *refer to carbon disulphide solutions: ultraviolet maxima* (Å) *of 2,4-dinitrophenylhydrazones* (DNP) *refer to chloroform solutions, and those of conjugated ketones to ethanolic solutions.*]

		Infrared		Ultraviolet			Infrared		Ultraviolet	
	5β-Series	C=O stretching	Olefin CH bending	$\lambda_{max.}$	ε	5α-Series	C=O stretching	Olefin CH bending	$\lambda_{max.}$	ε
Parent ketones	(XII)	1715				(XV)	1714			
	DNP			3670	25,800	DNP			3670	25,200
Bromo-ketone	(XVII)	1732				(XIV)	1735			
Dehydrobromination product	(XXI)	1682	777	2320	8,000	(XIII)	1674	860	2420	18,600
	DNP			3840	30,200	DNP			3940	30,900
Other compounds						(XIX)	1759			
						(XXIII)	1683	770	2320	12,700
						DNP			3860	31,300

*Reference data (for derivatives of cholestanone and coprostanone).**

	Infrared					Infrared			
5α-Series	C=O stretching	Olefin CH bending	Ultraviolet $\lambda_{max.}$	ε	5β-Series	C=O stretching	Olefin CH bending	Ultraviolet $\lambda_{max.}$	ε
									
R = H	1718				R = R′ = H	1716			
R = Br	1733				R = H, R′ = Br	1733			
					R = R′ = Br	1756			
	1684	778	2300	10,700		1674	863	2410	16,600
DNP			3830	28,600	DNP			3920	31,200

* Leading references: R. N. Jones and his co-workers, *J. Amer. Chem. Soc.*, 1955, **77**, 651, and previous papers; Henbest, Meakins, Nicholls, and Wilson, *J.*, 1957, 997; Dorfman, *Chem. Rev.*, 1953, **53**, 47.

Study of the 3-ketones (XII) and (XV) was expected to reveal the $C_{(5)}$-orientations since the direction of enolisation of 3-oxo-steroids is known to depend on the nature of the A/B ring fusion. Monobromination of lumistanone A (XII) gave a single bromo-ketone (XVII) which was dehydrobrominated to a conjugated ketone (XXI) *via* its 2,4-dinitrophenylhydrazone. Although the final ketone (XXI) could not be obtained crystalline the light absorption (see Table 2) of these compounds shows that bromination at $C_{(2)}$ and dehydrobromination to a Δ^1-3-ketone had occurred. (The distinction between Δ^1- and Δ^4-3-ketones and between corresponding derivatives by their ultraviolet absorption is supplemented by the difference between the ketones in the olefinic CH bending region of the infrared spectrum.)

Bromination of lumistanone B (XV) was more complicated. With two mols. of bromine the dibromo-ketone (XIX) was formed in high yield, but one mol. of bromine produced a mixture from which the $C_{(4)}$-monobromo-ketone (XIV) and the dibromo-ketone (XIX) were isolated after chromatography on silica gel. Dehydrobromination of the monobromo-ketone (XIV) afforded a product shown by its light absorption (Table 2) to be a Δ^4-3-ketone (XIII). When the material in the mother liquors from the crystallisation of the monobromo-ketone (XIV) was dehydrobrominated a third conjugated ketone, the Δ^1-3-ketone (XXIII) (light absorption shown in Table 2) was obtained. This presumably arises from the presence of a small amount of a $C_{(2)}$-bromo-ketone (XX) in the original bromination mixture: the alternative, that the Δ^1-3-ketone (XXII) is formed from the $C_{(4)}$-bromo-ketone (XIV) by $C_{(4)} \longrightarrow C_{(2)}$ bromine migration during dehydrobromination, seems unlikely in that the $C_{(4)}$-bromo-ketone gives the dinitrophenylhydrazone of the Δ^4-3-ketone (XIV) in high yield. [The carbonyl stretching frequencies of the bromo-ketones (XIV), (XVII), and (XIX) derived from lumistanones A and B together with the light absorption properties of the dehydrobromination products establish the positions and conformations of the bromine substituents. The configurations of the bromine atoms are, however, dependent upon the $C_{(5)}$-orientations in these compounds.]

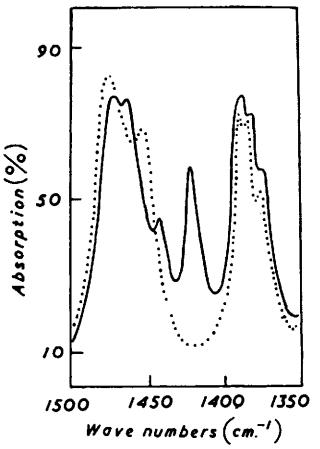


FIG. 1. *Methylene scissoring bands (in carbon tetrachloride) of* ·CH_2·CO· *groups in five-membered rings.*

A-Nor-5β-lumistan-2-one (XXII; R = O), full line.
A-Nor-5β-lumistane (XXII; R = H_2), dotted line.

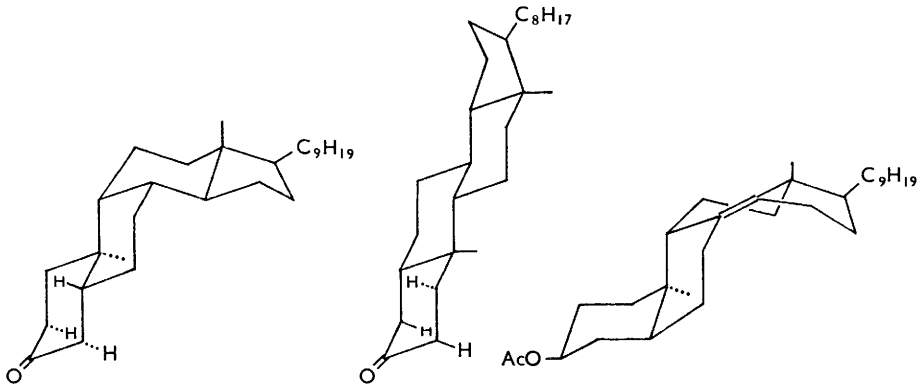
Ketone	Perturbed methylene band, $\nu_{max.}$ (cm.$^{-1}$)	ε (mole.$^{-1}$ l. cm.$^{-1}$) at $\nu_{max.}$ of ketone	ε (mole.$^{-1}$ l. cm.$^{-1}$) at $\nu_{max.}$ of hydrocarbon	Δε ketone–hydrocarbon
A-Nor-5β-lumistan-2-one (XXII; R = O).....	1416	75	11	64
A-Norcholestan-2-one ...	1413	75	10	65
A-Norcoprostan-3-one ...	1413	46	11	35

Enolisation of lumistanone A (XII) towards position 2 was confirmed by showing that oxidative fission produced a 2,3-seco-diacid (XVIII), converted into an A-nor-ketone with a 2-oxo-structure (XXII; R = O). (Enolisation to $C_{(4)}$ would have produced a 3-oxonor-ketone *via* a 3,4-seco-diacid.) Proof of the 2-oxo-structure for the nor-ketone (XXII; R = O) is based on the characteristic infrared absorption near 1410 cm.$^{-1}$ shown by the α-methylene group of a cyclopentanone.[7] From the spectrum of the norlumistanone (see Figure 1) it is clear that the intensity (ε = 75) of the perturbed methylene band at 1416 cm.$^{-1}$ is enhanced by contributions from neighbouring CH bending bands. To allow for this the intensity (ε = 11) of the non-selective absorption in the corresponding hydrocarbon (XXII; R = H_2) was subtracted to give a more correct representation (ε = 64) of the absorption due to perturbed methylene groups. Comparison with the data for authentic A-nor-2- and -3-ketones (Figure 1) establishes the presence of two α-methylene groups in the norlumistanone, which must be (XXII; R = O).

[7] R. N. Jones and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 5648, 5662.

The direction of enolisation of a 3-oxo-steroid is largely determined by two factors,[8-10] the non-bonded interactions that are modified by enolisation and the strain caused by the introduction of a double bond into ring A. With 5β- and 5α-lumistanones the consequences of enolisation closely resemble those occurring with cholestanone and coprostanone, respectively. [See Fig. 2*a* and *b* where 5β-lumistanone is represented so as to show its general relation to cholestanone.] From this the identification of lumistanone A (enolising to the Δ^2-position) as the 5β(*trans*-A/B)-compound and lumistanone B (enolising predominantly to the Δ^3-position) as the 5α(*cis*-A/B)-isomer follows. The optical rotatory dispersion curves of the ketones,[11] kindly determined by Professor C. Djerassi, strongly support these proposals.

FIG. 2.



(*a*) 5β-lumistanone (*b*) cholestanone (*c*) 3β-acetoxylumist-8(14)-ene (IV)

Table 1 shows that the 3β-hydroxyl groups in lumistanols A and B (VI and VII; R = H) should adopt axial and equatorial conformations, respectively. The infrared spectra of the alcohols and acetates conform with these predictions, as does the formation of epilumistanol A (XI; R = H) in 80% yield in the sodium–isopropyl alcohol reduction of lumistanone A (XII). Cole's suggestion [4] for the structure of lumistanol A (as a 5α,8β,9α-stanol) was based largely on the axial nature of the 3β-hydroxyl group and on the supposition [12] that lumistanol A differs from hexahydro-9α-lumisterol (hexahydropyrocalciferol) only in stereochemistry at position 9. {Hexahydro-9α-lumisterol has been obtained [13,14] from both dehydrolumisterol [lumista-5,7,9(11)-trien-3β-ol] and 9α-lumisterol (pyrocalciferol).} This representation for lumisterol A is invalidated by the 9β-configuration of lumisterol and its derivatives established recently [1] and by the 5β-orientation now proved for the A series of reduction products. Hexahydro-9α-lumisterol is in fact the $C_{(9)}$-epimer of lumistanol B.[5]

With lumistanol C, formed (*a*) (as acetate) by hydrogenation of the $\Delta^{8(14)}$-compound (IV; R = Ac) and (*b*) as the minor product in the reduction of lumistenyl acetate (III; R = Ac), stereochemical assignment is less certain. The $\Delta^{8(14)}$-bond in compound (IV; R = Ac) is clearly more accessible from the β- than from the α-face of the molecule (see Fig. 2*c*): *cis*-hydrogenation then leads to the 8β,14β-structure (VIII; R = Ac) provisionally assigned to lumistanyl C acetate. [This assumes that the 8,14 double bond in compound

[8] Dreiding, *Chem. and Ind.*, 1954, 1419.
[9] Corey and Sneen, *J. Amer. Chem. Soc.*, 1955, **77**, 2505.
[10] Turner, Meador, and Winkler, *J. Amer. Chem. Soc.*, 1957, **79**, 4122.
[11] Forthcoming publication with Professor C. Djerassi.
[12] Fieser and Fieser, " Natural Products related to Phenanthrene," Reinhold Publ. Co., New York, 1949, p. 173.
[13] Dimroth, *Ber.*, 1936, **69**, 1123.
[14] Busse, *Z. physiol. Chem.*, 1933, **214**, 211.

(IV; R = Ac) is hydrogenated directly, without prior isomerisation to the 8,9 or 14,15 positions. Compound (IV; R = Ac) is stable to treatment with pre-reduced Adams catalyst: acidic reagents cause slow isomerisation to the Δ^8-isomer (3β-acetoxy-5α,14β-lumist-8-ene) which is unchanged under the conditions used to reduce compound (IV; R = Ac).[5]]

Conformational analysis of structure (VIII) shows the somewhat unexpected result that two all-chair forms are possible. In the first the 3β-substituent is equatorial and the C/D ring fusion " unfavourable " (in Dreiding's sense [15]) while the 3β-substituent is axial and the ring fusion " favourable " in the second. Chemical evidence, isolation of lumistanol C in high yield from the reduction of lumistanone C (XVI) by sodium–isopropyl alcohol, indicates the adoption of the first form, and the equatorial nature of the 3β-substituent is confirmed by the infrared spectra of lumistanol C and its acetate (VIII; R = Ac).

On the basis of these results the hydrogenation of lumisterol can be represented as follows, the nature of the 3β-group, hydroxyl or acetoxyl, not being specified. Reduction of the Δ^5- and Δ^{22}-bonds proceeds quickly, giving a mixture of *cis*- and *trans*-A/B-compounds which differ markedly in the rate at which the remaining (Δ^7) double bond is hydrogenated. The trans-A/B-compound, tetrahydrolumisterol (V), is not isolated in the direct reduction of lumisterol since it passes easily into lumistanol A (VI). Reduction of the *cis*-A/B-compound, lumistenol (III), to a mixture of lumistanols B and C, is much slower and unless the hydrogenation is prolonged an appreciable amount of lumistenol persists in the reaction mixture. Lumistanol B (VII) arises from direct reduction of the Δ^7-bond in lumistenol but formation of lumistanol C (VIII) involves prior isomerisation of the double bond to the 8,14 position, the opportunity for migration arising because of the slowness of the direct reduction.

It is to be noted that the lumistanols are formed from the Δ^7- and $\Delta^{8(14)}$-compounds by attack on the β-faces of the molecules. [Similar hydrogenation of Δ^7-bonds was first encountered in certain ergosterol derivatives which, as in the present examples, possessed the 9β-configuration: [18] the occurrence of β-face reduction was shown to be a consequence of the stereochemical changes attending inversion at position 9 (cf. 9α-Δ^7-steroids in which the Δ^7-bonds cannot be directly reduced).] That the reduction of the *cis*-A/B-Δ^7-compound (III) is slower than that of the *trans*-A/B-Δ^7-isomer (V) agrees with the geometry of these compounds. Inversion at position 5 from the β- to the α-configuration increases the extent to which ring A projects above the general plane of the molecule, thus causing more hindrance to approach from the β-side. This subject will be discussed further after the reduction products of 9α-lumisterol (pyrocalciferol) and 9β-ergosterol (isopyrocalciferol) have been described.

Experimental

For general directions see *J.*, 1958, 2156. Spectroscopic data for compounds marked * are shown in Table 2.

Lumisterol (I; R = H) *and Derived Esters.*—Lumisteryl 3,5-dinitrobenzoate was obtained as bright yellow plates, m. p. 140—142°, $[\alpha]_D$ +21° (*c* 0·9), after several crystallisations from benzene. Hydrolysis with ethanolic potassium hydroxide gave lumisterol which crystallised from ethanol as needles, m. p. 118—120°, $[\alpha]_D$ +192° (*c* 0·8), $\lambda_{max.}$ 2720 (ε 9290) and 2800 Å (ε 8780). Lumisteryl acetate, prepared with acetic anhydride–pyridine, was first obtained as needles, m. p. 100—101° after crystallisation from ethanol or acetone–methanol, $[\alpha]_D$ +127° (*c* 1·1). Subsequent preparations gave hexagonal plates, m. p. 109—111°, $[\alpha]_D$ +123° (*c* 1·2). The two forms had identical infrared and ultraviolet spectra, and were interconverted by the

[15] Dreiding, *Chem. and Ind.*, 1954, 992.
[16] Castells and Fletcher, *J.*, 1956, 3245.
[17] Windaus and Vibrig, *Ber.*, 1914, **47**, 2384; Windaus and Dalmer, *ibid.*, 1919, **52**, 162; Lettré, *Z. physiol. Chem.*, 1933, **221**, 73.
[18] Bladon, Henbest, Jones, Lovell, Wood, Woods, Elks, Evans, Hathway, Oughton, and Thomas, *J.*, 1953, 2921.

usual seeding procedure. (Windaus *et al.*[2] report similar constants, but they obtained only the lower-melting form of the acetate.)

5β-*Lumistan*-3β-*ol* (*Lumistanol A*) (VI; R = H).—(a) *By reduction of* 5β-*lumista*-7,22-*dien*-3β-*ol* (*dihydrolumisterol*) (II; R = H). A solution of the lumistadienol [5] (20 g.) in ethyl acetate (600 c.c.) and perchloric acid [0·7 c.c. of a solution made from 60% aqueous perchloric acid (10 c.c.) and ethyl acetate (90 c.c.)] was shaken in hydrogen with Adams catalyst (1·3 g.) for 1·5 hr. After filtration and addition of ether the solution was washed with aqueous sodium carbonate and then water, dried, and evaporated. Crystallisation of the residue from ethanol afforded 5β-lumistan-3β-ol (16·5 g.), m. p. 126—128°, $[\alpha]_D$ +8° (*c* 1·0) (Found: C, 83·3; H, 12·6. Calc. for $C_{28}H_{50}O$: C, 83·5; H, 12·5%), $\nu_{max.}$ 3617 and 1010 cm.$^{-1}$ (hydroxyl), which gave no colour with tetranitromethane. Treatment with acetic anhydride–pyridine afforded 3β-acetoxy-5β-lumistane as cubes (from ethanol), m. p. 82—84·5°, $[\alpha]_D$ +9° (*c* 1·0) (Found: C, 80·7; H, 12·0. Calc. for $C_{30}H_{50}O_2$: C, 81·0; H, 11·8%), $\nu_{max.}$ 1733, 1247, and 1231 (complex acetate band), and 1117 cm.$^{-1}$. (The m. p. and $[\alpha]_D$ figures for the lumistanol and its acetate are close to those recorded by Ahrens [2] and Heilbron [3] and their collaborators.) 5β-*Lumistan*-3β-*yl* 3,5-*dinitrobenzoate*, prepared in the usual manner and crystallised from chloroform–ethanol, had m. p. 176·5—177·5°, $[\alpha]_D$ +21° (*c* 1·4) (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%).

(b) *By reduction of* 3β-*acetoxy*-5β-*lumist*-7-*ene* (*tetrahydrolumisteryl acetate*) (V; R = Ac). The acetate [5] (700 mg.) in ethyl acetate (52 c.c.) containing perchloric acid (0·1 c.c. of the reagent described above) was hydrogenated over Adams catalyst (70 mg.). After the completion of hydrogen absorption (30 min.) the mixture was treated as in the preceding experiment and yielded 3β-acetoxy-5β-lumistane (550 mg.), m. p. 80—82°, $[\alpha]_D$ +8° (*c* 0·9), identified by mixed m. p. and comparison of infrared spectra with an authentic specimen.

(c) *By the sequence involving hydroxylation of* 3β-*acetoxy*-5β-*lumist*-7-*ene* (V; R = Ac). Solutions of osmium tetroxide (2 g.) in dry ether (30 c.c.) and the acetate (1·7 g.) in dry ether (30 c.c.) and pyridine (6 c.c.) were mixed and refluxed for 1 hr. The residue obtained by evaporating the solution at 20 mm. was dissolved in tetrahydrofuran (30 c.c.) and refluxed for 30 min. with an excess of lithium aluminium hydride. Standard manipulation was followed by adsorption of the product (1·7 g.) on deactivated alumina (120 g.). Elution with benzene–ether (4 : 1; 250 c.c.) gave 5β-lumist-7-en-3β-ol [5] (V; R = H) (0·6 g.), m. p. 127—131°. Ether–methanol (50 : 1; 500 c.c.) gave 5β-*lumistan*-3β,7ξ,8ξ-*triol* (IX) (1 g.), m. p. 80—85° after crystallisation from aqueous methanol, $[\alpha]_D$ +23° (*c* 1·2) (Found: C, 77·2; H, 11·3. $C_{28}H_{50}O_3$ requires C, 77·4; H, 11·5%).

A solution of the triol (1·0 g.) in methanol (75 c.c.) was warmed with 10% methanolic sulphuric acid (75 c.c.) to 60°, then kept at 20° for 2 hr. Water was added and the product isolated by filtration was dried and chromatographed on deactivated alumina (70 g.). Benzene–ether (3 : 1; 100 c.c.) eluted material (0·35 g.) which after crystallisation from methanol afforded 5β-lumista-8,14-dien-3β-ol,[5] m. p. 132·5—133·5°. Further elution with the same solvent mixture (250 c.c.) gave 3β-*hydroxy*-5β-*lumistan*-7-*one* (X) (0·6 g.) which after crystallisation from methanol had m. p. 131—134°, $[\alpha]_D$ +105° (*c* 0·6) (Found: C, 80·7; H, 11·7. $C_{28}H_{48}O_2$ requires C, 80·8; H, 11·55%), $\nu_{max.}$ 3610, 1019 (hydroxyl), and 1712 cm.$^{-1}$ (ketone). This ketone was recovered unchanged (m. p., mixed m. p., and comparison of infrared spectrum with starting material) after being refluxed for 30 min. with 5% ethanolic potassium hydroxide.

The above ketone (200 mg.) was reduced by the standard Huang-Minlon procedure, and the product chromatographed on deactivated alumina (20 g.). The material eluted with light petroleum–benzene (3 : 2; 250 c.c.) crystallised from methanol to give 5β-lumistan-3β-ol (130 mg.), m. p. 125—127°, $[\alpha]_D$ +5° (*c* 0·5), identified by mixed m. p. and comparison of infrared spectra with authentic material.

5β-*Lumistan*-3-*one* (*Lumistanone A*) (XII).—(a) *From* 5β-*lumistan*-3β-*ol* (VI; R = H). A solution of the lumistanol (4 g.) in acetone (250 c.c.) was titrated with a solution of chromic acid in dilute sulphuric acid (8N with respect to active oxygen) until the supernatant liquid became yellow. The mixture was poured into iced water (1 l.), and the insoluble material collected, dried, and crystallised from acetone to give 5β-lumistan-3-one * (3·2 g.), m. p. 123—125°, $[\alpha]_D$ −11° (*c* 1·3) (Found: C, 83·65; H, 11·9. Calc. for $C_{28}H_{48}O$: C, 83·9; H, 12·1%). Heilbron *et al.*[3] record m. p. 121—122°, $[\alpha]_D$ −17·5°. The 2,4-*dinitrophenylhydrazone* * crystallised from chloroform–ethanol as yellow granules, m. p. 214—216° (Found: C, 70·2; H, 8·9; N, 9·95. $C_{34}H_{52}O_4N_4$ requires C, 70·3; H, 9·0; N, 9·65%).

(b) *From lumisterol* (I; R = H). A solution of lumisterol (6·3 g.) in ethyl acetate (100 c.c.) and perchloric acid (0·25 c.c. of the standard reagent) was stirred in hydrogen at 100°/70 atm. with Adams catalyst (500 mg.) for 6 hr. After being worked up as in the previous experiments the product was dissolved in acetone (200 c.c.) and oxidised with 8N-chromic acid (6 c.c.). Dilution with water and extraction with ether afforded material which was chromatographed on alumina (200 g.; Grade H). The fraction (4·5 g.) eluted with benzene was crystallised from ethanol to give 5β-lumistan-3-one (3·8 g.), m. p. 121·5—123°, $[\alpha]_D$ −9° (*c* 0·9), identified by mixed m. p. and comparison of infrared spectra with an authentic sample.

(c) *From lumist-4-en-3-one* (XIII). Lithium (250 mg.) was added to a solution of the lumistenone (36 mg.) in dry ether (10 c.c.) and liquid ammonia (20 c.c.). After the lithium had dissolved absolute ethanol was added slowly until the blue colour was discharged. The ammonia was allowed to evaporate, water was added, and the ether layer was separated and washed with dilute hydrochloric acid and then water. Evaporation of the dried ether solution gave a residue which was dissolved in acetone (5 c.c.) and treated for 2 min. with 8N-chromic acid (0·2 c.c.). The product, isolated by dilution with water and extraction with ether, was chromatographed on alumina (2 g.; Grade 0). The material eluted with benzene–ether (3 : 1; 5 c.c.) was crystallised from ethanol to give 5β-lumistan-3-one (25 mg.), m. p. 123—125°, identified as in experiment (b).

Sodium–Isopropyl Alcohol Reduction of 5β-*Lumistan*-3-*one* (XII).—Sodium (10 g.) was added during 3 hr. to a refluxing solution of the lumistanone (1 g.) in isopropyl alcohol (150 c.c.). Dilution with water and extraction with ether gave material (1 g.) which was adsorbed on deactivated alumina (70 g.). Light petroleum–benzene (2 : 1; 400 c.c.) eluted 5β-lumistan-3β-ol (VI; R = H) (220 mg.), m. p. 124—126° after crystallisation from methanol.

Further elution with the same solvent mixture afforded 5β-lumistan-3α-ol (XI; R = H) (780 mg.) which after crystallisation from methanol had m. p. 78—82°, $[\alpha]_D$ +10° (*c* 1·1), $\nu_{max.}$ 3600 and 1035 cm.$^{-1}$ (hydroxyl). Acetylation of this compound with acetic anhydride–pyridine at 20° afforded 3α-acetoxy-5β-lumistane (XI; R = Ac), m. p. 67—69°, $[\alpha]_D$ +18° (*c* 0·6), $\nu_{max.}$ 1736 and 1244 (simple band) cm.$^{-1}$ (acetate). (Ahrens *et al.*[2] record m. p. 86—95°, $[\alpha]_D$ +10°, for the alcohol, and m. p. 64—65°, $[\alpha]_D$ +20°, for the acetate.)

5α-*Lumistan*-3β-*ol* (*Lumistanol B*) (VII; R = H) *and* 5α,14β-*Lumistan*-3β-*ol* (*Lumistanol C*) (VIII; R = H).—Two procedures, experiments (*a*) and (*b*), for the reduction of 3β-acetoxy-5α-lumist-7-ene (lumistenyl acetate) (III; R = Ac) are described, together with the reduction, experiment (*c*), of 3β-acetoxy-5α-lumist-8(14)-ene (IV; R = Ac). Experiment (*a*) gives both lumistanols but is extremely laborious: experiment (*b*) leading to lumistanol B, and experiment (*c*) leading to lumistanol C are more convenient methods.

Hydrogenation of 3β-*Acetoxy*-5α-*lumist*-7-*ene* (*Lumistenyl acetate*) (III; R = Ac). (*a*) A suspension of the acetate (9·49 g.) in glacial acetic acid (450 c.c.) at 40° was allowed to cool while being shaken in hydrogen with Adams catalyst (3·5 g.). After 30 min. all the organic material had dissolved, and hydrogenation was continued for 23 hr. at 20°. Filtration of the solution and removal of solvent at 15 mm. afforded a gum which was dissolved in ethanol (90 c.c.) and refluxed for 30 min. with a solution of potassium hydroxide (9 g.) in water (10 c.c.). The solution was concentrated by distillation and poured into ice-water. The material collected by filtration was dried, dissolved in ether, and adsorbed on alumina (800 g.; grade H). After elution with ether (36 × 100 c.c. portions) and removal of solvent the specific rotation of the material in each fraction was determined. The $[\alpha]_D$ values decreased steadily, and this was used as a basis for combining the fractions into five main materials.

3,5-Dinitrobenzoyl chloride (500 mg.) was added to material 1 (428 mg., comprising fractions 1—5 with $[\alpha]_D$ values of +100° to +37°) in pyridine (5 c.c.), and the solution kept for 12 hr. at 20°. The dinitrobenzoate, isolated by dilution with water and benzene extraction, crystallised from ethyl acetate–ethanol to give coarse needles (215 mg.) the m. p. of which, 98—140°, was not improved by further crystallisation.

Material 2 (1·441 g., fractions 6—13 with $[\alpha]_D$ values between +27° and +26°) in pyridine (15 c.c.) was esterified with 3,5-dinitrobenzoyl chloride (1·5 g.). The product was dissolved in benzene and the solution filtered through a short column of deactivated alumina. Removal of solvent and 3 crystallisations of the residue from ethyl acetate–ethanol gave 5α,14β-*lumistan*-3β-*yl* 3,5-*dinitrobenzoate* as needles (721 mg.), m. p. 141·5—142·5°, $[\alpha]_D$ −5° (*c* 1·0) (Found: C, 70·7; H, 8·6; N, 4·7. $C_{35}H_{52}O_6N_2$ requires C, 70·4; H, 8·8; N, 4·7%). Hydrolysis of the ester with alkaline alumina [16] afforded 5α,14β-*lumistan*-3β-*ol* (lumistanol C) (VIII; R = H), m. p. 75—78°

after crystallisation from light petroleum, $[\alpha]_D$ +23° (*c* 1·3) (Found: C, 83·6; H, 12·5. $C_{28}H_{50}O$ requires C, 83·5; H, 12·5%), $\nu_{max.}$ 3630 and 1035 cm.$^{-1}$ (hydroxyl), negative tetranitromethane test. 3β-*Acetoxy*-5α,14β-*lumistane* (lumistanyl C acetate) (VIII; R = Ac), prepared in the usual way, crystallised from ethanol as needles, m. p. 70—72°, $[\alpha]_D$ −7° (*c* 0·5) (Found: C, 81·1; H, 11·9. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%), $\nu_{max.}$ 1732 and 1239 (simple band) cm.$^{-1}$ (acetate).

Material 3 (1·286 g., fractions 14—19 with $[\alpha]_D$ +23° to +15°) was esterified with 3,5-dinitrobenzoyl chloride–pyridine, and the product in benzene was filtered through deactivated alumina. The residue obtained on evaporation crystallised from ethyl acetate–ethanol to give crystals (1·48 g., m. p. 145—168°) presumed to be a mixture of the esters of lumistanols B and C. From the mother liquor pure lumistanyl C 3,5-dinitrobenzoate was obtained as needles (120 mg.), m. p. 140—142°.

Material 4 (1·875 g., fractions 20—26 with $[\alpha]_D$ +13° to +9°) was esterified as above. Three crystallisations of the product from ethyl acetate–ethanol gave 5α-*lumistan*-3β-*yl* 3,5-*dinitrobenzoate* as fine needles (1·29 g.), m. p. 190—190·5°, $[\alpha]_D$ −9° (*c* 1·1) (Found: C, 70·25; H, 8·7; N, 4·75. $C_{35}H_{52}O_6N_2$ requires C, 70·4; H, 8·8; N, 4·7%). Hydrolysis in the usual way [16] afforded 5α-*lumistan*-3β-*ol* (lumistanol B) (VII; R = H) as needles (from methanol), double m. p. 87—90° and 115—118°, $[\alpha]_D$ +5° (*c* 1·0) (Found: C, 83·6; H, 12·7. $C_{28}H_{50}O$ requires C, 83·5; H, 12·5%), $\nu_{max.}$ 3600, 1065, and 1030 cm.$^{-1}$ (hydroxyl), no colour with tetranitromethane. 3β-*Acetoxy*-5α-*lumistane* (lumistanyl B acetate) (VII; R = Ac) crystallised from methanol as plates, m. p. 83—85°, $[\alpha]_D$ −12° (*c* 1·1) (Found: C, 81·0; H, 12·05. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%), $\nu_{max.}$ 1241 (simple band) cm.$^{-1}$ (acetate).

Material 5 (2·52 g., fractions 27—36 with $[\alpha]_D$ *ca.* +5°) was dissolved in methanol. After being seeded the solution deposited 5α-lumistan-3β-ol (VII; R = H) as needles (1·47 g.), m. p 88—91°, $[\alpha]_D$ +5° (*c* 1·5). Identification of this material was confirmed by comparing its infrared spectrum with that of authentic material; the double m. p. of lumistanol B was observed only with specimens obtained *via* the pure dinitrobenzoate.

(*b*) 3β-Acetoxy-5α-lumist-7-ene (III; R = Ac) (200 mg.) in acetic acid (10 c.c.) was hydrogenated at 20° in the presence of Adams catalyst (40 mg.). Absorption of hydrogen ceased after 1 hr. (uptake 18 c.c.). More catalyst (40 mg.) was added and the hydrogenation was continued for 4 hr. at 80°. The filtered solution was evaporated at 15 mm. and the residue hydrolysed with ethanolic potassium hydroxide. Esterification of the product with 3,5-dinitrobenzoyl chloride–pyridine and three crystallisations of the ester from ethyl acetate–ethanol yielded 5α-lumistan-3β-yl 3,5-dinitrobenzoate (66 mg.), m. p. and mixed m. p. with authentic material, 188—190°, $[\alpha]_D$ −8° (*c* 0·7).

(*c*) 3β-Acetoxy-5α-lumist-8(14)-ene [5] (IV; R = Ac) (220 mg.) in warm acetic acid (11 c.c.) was shaken in hydrogen with Adams catalyst (90 mg.) for 22 hr. Hydrolysis of the residue obtained after removing catalyst and solvent, and treatment of the product with 3,5-dinitrobenzoyl chloride–pyridine gave a crude ester which was adsorbed on deactivated alumina (3 g.). The fraction eluted with benzene was thrice crystallised from ethyl acetate–ethanol to give 5α,14β-lumistan-3β-yl 3,5-dinitrobenzoate as needles (98 mg.), m. p. and mixed m. p. with authentic material, 139—142°, $[\alpha]_D$ −4° (*c* 1·6). Hydrolysis afforded 5α,14β-lumistan-3β-ol (VIII; R = H), m. p. 76—78°, $[\alpha]_D$ +24° (*c* 1·6).

Lumistan-3-*one* (*Lumistanone B*) (XV).—A solution of 5α-lumistan-3β-ol (VII; R = H) (1·2 g.) in acetone (20 c.c.) was titrated with 8N-chromic acid until the supernatant liquid became yellow (*ca.* 2 c.c. of chromic acid solution required). The material precipitated by addition of water was collected, washed with aqueous sodium hydrogen carbonate and then water; it crystallised from ethanol to give 5α-*lumistan*-3-*one* * as needles (0·9 g.), m. p. 89·5—91°, $[\alpha]_D$ +38° (*c* 0·7). Reproducible analyses on different specimens (*e.g.*, Found: C, 82·1; H, 11·9%) indicated the presence of solvent of crystallisation ($C_{28}H_{48}O$ requires C, 83·9; H, 12·1. $C_{28}H_{48}O,0{\cdot}5H_2O$ requires C, 82·1; H, 12·1%), but even after sublimation at 100°/0·4 mm. satisfactory values were not obtained (Found: C, 82·55; H, 12·0%), $\nu_{max.}$ (Nujol) of sublimed specimen 3575 (hydroxyl) as well as 1703 cm.$^{-1}$ (ketone). The 2,4-*dinitrophenylhydrazone* * crystallised from ethyl acetate–ethanol as orange-yellow needles, m. p. 178—180° (Found: C, 70·4; H, 8·9; N, 9·85. $C_{34}H_{52}O_4N_4$ requires C, 70·3; H, 9·0; N, 9·65%).

5α,14β-*Lumistan*-3-*one* (*Lumistanone C*) (XVI).—5α,14β-Lumistan-3β-ol (VIII; R = H) (1·5 g.) in acetone (35 c.c.) was oxidised with 8N-chromic acid in the usual way. The product crystallised from acetone–methanol to give 5α,14β-*lumistan*-3-*one* (1·2 g.), m. p. 84—86°, $[\alpha]_D$

+27° (*c* 0·7) (Found: C, 84·2; H, 12·2. $C_{28}H_{48}O$ requires C, 84·0; H, 12·0%), $\nu_{max.}$ 1718 cm.$^{-1}$ (ketone).

Reduction of 5α,14β-*Lumistan*-3-*one* (XVI) *with Sodium–Isopropyl Alcohol.*—Sodium (5 g.) was added during 3 hr. to a refluxing solution of the lumistanone (500 mg.) in isopropyl alcohol (100 c.c.). Dilution with water and extraction with ether gave material (490 mg.) which was adsorbed on deactivated alumina (40 g.). The material eluted with light petroleum–benzene (1 : 1; 200 c.c.) crystallised from pentane to give 5α,14β-lumistan-3β-ol (VIII; R = H) (410 mg.), m. p. 76—78°, $[\alpha]_D$ +26° (*c* 0·8).

2β-*Bromo*-5β-*lumistan*-3-*one* (XVII).—A 0·98M-solution of bromine in acetic acid (4 c.c.) and a 50% solution of hydrogen bromide in acetic acid (0·15 c.c.) were mixed and added to a solution of 5β-lumistan-3-one (XII) (1·5 g.) in acetic acid (100 c.c.). The mixture was warmed on the steam-bath for 3 min. and then kept at room temperature for 12 hr. The precipitate was collected and crystallised from ethyl acetate to give 2β-*bromo*-5β-*lumistan*-3-*one* * as needles, m. p. 201—203°, $[\alpha]_D$ −39° (*c* 0·8) (Found: C, 70·25; H, 10·0; Br, 17·1. $C_{28}H_{47}OBr$ requires C, 70·1; H, 9·9; Br, 16·7%).

This compound was recovered unchanged after treatment with hydrogen bromide in warm acetic acid. In attempts to introduce a second bromine substituent starting material was recovered in low yield but no other crystalline products were obtained.

5β-*Lumist*-1-*en*-3-*one* (XXI).—A solution of 2,4-dinitrophenylhydrazine (165 mg.) and 2β-bromo-5β-lumistan-3-one (400 mg.) in acetic acid (25 c.c.) was refluxed under nitrogen for 5 min. 5β-*Lumist*-1-*en*-3-*one* 2,4-*dinitrophenylhydrazone* * was precipitated from the cold solution and after crystallisation from chloroform–ethanol formed orange-red needles (331 mg.), m. p. 208·5—209·5° (Found: C, 70·4; H, 8·8; N, 10·0. $C_{34}H_{50}O_4N_4$ requires C, 70·55; H, 8·7; N, 9·7%). The dinitrophenylhydrazone (300 mg.) was refluxed under nitrogen for 45 min. with a mixture of acetone (65 c.c.) and 10N-hydrochloric acid (1·6 c.c.), stannous chloride (1·6 g.) in 10N-hydrochloric acid (6 c.c.) was added, and the refluxing continued for 40 min. After removal of acetone under reduced pressure and dilution with water the mixture was thoroughly extracted with benzene. The extract was washed with dilute hydrochloric acid and then water, dried, and filtered through alumina (20 g.; grade 0). Evaporation of the solution afforded 5β-*lumist*-1-*en*-3-*one* * as an oil (171 mg.), $[\alpha]_D$ +32° (*c* 1·1) (Found: C, 84·0; H, 11·3. $C_{28}H_{46}O$ requires C, 84·35; H, 11·6%).

Bromination of 5α-*Lumistan*-3-*one* (XV).—(a) *With 2 mols. of bromine.* A 1·03M-solution of bromine in acetic acid (1·3 c.c.) and a 50% solution of hydrogen bromide in acetic acid (0·01 c.c.) were added to the lumistanone (250 mg.) dissolved in acetic acid (2 c.c.), and the mixture was kept at 20° for 12 hr. The precipitate was collected and crystallised from ethyl acetate, giving 2α,4β-*dibromo*-5α-*lumistan*-3-*one* * (XIX) as needles (300 mg.), m. p. 202—203° (decomp.), $[\alpha]_D$ +23° (*c* 0·8) (Found: C, 60·2; H, 8·2. $C_{28}H_{46}OBr_2$ requires C, 60·2; H, 8·3%).

(b) *With 1 mol. of bromine.* Solutions of bromine in acetic acid (1·56 c.c.; 1·03M), hydrogen bromide in acetic acid (0·02 c.c., 50%), and 5α-lumistan-3-one (600 mg.) in acetic acid (5 c.c.) were mixed and kept at 20° for 12 hr. Dilution with water and extraction with light petroleum gave a product (751 mg.) which was dissolved in benzene and adsorbed on silica gel (75 g.; B.D.H. chromatographic grade). Elution with benzene (2 × 100 c.c.) and evaporation of solvent gave two fractions. The first (65 mg.) crystallised from ethyl acetate affording 2α,4α-dibromo-5α-lumistan-3-one (XIX) (27 mg.), m. p. 199—203° (decomp.), $[\alpha]_D$ +21° (*c* 0·6), further identified by its characteristic infrared spectrum.

The second fraction (570 mg.) was crystallised three times from ethanol–ethyl acetate (9 : 1) to give 4α-*bromo*-5α-*lumistan*-3-*one* * (XIV) (174 mg.), m. p. 194—197°, $[\alpha]_D$ +21° (*c* 0·8) (Found: C, 69·95; H, 10·15. $C_{28}H_{47}OBr$ requires C, 70·1; H, 9·9%). The material obtained by evaporating the mother-liquors from these three crystallisations was again crystallised from ethanol–ethyl acetate (9 : 1). Impure 4α-bromo-5α-lumistan-3-one (23 mg.), m. p. 189—194°, was collected and the filtrate retained for the preparation of 5α-lumist-1-en-3-one (XXIII) described below.

5α-*Lumist*-1-*en*-3-*one* (XXIII).—The filtrate obtained in the crystallisation of 4α-bromo-5α-lumistan-3-one (preceding experiment) was evaporated and the residue dissolved in acetic acid (15 c.c.). 2,4-Dinitrophenylhydrazine (190 mg.) was added, and the mixture heated at 100° under nitrogen for 45 min., diluted with water, and extracted with benzene. The extract was washed with aqueous sodium carbonate and then water, dried, and filtered through a column of

alumina (20 g.; grade H). Evaporation of the solvent and repeated crystallisation of the residue from chloroform–ethanol gave 5α-*lumist*-1-*en*-3-*one* 2,4-*dinitrophenylhydrazone* * as orange-red granules (83 mg.), m. p. 183—185° (Found: C, 70·3; H, 8·8; N, 9·6. $C_{34}H_{50}O_4N_4$ requires C, 70·55; H, 8·7; N, 9·7%).

The dinitrophenylhydrazone (40 mg.) was hydrolysed by the hydrochloric acid–stannous chloride–acetone method [see details described in the preparation of 5β-lumist-1-en-3-one (XXI)]. Evaporation of the benzene solution so obtained gave 5α-lumist-1-en-3-one as an oil (22 mg.; not analysed), $[\alpha]_D$ −29° (*c* 0·3). This material was converted in high yield into the 2,4-dinitrophenylhydrazone, m. p. 183—185°, for which correct analytical figures had already been obtained.

Lumist-4-*en*-3-*one* (XIII).—A solution of 2,4-dinitrophenylhydrazine (45 mg.) and 4α-bromo-5α-lumistan-3-one (XIV) (97 mg.) in acetic acid (10 c.c.) was refluxed under nitrogen for 5 min. The mixture was diluted with water and extracted with benzene, and the dried benzene solution passed through a short column of alumina (Grade H). Evaporation of solvent and crystallisation of the residue from chloroform–ethanol gave *lumist*-4-*en*-3-*one* 2,4-*dinitrophenylhydrazone* * as orange-red blades (65 mg.), m. p. 207—209° (Found: C, 70·9; H, 8·7; N, 9·5. $C_{34}H_{50}O_4N_4$ requires C, 70·55; H, 8·7; N, 9·7%). The dinitrophenylhydrazone (65 mg.) was hydrolysed with hydrochloric acid–stannous chloride–acetone, as described previously. Lumist-4-en-3-one was obtained as an oil (38 mg.; not analysed), $[\alpha]_D$ −124° (*c* 0·7). The compound was converted quantitatively into the 2,4-dinitrophenylhydrazone, m. p. 207—209°, which gave satisfactory analytical results.

2,3-*Seco*-5β-*lumistan*-2,3-*dioic Acid* (XVIII).—Chromium trioxide (22 g.) in water (20 c.c.) and acetic acid (200 c.c.) was added during 1 hr. to a stirred solution of 5β-lumistan-3β-ol (VI; R = H) (9 g.) in acetic acid (180 c.c.) at 60° and the stirring continued for a further hour. Sulphur dioxide was passed through the solution and most of the acetic acid removed by distillation at 20 mm. Water was added and the mixture extracted with ether. The ether solution was washed with water and then extracted with 2N-sodium hydroxide solution (2 × 50 c.c.). The alkaline extract was warmed to remove dissolved ether, cooled, and slowly added to stirred 4N-hydrochloric acid (200 c.c.) at 0°. After 30 min. the precipitate was collected, dried, and crystallised several times from ethyl acetate to give the seco-diacid (XVIII) as blades (1·12 g.), m. p. 223—226°, $[\alpha]_D$ +25° (*c* 1·2) (Found: C, 74·6; H, 10·8. Calc. for $C_{28}H_{48}O$: C, 74·95; H, 10·8%). Heilbron *et al.*[3] record m. p. 208—210°, $[\alpha]_D$ +24·6°.

A-*Nor*-5β-*lumistan*-2-*one* (XXII; R = O).—A solution of the above seco-diacid (1·5 g.) in ethanol (36 c.c.) and water (4 c.c.) was gently refluxed for 4 hr., the condensed liquid returning to the boiling solution through a small funnel containing barium hydroxide (1·6 g.). Filtration of the cooled mixture gave precipitate (containing the seco-acid and its barium salt) and filtrate (containing some seco-diacid). The precipitate was washed with ether, and the residue obtained by evaporating the ether washings was combined with the alcoholic filtrate which was then re-treated with barium hydroxide as described above. This process was repeated until a portion of the alcoholic filtrate no longer gave a precipitate on dilution with water. The combined precipitates were dried, finely ground, and heated at 300—350°/0·03 mm. in a glass retort. The distillate (800 mg.) was adsorbed from benzene (5 c.c.) on alumina (50 g.; grade 0). Elution with benzene (150 c.c.) gave the *nor-ketone* which crystallised from acetone–methanol as plates (631 mg.), m. p. 93—96°. After several crystallisations from acetone the compound had m. p. 97·5—99°, $[\alpha]_D$ −116° (*c* 1·0) (Found: C, 83·8; H, 11·9. $C_{27}H_{46}O$ requires C, 83·9; H, 12·0%), $\nu_{max.}$ 1750 cm.$^{-1}$ (ketone). The 2,4-*dinitrophenylhydrazone* crystallised from benzene in small orange needles, m. p. 214—216° (Found: C, 69·75; H, 9·0; N, 10·0. $C_{33}H_{50}O_4N_4$ requires C, 69·9; H, 8·9; N, 9·9%), $\lambda_{max.}$ (in chloroform) 3660 Å (ε 24,100).

A-*Nor*-5β-*lumistane* (XXII; R = H_2).—The preceding nor-ketone (250 mg.) was reduced by the standard Huang-Minlon procedure, and the product chromatographed on alumina (15 g., grade 0). Elution with light petroleum (100 c.c.) gave A-*nor*-5β-*lumistane* which crystallised from acetone as plates (205 mg.), m. p. 65—68°. The pure product had m. p. 69—71°, $[\alpha]_D$ −27° (*c* 0·8) (Found: C, 87·1; H, 12·7. $C_{27}H_{48}$ requires C, 87·0; H, 13·0%).

Reference Compounds in Table 2.—The methods described above for the lumisterol derivatives were found to be more efficient than the published ones [17] for the preparation of these known compounds. Satisfactory analytical results were obtained in each case, and the observed constants were: 2,3-secocholestane-2,3-dioic acid, m. p. 197—200°, $[\alpha]_D$ +34° (*c* 1·1); A-norcholestan-2-one, m. p. 101—102°, $[\alpha]_D$ +147° (*c* 1·4); A-norcholestane, m. p. 81—82°, $[\alpha]_D$ +27°

(*c* 1·0); 3,4-secocoprostane-3,4-dioic acid, m. p. 255—256°, $[\alpha]_D$ +57° (*c* 0·6); A-norcoprostan-3-one, m. p. 78—80°, $[\alpha]_D$ +131° (*c* 0·9); A-norcoprostane, m. p. 47—51°, $[\alpha]_D$ +28° (*c* 1·1).

The authors are indebted to the Department of Scientific and Industrial Research for maintenance grants (to G. A. F. and R. S.), to the British Council and the Consejo Superior de Investigaciones Cientificas de España for grants (to J. C.), to Miss S. Hackney and Miss W. Peadon for recording the spectroscopic data, and to Mr. E. S. Morton for performing the microanalyses.

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