212. *Steroids and Related Compounds. Part III. The Constitution of Westphalen's Diol.*

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A retropinacolinic change, involving a hitherto unrecorded structural rearrangement of the steroid molecule, has been held responsible for the formation of Westphalen's diol during the dehydration of cholestane-3 : 5 : 6-triol (I; R = R_1 = H), leading to 5-methyl-$\Delta^{8:9}$-norcholestene-3 : 6-diol (II; R = H) (cf. Part II). Further evidence in support of this formulation has now been obtained by a study of the interrelationship of a series of oxidation products of the diol.

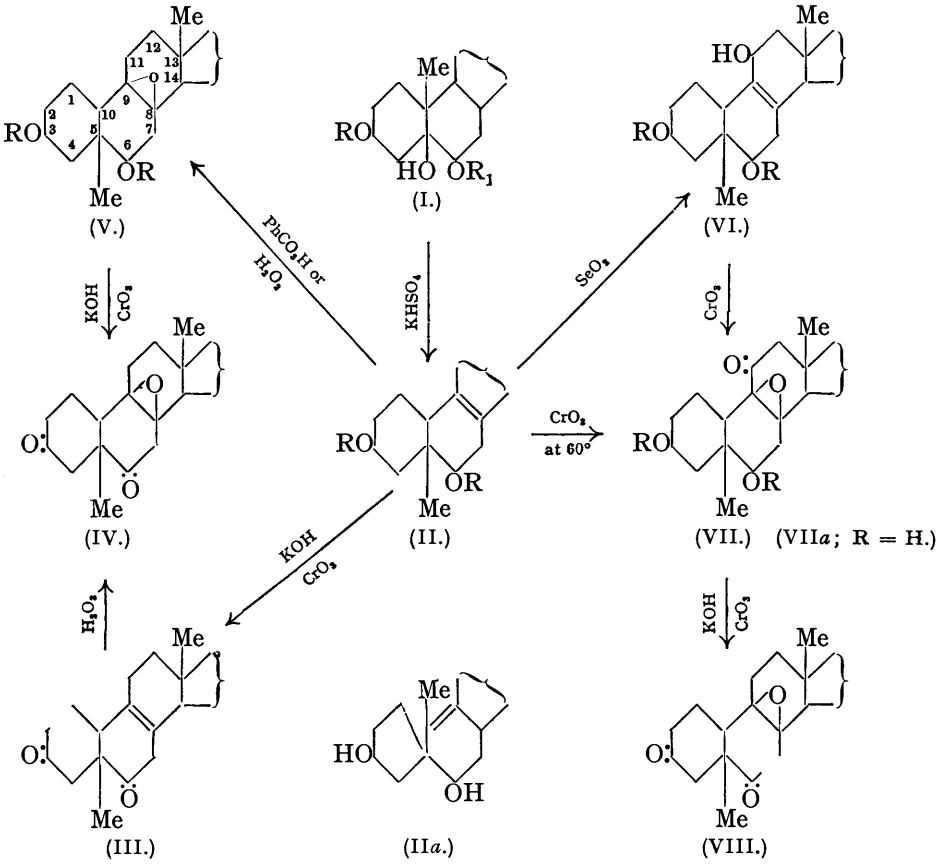
THE constitution of a 5-methyl-$\Delta^{8:9}$-norcholestene-3 : 6-diol (II; R = H) has been assigned by Petrow, Rosenheim, and Starling (J., 1938, 677) to the diol obtained as a diacetate by Westphalen (*Ber.*, 1915, **48**, 1064) when he dehydrated 5-hydroxy-3 : 6-diacetoxycholestane (I; R = R_1 = Ac) with concentrated sulphuric acid in acetic anhydride solution. The method of preparation has now been improved, and the yield of Westphalen's diacetate increased, by the use of potassium hydrogen sulphate as the dehydrating agent. Further, under these conditions the same diacetate is obtained when 5-hydroxy-3 : 6-diacetoxycholestane (I; R = R_1 = Ac) is dehydrated in propionic anhydride solution. Evidence is thus supplied for the position at C_3 and C_6 of the two secondary hydroxyl groups in Westphalen's diol. This fact, together with the analogous result of the dehydration of 5-hydroxy-6-acetoxy-3-methoxycholestane (I; R = Me, R_1 = Ac) (Petrow, J., 1937, 1077), proves conclusively that the elimination of the tertiary group from C_5 (or C_{10}) is the determining factor of the reaction and the final outcome of the retropinacolinic rearrangement (cf. Lettré and Müller, *Ber.*, 1937, **70**, 1947). The possibility of a spiran formation (II*a*) during this rearrangement is excluded by the result of the dehydrogenation with selenium of the diacetate of Westphalen's diol, which furnished the hydrocarbon " $C_{25}H_{24}$", a typical dehydrogenation product of cholesterol containing the *cyclo*pentenophenanthrene ring system.

The experimental results obtained by oxidation of Westphalen's diacetate find a ready interpretation if the position $C_{8:9}$ for the ethylenic linkage of the diol, assigned to it for other reasons in Part II (Petrow, Rosenheim, and Starling, *loc. cit.*), is assumed. This conclusion is confirmed, although not definitely proved, by a study of the inter-relationship of the whole series of oxidation products with perbenzoic acid, hydrogen peroxide, selenium dioxide, and chromic acid, which will be conveniently discussed on the basis of a $C_{8:9}$ ethylenic linkage in Westphalen's diol.

On oxidation with chromic acid, Westphalen's diol (II; R = H) furnishes 5-methyl-$\Delta^{8:9}$-norcholestene-3 : 6-dione (III) (Part II, *loc. cit.*). When this unsaturated diketone in acetic acid solution is treated with hydrogen peroxide at room temperature, a saturated dione-oxide, $C_{27}H_{42}O_3$, m. p. 133°, is obtained which is characterised by a *mono-o-tolylsemicarbazone*, m. p. 225°. The structure of this compound follows from the observation that the identical dione-oxide results as the end-product of the following series of reactions : The diacetate (II; R = Ac) yields with perbenzoic acid or with hydrogen peroxide a saturated *diacetate*, $C_{31}H_{50}O_5$, m. p. 133·5°, from which 5-methylnorcholestane-3 : 6-diol-8 : 9-oxide (V; R = H) is obtained on hydrolysis. The diacetate (V; R = Ac) is recovered unchanged on acetylation of the diol, and also after treatment with dinitrophenylhydrazine, proving the absence of alcoholic or ketonic functions of the newly introduced oxygen atom. On oxidation of the diol (V; R = H) with chromic acid the dione-oxide, m. p. 133° (see above), is obtained, which may therefore be formulated as 5-*methylnorcholestane*-3 : 6-*dione*-8 : 9-*oxide* (IV). The oxide ring of both (IV) and (V) is thus unaffected by the oxidising agent in agreement with the view that the two tertiary carbon atoms C_8 and C_9 are bridged by oxygen (cf. Ruzicka and Bosshard, *Helv. Chim. Acta*, 1937, **20**, 224).

Westphalen's diol reacts readily with selenium dioxide in alcoholic solution (Part II, *loc. cit.*), a reaction which has now been found to give rise to the introduction of a hydroxyl group, in analogy to the reaction of selenium dioxide on cholesterol (cf. Rosenheim and

Starling, J., 1937, 377). Owing to its relatively sparing solubility in the usual solvents the main reaction product, an unsaturated *triol*, $C_{27}H_{46}O_3$, m. p. 223°, is easily isolated. The position at C_{11} has been assigned to the newly introduced hydroxyl group, the alternative position at C_7 being excluded since the triol does not function as an α-glycol and does not react with lead tetra-acetate (Criegee, *Ber.*, 1931, **64**, 260). On acetylation the triol yields

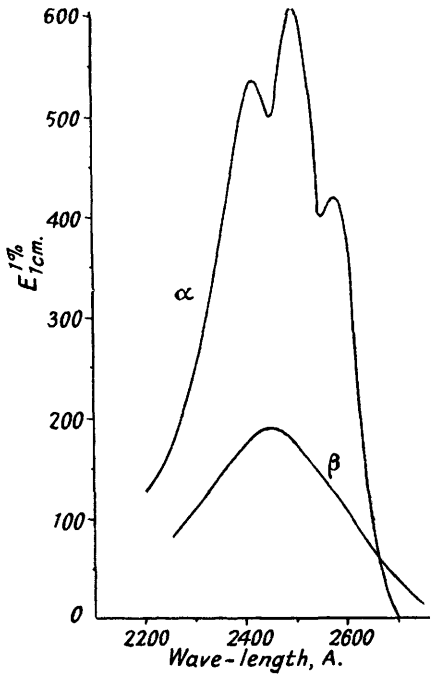


only a diacetate, $C_{31}H_{50}O_5$, m. p. 184·5°, which is formulated as 3 : 6-*diacetoxy*-5-*methyl*-$\Delta^{8:9}$-*norcholesten*-11-*ol* (VI; R = Ac). The inert character of the hydroxyl group at C_{11} in the diacetate is also shown by its resistance to benzoylation and to the Oppenauer oxidation with aluminium *tert.*-butoxide in acetone–benzene solution (*Rec. Trav. chim.*, 1937, **56**, 137). Its function as a secondary alcohol, however, is demonstrated by the ready formation in high yield of 3 : 6-*diacetoxy*-5-*methylnorcholestane*-11-*one*-8 : 9-*oxide* (VII; R = Ac), m. p. 160·5°, when the diacetate (VI; R = Ac) is oxidised with chromic acid. The simultaneous formation of an oxide ring on the ethylenic linkage of an αβ-unsaturated steroid alcohol with chromic acid has previously been observed (Rosenheim and King, *Nature*, 1937, **139**, 1015).

The constitution assigned to (VII) is confirmed by the observation that the same compound, m. p. 160·5°, is obtained by direct oxidation of Westphalen's diacetate (II; R = Ac) with chromic acid at 55—60°, presumably by way of (VI) as an intermediate. In analogy with the corresponding corticosterone derivative (Reichstein, *Helv. Chim. Acta*, 1937, **19**, 29), the carbonyl group at C_{11} does not react with ketonic reagents. Its inert character may be ascribed to steric hindrance of the oxide ring at $C_{8:9}$ in the present case.

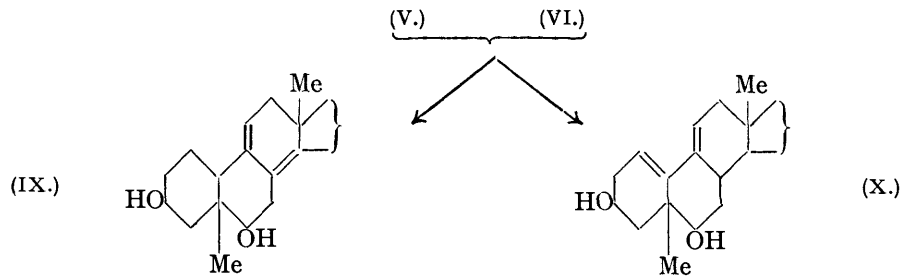
On hydrolysis with alcoholic potassium hydroxide, (VII) yields 5-*methylnorcholestane*-3 : 6-*diol*-11-*one*-8 : 9-*oxide* (VII*a*), m. p. 220°, which is readily oxidised to 5-*methylnorcholestane*-

3 : 6 : 11-*trione*-8 : 9-*oxide* (VIII), m. p. 166·5°. The trione does not react with lead tetra-acetate and its failure to yield a quinoxaline derivative with *o*-phenylenediamine and to give a coloration with ferric chloride proves the absence of an *o*-ketonic grouping. These observations supplement the evidence (see above) against the assignation to C_7 of the newly introduced hydroxyl or carbonyl group.



Absorption spectra of α- *and* β-3 : 6-*diacetoxy*-5-*methylnorcholestadienes in* cyclo*hexane solution.*

An interesting relationship has been found to exist between the oxidation products of Westphalen's diol obtained with selenium dioxide and with perbenzoic acid, which is unambiguously interpreted on the basis of the formulæ assigned to them (V and VI respectively). Both compounds easily undergo partial dehydration, (V) by treatment with alcoholic hydrochloric acid and (VI) by dehydration with sodium acetate–acetic anhydride. The main product in both cases is a doubly unsaturated diol, $C_{27}H_{44}O_2$, m. p. 102° (α-compound), accompanied by an isomeride, m. p. 182° (β-compound). The isomerides differ characteristically in their ultra-violet absorption spectra. The α-compound, to which the formula of 5-*methyl*-$\Delta^{8(14):9(11)}$-*norcholestadiene*-3 : 6-*diol* (IX) is assigned, shows a typical three-banded spectrum of high intensity (Figure), resembling that of ergosterol (Pohl, *Nachr. Ges. Wiss. Göttingen*, 1926, 185) and indicating a system of conjugated linkages situated in one ring. The absorption, however, is at a shorter wave-length than that of ergosterol and is of about twice the intensity. The ultra-violet absorption of the β-compound, on the other hand, shows a single band of low intensity, concordant with a system of conjugated ethylenic linkages spread over three rings as in (X).



In agreement with this assumption the β-compound forms easily and in good yield an adduct with maleic anhydride at 80°, whereas the α-compound behaves like ergosterol (Windaus and Luttringhaus, *Ber.*, 1931, **64**, 850) and is recovered unchanged under these conditions, forming an adduct only at 135°. Both compounds give an intense green Tortelli–Jaffé reaction and a blue colour with arsenic and antimony trichloride, and regenerate, in poor yield, Westphalen's diol on catalytic hydrogenation.

Experimental.

The analyses are microanalyses by Dr. G. Weiler, Oxford. Optical rotations were measured in chloroform solution in a 2-dm. tube. All melting points are corrected.

Dehydration of 5-*Hydroxy*-3 : 6-*diacetoxycholestane*.—(a) The sulphuric acid method of dehy-

dration employed by Westphalen (*loc. cit.*) is suitable only for quantities of material up to 2 g. (cf. J., 1934, 1580). For the preparation of larger quantities the following improved method was adopted: 50 G. of 5-hydroxy-3 : 6-diacetoxycholestane and 12 g. of potassium hydrogen sulphate were heated with 250 ml. of acetic anhydride for 15 mins. on the water-bath. The solution was poured into saturated brine and kept overnight. The crystalline precipitate was collected and recrystallised once (norit) from aqueous acetone. Yield 45—50%, m. p. 128°.

(b) 2 G. of 5-hydroxy-3 : 6-diacetoxycholestane, 0·5 g. of potassium hydrogen sulphate, and 8 ml. of propionic anhydride were heated for 15 minutes on the water-bath. The product, worked up as in (a), yielded prisms of the Westphalen diacetate, m. p. 127—128° alone or in admixture with an authentic specimen. Yield, 35%.

Dehydrogenation.—Westphalen's diacetate (40 g.) and selenium (40 g.) were heated for 1 hour at 300—310° and for a further 40 hours at 340—360°. The product was extracted (benzene), and the solution filtered through a column of active alumina. The fluorescent oil left on removal of the solvent (20 g.) was distilled in a vacuum. The fraction, b. p. 285—305°/15 mm., was dissolved in light petroleum; the yellow solid (150 mg.) deposited after 24 hours crystallised from acetic acid and acetic anhydride in faintly yellow plates of the "$C_{25}H_{24}$" hydrocarbon, m. p. 224—225° (Found: C, 92·9; H, 7·0. Calc.: C, 92·5; H, 7·5%), identified by its mixed melting point with an authentic specimen kindly supplied by Prof. J. W. Cook, no depression being obtained, and by its ultra-violet absorption spectrum (cf. Diels and Klare, *Ber.*, 1934, **67**, 113).

3 : 6-*Diacetoxy*-5-*methylnorcholestane*-8 : 9-*oxide* (V; R = Ac).—(a) 1 G. of Westphalen's diacetate in 25 ml. of acetic acid was treated for 2 days at room temperature with 1 ml. of perhydrol. The product was poured into saturated brine, and the precipitated solids crystallised from aqueous methyl alcohol–acetone. 3 : 6-*Diacetoxy*-5-*methylnorcholestane*-8 : 9-*oxide* formed flat needles, m. p. 132·5—133·5°, $[\alpha]_D^{18°}$ + 8·7° (*c*, 2·865) (Found: C, 74·2; H, 9·9. $C_{31}H_{50}O_5$ requires C, 74·1; H, 10·0%), readily soluble in the usual solvents. The compound gave no colour with tetranitromethane, and was unaffected by sodium acetate–acetic anhydride, 2 : 4-dinitrophenylhydrazine, and thionyl chloride in pyridine. It gave a positive Tortelli–Jaffé reaction and blue colours with arsenic trichloride and Rosenheim's mercury reagent (Rosenheim and Callow, *Biochem. J.*, 1931, **25**, 74). Yield, 30%.

(b) 1 G. of Westphalen's diacetate was treated with 4 ml. of a chloroform solution of perbenzoic acid containing 0·032 g. of active oxygen (equiv. to 1·1 atoms of oxygen) for 3 days at room temperature. The solution was washed with potassium hydroxide, the solvent removed, and the residue crystallised from aqueous acetone–methyl alcohol. 3 : 6-Diacetoxy-5-methylnorcholestane-8 : 9-oxide, obtained in a yield of 20%, was identified by m. p., mixed m. p., and optical rotation with the compound obtained by the action of perhydrol (above).

5-Methylnorcholestane-3 : 6-diol-8 : 9-oxide (V; R = H), obtained from the diacetate by hydrolysis with alcoholic potassium hydroxide, separated from aqueous acetone or from benzene as a jelly which became granular on standing, m. p. 174·5—175·5°, $[\alpha]_D^{19°}$ + 35·3° (*c*, 2·125).

5-*Methylnorcholestane*-3 : 6-*dione*-8 : 9-*oxide* (IV).—(a) 1 G. of Westphalen's diketone (Part II, *loc. cit.*) in 25 ml. of acetic acid was treated with 1 ml. of perhydrol for 3 days at room temperature. The product was poured into saturated brine and next day the precipitated solids were collected and crystallised from aqueous acetone. 5-*Methylnorcholestane*-3 : 6-*dione*-8 : 9-*oxide* formed long needles, m. p. 132—133° (softens at 120°), $[\alpha]_D^{19°}$ − 35° (*c*, 2·0) (Found: C, 78·1; H, 9·8. $C_{27}H_{42}O_3$ requires C, 78·2; H, 10·1%), readily soluble in most organic solvents. Yield, 55%. The *mono*-o-*tolylsemicarbazone* was obtained by warming a solution of the diketone (50 mg.) in alcohol (1 ml.) with a solution of *o*-tolylsemicarbazide in alcohol (5 ml., containing 2 drops of acetic acid) on the steam-bath; recrystallised from chloroform–alcohol, it formed rectangular plates, m. p. 224—225° (decomp.) (Found: N, 7·0. $C_{35}H_{51}O_2N_3$ requires N, 7·7%).

(b) 1 G. of 5-methylnorcholestane-3 : 6-diol-8 : 9-oxide in 15 ml. of benzene was shaken with 0·7 g. of chromic acid in 2 ml. of water and 20 ml. of acetic acid for 5 hours at room temperature. The neutral fraction of the oxidation product, on crystallisation from aqueous acetone–methyl alcohol, gave long needles of 5-methylnorcholestane-3 : 6-dione-8 : 9-oxide, m. p. 132—133°, $[\alpha]_D^{19°}$ − 35° (*c*, 2·0) (Found: C, 78·1; H, 9·9%). Yield, 65%.

5-*Methyl*-$\Delta^{8:9}$-*norcholestene*-3 : 6 : 11-*triol* (VI; R = H).—9 G. of Westphalen's diol in 300 ml. of spirit were treated with 9 g. of selenium dioxide in 30 ml. of water. Precipitation of selenium began almost immediately. After 5 hours at room temperature the precipitated selenium (1·28 g., equiv. to 0·87 atom of selenium) was filtered off, and the solution poured into water and extracted with ether. The extract was washed with potassium cyanide solution

until free from selenium, and the ether removed. The residual oil was refluxed with 150 ml. of light petroleum and kept overnight. The precipitated microcrystalline deposit was purified from boiling alcohol and boiling benzene. *5-Methyl-*$\Delta^{8:9}$*-norcholestene-3 : 6 : 11-triol* formed needles, m. p. 223° (decomp.) (Found : C, 77·2; H, 10·8. $C_{27}H_{46}O_3$ requires C, 77·5; H, 11·0%), sparingly soluble in the usual solvents. Yield, 25%. The compound gave a blue-green Tortelli–Jaffé reaction and a transient pink colour, followed by a peacock-blue, with arsenic trichloride.

3 : 6-Diacetoxy-5-methyl-$\Delta^{8:9}$*-norcholesten-11-ol* was prepared by treating the triol (1 g.) in pyridine (16 ml.) with 8 ml. of redistilled acetic anhydride for 3 days at room temperature. The liquid was poured into water, and the precipitated solids purified from aqueous acetone–methyl alcohol. The compound formed flat needles, m. p. 183·5—184·5°, $[\alpha]_D^{19°}$ — 21·0° (*c*, 2·49) (Found : C, 73·7; H, 9·9. $C_{31}H_{50}O_5$ requires C, 74·1; H, 10·0%), moderately readily soluble in the usual solvents. Yield, almost quantitative.

Attempts to acetylate the free hydroxyl group at C_{11} were not successful, dehydration occurring. Benzoyl chloride in pyridine was without effect. The compound was recovered unchanged after refluxing for 10 hours with the Oppenauer reagent in benzene–acetone solution.

3 : 6-Diacetoxy-5-methylnorcholestan-11-one-8 : 9-oxide (VII; R = Ac).—(a) 400 Mg. of 3 : 6-diacetoxy-5-methyl-$\Delta^{8:9}$-norcholesten-11-ol in 6 ml. of benzene were shaken with 250 mg. of chromic acid in 2 ml. of water and 8 ml. of acetic acid for 6 hours at room temperature. The neutral fraction of the oxidation product, purified from aqueous acetone–methyl alcohol, yielded needles of *3 : 6-diacetoxy-5-methylnorcholestan-11-one-8 : 9-oxide*, m. p. 159·5—160·5°, $[\alpha]_D^{19°}$ + 121° (*c*, 1·9) (Found : C, 71·4; H, 9·2. $C_{31}H_{48}O_8$ requires C, 72·1; H, 9·3%). Yield, 40%.

(b) To 400 mg. of 3 : 6-diacetoxy-5-methyl-$\Delta^{8:9}$-norcholesten-11-ol in 8 ml. of benzene were added dropwise with vigorous stirring during 4 hours at 0° 1·2 ml. of Kiliani's chromic acid mixture in 2 ml. of acetic acid. The neutral fraction of the oxidation product yielded 3 : 6-diacetoxy-5-methylnorcholestan-11-one-8 : 9-oxide in a yield of 60%.

(c) 2 G. of Westphalen's diacetate in 25 ml. of acetic acid were treated at 55—60°, with stirring, with a solution of 1·5 g. of chromic acid in 2 ml. of water and 3 ml. of acetic acid, added dropwise during 2 hours. After being kept for a further hour at this temperature, the liquid was diluted with water and extracted with ether. The neutral portion of the oxidation product was crystallised from aqueous methyl alcohol. 3 : 6-Diacetoxy-5-methylnorcholestan-11-one-8 : 9-oxide formed flat needles, m. p. 159·5—160·5°, $[\alpha]_D^{19°}$ + 120° (*c*, 2·035) (Found : C, 72·1; H, 9·2%). Yield, 30%. The compound did not show the steroid colour reactions and did not contain a hydroxyl group (negative Zerewitinoff test). It was recovered unchanged after treatment with acetic anhydride, hydroxylamine, and 2 : 4-dinitrophenylhydrazine. Bromine was absorbed after a short period of induction. The compound did not show selective absorption in the ultra-violet.

Attempts to reduce the keto-group were not successful. Aluminium *iso*propoxide was without effect; sodium in alcohol yielded a gum. Attempts to hydrolyse the oxide ring with alcoholic hydrochloric acid failed owing to resinification.

Hydrolysis of the diacetate with excess of 5% methyl-alcoholic potassium hydroxide, followed by crystallisation from aqueous methyl alcohol, gave *5-methylnorcholestane-3 : 6-diol-11-one-8 : 9-oxide* (VII*a*) in fine silky needles, m. p. 219—220° (sintering at 203°), $[\alpha]_D^{19°}$ + 123° (*c*, 1·5) (Found : C, 74·6; H, 10·3. $C_{27}H_{44}O_4$ requires C, 75·0; H, 10·2%), readily soluble in acetone and alcohol, and sparingly soluble in light petroleum. Yield, almost quantitative. On acetylation the original diacetate, m. p. 160·5°, was obtained. The compound was unaffected by lead tetra-acetate.

5-Methylnorcholestane-3 : 6 : 11-trione-8 : 9-oxide (VIII).—A suspension of 1 g. of 5-methylnorcholestane-3 : 6-diol-11-one-8 : 9-oxide in 15 ml. of benzene was shaken for 6 hours with a solution of 0·66 g. of chromic acid in 7 ml. of water and 15 ml. of acetic acid. The neutral fraction of the oxidation product was purified from aqueous acetone–methyl alcohol and yielded flat needles (0·58 g.) of *5-methylnorcholestane-3 : 6 : 11-trione-8 : 9-oxide*, m. p. 165·5—166·5°, $[\alpha]_D^{19°}$ + 134° (*c*, 2·0) (Found : C, 75·4; H, 9·2. $C_{27}H_{40}O_4$ requires C, 75·7; H, 9·3%), readily soluble in the usual solvents. The compound was recovered unchanged after (a) refluxing with acetic anhydride–sodium acetate, (b) treatment with hydrogen chloride in chloroform, and (c) refluxing for 1 hour with 5% alcoholic sulphuric acid. It did not give a coloration with ferric chloride or yield a quinoxaline derivative on heating with *o*-phenylenediamine at 140—150° for 35 minutes. Lead tetra-acetate at room temperature was without effect.

α- *and* β-*5-Methylnorcholestadiene-3 : 6-diols*.—(a) 1 G. of 3 : 6-diacetoxy-5-methylnorcholestane-8 : 9-oxide in 20 ml. of spirit was refluxed for 30 minutes with 1 ml. of concentrated

hydrochloric acid, the solution turning pink. The oily product, isolated with ether, was refluxed for 1 hour with 8 ml. of acetic anhydride and 1 g. of anhydrous sodium acetate, and the excess of acetic anhydride decomposed with water. The product was fractionated from aqueous methyl alcohol–acetone (norit), β-**3** : 6-*diacetoxy-5-methylnorcholestadiene* separating first in large needles, m. p. 167·5°, $[\alpha]_D^{19°}$ — 36·6° (*c*, 2·05) (Found : C, 76·8; H, 9·8. $C_{31}H_{48}O_4$ requires C, 76·8; H, 9·9%). Yield, 15%. The mother-liquors yielded fine needles of the α-**3** : 6-*diacetoxy-5-methyl-*$\Delta^{8(14):9(11)}$*-norcholestadiene*, m. p. 126—127°, $[\alpha]_D^{19°}$, — 45·8° (*c*, 2·075) (Found : C, 76·7; H, 9·8. $C_{31}H_{48}O_4$ requires C, 76·8; H, 9·9%). Yield, 30%.

(b) 350 Mg. of **3** : 6-diacetoxy-5-methyl-$\Delta^{8:9}$-norcholesten-11-ol were refluxed for 3 hours with 10 ml. of acetic anhydride and 1 g. of anhydrous sodium acetate. The product was poured into water, and the precipitated material collected and fractionally crystallised from aqueous acetone–methyl alcohol (norit). β-**3** : 6-Diacetoxy-5-methylnorcholestadiene, m. p. 167·5°, was obtained from the least soluble fraction, and α-**3** : 6-diacetoxy-5-methylnorcholestadiene, m. p. 126—127°, from the more soluble fraction, identified in each case by mixed m. p.

The absorption spectrum of the α-isomeride showed a main maximum at 2500 A. ($E_{1cm.}^{1\%}$ = 610) and two subsidiary maxima at 2420 A. ($E_{1cm.}^{1\%}$ = 535) and 2580 A. ($E_{1cm.}^{1\%}$ = 420). The β-compound, on the other hand, showed a broad maximum at 2540 A. ($E_{1cm.}^{1\%}$ = 190).

Hydrolysis of the diacetates with alcoholic potassium hydroxide gave the corresponding diols. The α-isomeride, *5-methyl-*$\Delta^{8(14):9(11)}$*-norcholestadiene*-**3** : 6-*diol* (IX), formed large irregular plates from aqueous methyl alcohol, m. p. 95—102°, $[\alpha]_D^{19°}$ — 46·7° (*c*, 2·035) (Found : C, 77·7; H, 10·7. $C_{27}H_{44}O_2,H_2O$ requires C, 77·5; H, 11·0%), readily soluble in alcohol and acetone, and sparingly soluble in light petroleum. The compound slowly turned yellow on exposure to light. The β-*isomeride* (X) formed needles from aqueous methyl alcohol, m. p. 182°, $[\alpha]_D^{19°}$ — 47° (*c*, 2·04) (Found : C, 80·8; H, 10·8. $C_{27}H_{44}O_2$ requires C, 81·0; H, 11·0%), readily soluble in most organic solvents except benzene and light petroleum.

Addition of Maleic Anhydride.—(a) 200 Mg. of α-**3** : 6-diacetoxy-5-methylnorcholestadiene, 200 mg. of maleic anhydride, and 2 ml. of xylene were heated for 14 hours in an evacuated tube at 135°. The xylene was removed in a vacuum, and the residue hydrolysed by refluxing for 1 hour with 0·5 g. of potassium hydroxide and 5 ml. of methyl alcohol. The solution was considerably diluted with water, and the unchanged material (0·08 g.) removed by three extractions with light petroleum (25 ml. per portion). The endo-*succinic acid*, obtained by acidification of the aqueous alkaline fraction with dilute hydrochloric acid and extraction with ether, formed silky needles from alcohol–light petroleum, m. p. 213° (Found : C, 71·7; H, 9·3. $C_{31}H_{48}O_6$ requires C, 72·1; H, 9·3%).

(b) 200 Mg. of β-**3** : 6-diacetoxy-5-methylnorcholestadiene, 200 mg. of maleic anhydride, and 2 ml. of benzene were heated in an evacuated tube at 80° for 14 hours. The product was worked up as in (a) (unchanged material, 0·005 g.). The endo-*succinic acid*, on crystallising from from alcohol–light petroleum, formed short hard needles, m. p. 190° (decomp.) (Found : C, 71·5; H, 9·0. $C_{31}H_{48}O_6$ requires C, 72·1; H, 9·3%).

The α-isomeride was recovered unchanged after similar treatment.

Reduction.—(a) *With sodium in ethyl alcohol.* 200 Mg. of β-**3** : 6-diacetoxy-5-methylnorcholestadiene in 12 ml. of alcohol were treated under reflux during 1 hour with 1 g. of sodium. The product, after acetylation, was fractionated from aqueous methyl alcohol. The least soluble fraction (110 mg.) was unchanged material; the mother-liquors yielded 30 mg. of Westphalen's diacetate, identified by m. p. and mixed m. p.

The α-isomeride was recovered unchanged after similar treatment.

(b) *Catalytic.* 300 Mg. of the diacetoxy-diene, 200 mg. of palladium–charcoal, and ether–acetic acid solvent were employed. Several experiments were carried out with each isomeride, the hydrogen absorbed varying from 1·3—1·7 molecular equivalents. Various quantities of Westphalen's diacetate, m. p. 125°, were isolated in each case, together with oily material which gave a blue arsenic trichloride reaction.

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