695. *Lanosterol. Part XIII.* Further Experiments on the Constitution of Lanostadienol.*

By J. F. CAVALLA, J. F. McGHIE, and M. K. PRADHAN.

Diketolanostanol and phosphorus pentachloride have been shown to give *iso*lanostenedione which may be further isomerized to give an αβ-unsaturated diketone. The isomerization of lanostenyl acetate has been reinvestigated, and pure *iso*lanostenyl acetate isolated by two routes. Some further examples of bond migration in substituted lanostadienol derivatives are given.

IN Part XII * we summarised the more important facts on the basis of which a partial formula for the tetracyclic triterpenoid alcohol lanostadienol might be suggested, although at the time no actual formula was put forward. Recently the Swiss school have advanced the partial formula (I) for lanostadienol (Voser, Montavon, Günthard, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 1893). This formula was suggested by Dr. D. H. R. Barton, in personal discussion with the senior author, considerably before the appearance of the Swiss communication. We have used this partial structure as a background for subsequent investigation and we now submit evidence which supports it.

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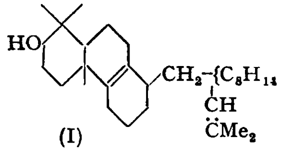
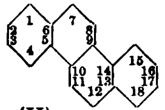
* Part XII, *J.*, 1951, 2474.

From the dehydrogenation of "lanosterol" with selenium (Schulze, *Z. physiol. Chem.*, 1936, **190**, 52) to 1 : 2 : 8-trimethylphenanthrene the presence of at least three six-membered rings in lanostadienol may be assumed. Furthermore, if we take into account the isolation of a tetramethylchrysene (Ruzicka, Rey, and Muhr, *Helv. Chim. Acta*, 1944, **27**, 472), provisionally assigned the 1 : 2 : 7 : 8-structure, we may interpret the ring system of lanostadienol



(I)



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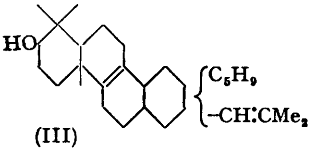
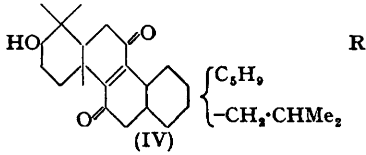


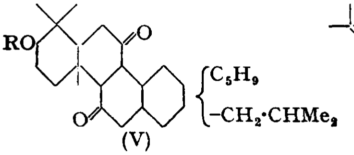
(III)

on the basis of perhydrochrysene (II; numbering as in triterpenes). This may be expanded to (III), by the incorporation of all the known structural features: the inert ethylenic bond is placed at the 9 : 10-bridgehead position, in accordance with formula (I), and we provide confirmatory evidence of this.

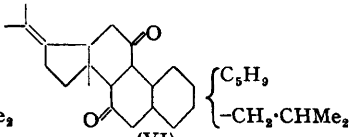
Oxidation of either lanostenyl or γ-lanostadienyl acetate is known to give diketolanostenyl acetate (Ruzicka, Rey, and Muhr, *loc. cit.*; Dorée and McGhie, *Nature*, 1944, **153**, 148; Cavalla and McGhie, *J.*, 1951, 834), which is reduced under fairly mild conditions to diketolanostanyl acetate (Dorée, McGhie, and Kurzer, *J.*, 1948, 988). On the basis of (III) for lanostadienol these may be formulated as (IV) and (V; R = Ac) respectively. Hydrolysis of (V; R = Ac) gave hydroxylanostanedione (V; R = H) and this on treatment with phosphorus pentachloride under the conditions resulting in a retropinacolinic change gave either of two products, depending on the reaction conditions. Under the conditions outlined by Dorée, McGhie, and Kurzer (*J.*, 1947, 1467), for the dehydration of lanostenol and γ-lanostadienol, the only crystalline compound which could be isolated had m. p. 183—184°, considerably depressed on admixture with the starting material. The compound on analysis was found to contain chlorine and was not further investigated. Modification of the reaction conditions gave a substance, m. p. 146—147°, $[\alpha]_D$ +79·4°, which gave analytical figures in good agreement for an *iso*lanostenedione, $C_{30}H_{48}O_2$ (VI), a retropinacolinic change having taken place in its formation from hydroxylanostanedione.



(IV)



(V)

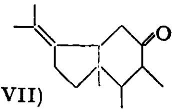


(VI)

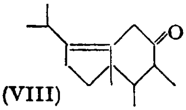
*iso*Lanostenedione was strongly unsaturated to tetranitromethane; lack of high-intensity absorption in the ultra-violet region indicated the absence of a conjugated system, *iso*lanostenedione being correctly represented as (VI).

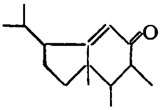
Treatment of *iso*lanostenedione with hydrochloric acid in acetic acid gave an isomer, m. p. 126°, $[\alpha]_D$ +71°, which unlike its precursor had an absorption maximum at 240 mμ. (log ε 3·98), indicative of the presence of an $\alpha\beta$-unsaturated keto-group. Its formation is readily explained by the partial formula (VII)—(IX), the $\gamma\delta$-ethylenic bond in (VII) passing through the unstable $\beta\gamma$-intermediate (VIII) to give the more stable $\alpha\beta$-unsaturated ketone (IX). These experiments strongly support formula (I) for lanostadienol.

(VII)



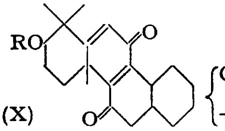
(VIII)



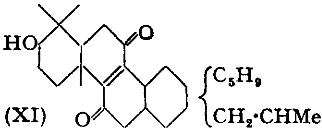


(IX)

In an attempt to avoid the necessity for acid isomerization of the intermediate olefin we turned our attention to dehydrodiketolanostenyl acetate (X; R = Ac) (Voser *et al.*, *loc. cit.*; Cavalla and McGhie, *J.*, 1951, 744). Voser *et al.* considered that this compound contained an ethylenic bond more than the starting material diketolanostenyl acetate (XI). We have confirmed this in the following manner: Mild reduction of (X; R = Ac) with zinc dust in acetic acid gave a compound, m. p. 177—179°, $[\alpha]_D$ +5·0°, possessing an absorption maximum at 237 mμ. (log ε 4·12); the characteristic maximum of the unsaturated 1 : 4-diketo-grouping ·CO·C:C·CO· at 275 mμ. (log ε 4·2) has disappeared, reduction occurring at the ethylenic bond between the two carbonyl groups. This reduction product was identical with a compound first obtained by Dorée McGhie, and Kurzer (*J.*, 1949, 570) by dehydrogenation of diketolanostanyl acetate with selenium dioxide; consequently the dehydrodiketolanostenyl acetate is correctly represented as (X).



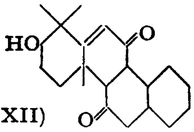
(X)



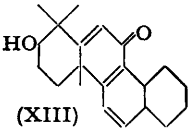
(XI)

Dehydration of the alcohol (X; R = H) with phosphorus pentachloride has, as yet, given no crystalline product (we are continuing our experiments).

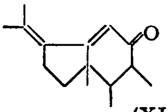
We early recognised that the most suitable compounds for further investigations of retropinacolinic change in the lanostadienol group were hydroxylanostenedione (XII) and hydroxylanostatrienone (XIII) (partial formulæ). Both compounds already contain the keto-group



(XII)



(XIII)



(XIV)

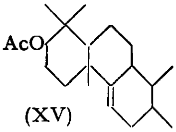
at $C_{(8)}$ and the αβ-ethylenic bond in the 6 : 7-position, and thus in the retropinacolinic rearrangement would give the extended conjugated system (XIV). Unfortunately, although the acetates are readily available, we have been unable to hydrolyse them satisfactorily, and we defer our report on this work.

The above-mentioned experiments are all primarily concerned with the inert 9 : 10-olefinic bond of lanostadienol. We next turned our attention to the isomeric *iso*lanostenyl acetate. Conflicting results have been reported concerning the product obtained by hydrogen chloride isomerization of lanostenol or its acetate. Marker, Wittle, and Mixon (*J. Amer. Chem. Soc.*, 1937, **59**, 1368) reported the values m. p. 147—149° and 162° for *iso*lanostenyl acetate and the alcohol respectively; Wieland and Benend (*Z. physiol. Chem.*, 1942, **274**, 215) reported m. p. 129—130°, $[\alpha]_D$ +46·6°, and m. p. 135—136°, $[\alpha]_D$ +38·0°, respectively; Muhr (Thesis, Zurich, 1945) gave m. p. 132—133°, $[\alpha]_D$ +45·6°, for *iso*lanostenol. Reinvestigation has shown that the compounds described by Wieland and Benend and by Muhr (*locc. cit.*) are mixtures of lanostenyl and *iso*lanostenyl acetates (or alcohols) in varying proportions, but the *iso*lanostenyl acetate described by Marker *et al.* (*loc. cit.*) is pure; when the mixtures obtained by Wieland *et al.* and by Muhr were worked up as laid down by Marker *et al.* (*loc. cit.*) they gave a product, m. p. 146—147°, $[\alpha]_D$ +28·9°, identical with that of Marker *et al.* Marker *et al.* separated their lanostenyl and *iso*lanostenyl acetates by making use of the observation that lanostenyl acetate is more readily attacked by chromic acid under mild conditions : however, these conditions are practically identical with those for the preparation of ketolanostenyl acetate (Marker *et al.*, *loc. cit.*; see also Birchenough and McGhie, *J.*, 1950, 1249), and the melting point of *iso*lanostenyl acetate (147—149°) is very close to that of ketolanostenyl acetate (151—152°). The possibility that the product might be impure ketolanostenyl acetate was ruled out, since analysis gave values agreeing well with the formula $C_{32}H_{54}O_2$. Conclusive evidence of non-identity was that *iso*lanostenyl acetate gave no high-intensity absorption at 255 mμ., characteristic of ketolanostenyl acetate.

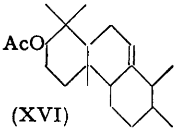
McGhie (Thesis, London, 1947) concluded that the ethylenic bond of *iso*lanostenyl acetate is close to the position occupied in lanostenyl acetate, since *iso*lanostenyl acetate on dehydrogenation with selenium dioxide, and on oxidation with chromic acid, gave the same products (γ-lanostadienyl acetate and diketolanostenyl acetate respectively) as are obtained from lanostenyl acetate. We have confirmed and extended these observations, and have found that either keto- or diketo-lanostenyl acetate may be obtained in the chromic acid oxidation depending on the reaction conditions. Furthermore, oxidation of *iso*lanostenyl acetate with perbenzoic acid afforded both γ-lanostadienyl acetate and ketolanostenyl acetate, the latter presumably arising from the former by further oxidation (see Birchenough and McGhie, *J.*, 1949, 2038; 1950, 1249).

We have also discovered an alternative, more convenient route to *iso*lanostenyl acetate : ketolanostenyl acetate is subjected to Wolff–Kishner reduction in diethylene glycol (Herr, Whitmore, and Schliessler, *J. Amer. Chem. Soc.*, 1945, **67**, 2061); *iso*lanostenyl acetate, m. p. 146—147°, $[\alpha]_D$ +30·0°, is obtained.

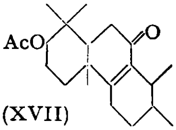
From these experiments it is apparent that bond migration has occurred both in the hydrogen chloride isomerization and in the Wolff–Kishner reduction, and if, as has been postulated, the position of the olefinic bond in *iso*lanostenyl acetate is very close to that in lanostenyl acetate, we can assign two possible partial formulæ (XV and XVI) to *iso*lanostenyl acetate. Formula



(XV)



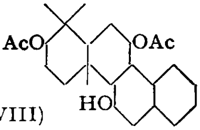
(XVI)



(XVII)

(XV) has already been provisionally assigned to a compound isomeric with *iso*lanostenyl acetate by Voser *et al.* (*loc. cit.*), leaving only (XVI) to be considered; ketolanostenyl acetate may then be represented by (XVII). This implies that the more reactive methylenic group in lanostadieno is at $C_{(8)}$, and we hope later to present confirmatory evidence of this.

It is of interest that bond migration also occurs in compounds derived from structures analogous to (XV). In Part XI (*J.*, 1951, 834) we reported the dehydration of diacetoxylanostanol (XVIII) to diacetoxylanostene which is best represented as (XIX; R = Ac).



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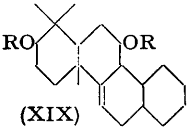
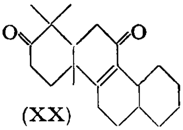
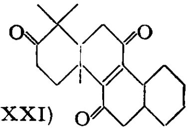


(XIX)



(XX)



(XXI)

Oxidation of the corresponding diol (XIX; R = H) has afforded a colourless diketone, m. p. 148—149°, $[\alpha]_D$ +17·8°, and a yellow triketone, m. p. 108—109°, $[\alpha]_D$ +16·9°. The former shows an absorption maxima at 254 mμ. (log ε 4·03), indicating the presence of an unsaturated keto-grouping, the ethylenic bond in the 10 : 11-position moving into conjugation with the keto-group at $C_{(8)}$. This diketone is identical with that obtained by the mild oxidation of lanostenol (Wieland and Joost, *Annalen*, 1941, **546**, 103; McGhie, *loc. cit.*), and is to be represented as (XX). The triketone is identical with triketolanostene prepared by the oxidation of diketolanostenol (Ruzicka, Rey, and Muhr, *loc. cit.*; see also McGhie, *loc. cit.*), and is to be represented by the partial formula (XXI).

After these experiments we learnt that Barton, Fawcett, and Thomas had independently reached similar conclusions about the position of the inert ethylenic bond in lanostadienol, and had also carried out some analogous experiments on the constitution of *iso*lanostenyl acetate (see following paper). The results reported in the two papers are in excellent agreement. We thank Dr. D. H. R. Barton for informing us of his results before their general publication.

EXPERIMENTAL.

All m. p.s are uncorrected. Specific rotations were measured in chloroform solution at 20°.* The aluminium oxide used in the chromatographic work was from Messrs. Peter Spence Ltd. (Grade " O "). Analyses are by Drs. Weiler and Strauss, Oxford. Light petroleum refers to the fraction of b. p. 60—80°.

Dehydration of Hydroxylanostanedione with Phosphorus Pentachloride.—Diketolanostanyl acetate on alkaline hydrolysis gave hydroxylanostanedione, m. p. 190—191°, $[\alpha]_D^{20}$ +57·7° (*c*, 2·947) (Doree, McGhie, and Kurzer, *J.*, 1948, 988, give m. p. 183—184°, $[\alpha]_D$ +26°).

(*a*) Hydroxylanostanedione (1·5 g.) in dry light petroleum (150 ml.), was treated at room temperature with phosphorus pentachloride (1·5 g.) for 2 hours with constant stirring. The mixture was refluxed for a further hour, then poured into water, the light petroleum layer was washed repeatedly with water, and the solvent removed *in vacuo*, leaving a viscous oil. Passage of this through a column of alumina (10 × 1·3 cm.), in light petroleum (200 ml.) as a carrier, and then elution of the column with light petroleum (500 ml.), followed by removal of the solvent, gave a white solid (0·4 g.). This after two further recrystallizations had m. p. 183—184°, depressed (by 20—30°) on admixture with the starting material, and gave a positive Beilstein test (Found: C, 70·5; H, 9·3%).

(*b*) Reaction was carried out as above, but with half the amount of phosphorus pentachloride. The reaction product, worked up as before, gave a semi-solid material. This was absorbed on alumina from light petroleum (100 ml.) and gave the following fractions on elution: (i) light petroleum (150 ml.), 0·05 g., m. p. 139—144° (from methanol); (ii) light petroleum (150 ml.), 0·09 g., m. p. 140—144° (from methanol); (iii) light petroleum–benzene (4 : 1), 0·4 g., m. p. 140—141° (from methanol); (iv) light petroleum–benzene (1 : 4), 0·15 g., amorphous, m. p. 119—124°. Fractions (i), (ii), and (iii), recrystallized together twice from methanol, gave white felting needles of iso*lanostenedione*, m. p. 146—147°, $[\alpha]_D^{20}$ +80·2 (*c*, 2·5) (Found: C, 81·9; H, 10·7. $C_{30}H_{48}O_2$ requires C, 81·8; H, 11·0%).

(*c*) The most satisfactory preparation of *iso*lanostenedione is as follows. A suspension of diketolanostanol (3 g.) and phosphorus pentachloride (1·8 g.) in light petroleum (250 ml.) was stirred for 90

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* In previous papers in this series (Part IV onwards), all concentrations were expressed as g. per c.c.

minutes, by which time dissolution was complete. The unchanged pentachloride was decomposed by water (70 ml.), and the product worked up to give a brownish solid. Chromatographic purification on alumina, with light petroleum (150 ml.) as the carrier, followed by elution with light petroleum (3 × 200 ml.), gave the following fractions (each crystallized from methanol) : 0·5 g., m. p. 138—142°; 0·4 g., m. p. 134—139°; 0·5 g., m. p. 112—122°. The first two fractions, recrystallized together from methanol, gave *iso*lanostenedione (0·7 g.), m. p. 145—146°, $[\alpha]_D^{20}$ +79·4 (*c*, 2·2).

Isomerization of iso*Lanostenedione.*—*iso*Lanostenedione (0·9 g.) was refluxed for 14 hours, with concentrated hydrochloric acid (50 ml.) and acetic acid (200 ml.). The solution was poured into water, and worked up in the usual manner, to give a pale brown oil (0·75 g.). This was adsorbed from light petroleum (100 ml.) on a column of alumina (12 × 1·3 cm.). Elution of the column with light petroleum (4 × 200 ml.) gave negligible quantities of oil which on crystallization from methanol gave amorphous products. Elution with light petroleum–benzene (1 : 1; 250 ml.) gave a pale yellow oil (0·55 g.) which crystallized from methanol in hard blades (0·45 g.), m. p. 94—98°. These were purified further by chromatography, to give the *αβ*-conjugated *isomer* in hard needles, m. p. 126° (0·2 g.), $[\alpha]_D^{20}$ +71·0° (*c*, 2·281) (Found : C, 81·6; H, 10·6. $C_{30}H_{48}O_2$ requires C, 81·8; H, 10·9%). Absorption : Max., 240 mμ. (log ε, 3·98) in alcohol.

Reduction of Dehydrodiketolanostenyl Acetate.—Dehydrodiketolanostenyl acetate (0·3 g.) (Voser, Montavon, Gunthard, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 1893; Cavalla and McGhie, *J.*, 1951, 744) in glacial acetic acid (40 ml.) was treated at 80° with zinc dust (approx. 2 g., added in portions). The lemon-yellow solution was rapidly decolorized, and was allowed to remain in contact with the zinc for 30 minutes with occasional shaking. The supernatant liquor was decanted, the residual zinc was washed with warm acetic acid, and the washings were combined with the main solution, and the whole was then diluted with water and extracted with ether. The ethereal solution was washed successively with water, dilute sodium carbonate solution, and water, and the solution dried (Na_2SO_4). Removal of the ether gave a white solid, which after two crystallizations from methanol gave felting white plates of dehydrodiketolanostanyl acetate (0·2 g.), m. p. 177—179°, $[\alpha]_D^{20}$ +5·0° (*c*, 3·0) (Found : C, 77·0; H, 19·1. Calc. for $C_{32}H_{50}O_4$: C, 77·1; H, 10·1%). Absorption : Max., 237 mμ. (log ε, 4·12) in alcohol.

Dehydration of Dehydrohydroxylanostenedione with Phosphorus Pentachloride.—Dehydrohydroxylanostenedione (1 g.) {obtained by hydrolysis of the corresponding acetate; m. p. 135—137°, $[\alpha]_D^{20}$ +82·2° (*c*, 3·2)} and phosphorus pentachloride (0·6 g.) in light petroleum (150 ml.), treated as described in (*b*) and (*c*) for hydroxylanostanedione, did not give a crystalline product, nor did reduction of the oil as described above for the conversion of dehydrodiketolanostanyl acetate.

Isomerization of Lanostenyl Acetate.—A solution of lanostenyl acetate (5 g.) in dry chloroform (80 ml.) was treated under reflux at 0°, for periods varying from 1 to 8 hours. The products so obtained (4·0—4·5 g.) had m. p.s in the range 126—134°. Each was worked up separately by the procedure of Marker, Wittle, and Mixon (*J. Amer. Chem. Soc.*, 1937, **59**, 1368) for *β*-dihydrolanosteryl acetate (*iso*lanostenyl acetate). Chromatographic purification then afforded identical products of m. p. 146—147°, $[\alpha]_D^{20}$ +30·0° (*c*, 4·0) (Found : C, 81·5; H, 11·6. Calc. for $C_{32}H_{54}O_2$: C, 81·6; H, 11·6%). These products were identical with an authentic specimen of *iso*lanostenyl acetate, m. p. 147—148°, $[\alpha]_D^{20}$ +28·9° (*c*, 3·6), prepared according to Marker *et al.* (*loc. cit.*).

Dehydrogenation of iso*Lanostenyl Acetate with Selenium Dioxide.*—To a solution of *iso*lanostenyl acetate (1 g.) in acetic acid (50 ml.) was added a solution of selenium dioxide (1 g.) in water (0·5 ml.). The mixture was heated under reflux for 3 hours, filtered from selenium, poured into water, and worked up in the usual manner, to give *γ*-lanostadienyl acetate, m. p. 168—169°, $[\alpha]_D^{20}$ +88·1° (*c*, 3·1) (Found : C, 81·92; H, 11·2%).

Oxidation of iso*Lanostenyl Acetate with Chromic Acid.*—(a) *Formation of ketolanostenyl acetate. iso*Lanostenyl acetate (1 g.) in glacial acetic acid (30 ml.) was treated with chromic acid (0·3 g.) in 90% acetic acid (4 ml.) as described by Marker *et al.* (*loc. cit.*) (see also Birchenough and McGhie, *J.*, 1950, 1249). The product, ketolanostenyl acetate (50—70 mg.), after chromatographic purification and repeated crystallization, had m. p. 151—152° alone or mixed with an authentic specimen, and $[\alpha]_D^{20}$ +20° (*c*, 3·2) Found : C, 79·2; H, 11·0. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%). Absorption : Max., 255 mμ. (log ε, 4·1) in alcohol.

(b) *Formation of diketolanostenyl acetate.* Oxidation of *iso*lanostenyl acetate as described by Cavalla and McGhie, *J.*, 1951, 834, gave pure lanostenedionyl acetate, m. p. 158° alone or in admixture with an authentic specimen, $[\alpha]_D^{20}$ +92·0 (*c*, 2·4).

Perbenzoic Acid Oxidation of iso*Lanostenyl Acetate.*—*iso*Lanostenyl acetate (1 g.) in chloroform (30 ml.) was treated with a chloroform solution of perbenzoic acid (equiv. to 0·08 g. of active oxygen), following the method of Birchenough and McGhie (*J.*, 1949, 2039). The product was worked up in the usual way, dissolved in light petroleum (100 ml.), and adsorbed on a column of alumina (15 × 1·3 cm.). Elution with light petroleum (200 ml.) gave *γ*-lanostadienyl acetate (0·3 g.), m. p. 167—169°, $[\alpha]_D^{20}$ +87·0° (*c*, 2·61) (Found : C, 81·9; H, 11·0. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%). Absorption : Max., 243 and 252 mμ. (log ε, 4·24 and 4·02 respectively). Further elution with light petroleum–benzene (1 : 1) gave ketolanostenyl acetate (0·1 g.), m. p. 151—152°, $[\alpha]_D^{20}$ +22·0° (*c*, 3·9) (Found : C, 79·2; H, 10·7%). Absorption : Max., 256 mμ. (log ε, 4·1) in alcohol.

Attempted Hydrogenation of iso*Lanostenyl Acetate.*—*iso*Lanostenyl acetate (0·5 g.) and a platinum catalyst (from platinic oxide, 0·3 g.) in glacial acetic acid (50 ml.) were shaken in hydrogen at 60° for 3 hours. No absorption took place, and *iso*lanostenyl acetate, m. p. 146°, $[\alpha]_D^{20}$ +29·0° (*c*, 2·23), was recovered.

Modified Wolff–Kishner Reduction of Ketolanostenyl Acetate.—Ketolanostenyl acetate (1·0 g.) in diethylene glycol (20 ml.) was refluxed with hydrazine hydrate (1 ml.; 100%), for 30 minutes. The mixture was cooled, a solution of sodium (1 g.) in diethylene glycol (10 ml.) was added, and the mixture heated under reflux at 210—220° for 6 hours. The cooled solution was diluted with water, extracted with ether, and washed with water, and the ethereal solution dried (Na_2SO_4). Removal of the ether gave a light brown solid (0·8 g.). This was acetylated with pyridine (5 ml.) and acetic anhydride (20 ml.) on a steam-bath for 3 hours. The product was worked up in the usual manner, to give the acetate (0·7 g.). This was absorbed on a column of alumina (12 × 1·3 cm.) from light petroleum (100 ml.); elution with light petroleum (300 ml.) gave a product (0·3 g.), m. p. 135—136° (from acetone–methanol); this was impure *iso*lanostenyl acetate, brought by several recrystallizations to m. p. 144—145°, $[\alpha]_D^{20}$ +28·1° (*c*, 2·0). Further elution with light petroleum–benzene (1 : 1) (150 ml.) gave a white solid (0·3 g.) which, recrystallized from benzene–methanol, gave pure *iso*lanostenyl acetate, m. p. 146°, $[\alpha]_D^{20}$ +28·8° (*c*, 3·3) (Found : C, 81·4; H, 11·8. Calc. for $C_{32}H_{54}O_2$: C, 81·6; H, 11·6%). This gave no m. p. depression with authentic *iso*lanostenyl acetate, but gave a depression of 25° with the starting material.

Oxidation of Lanostenediol.—Hydrolysis of diacetoxylanostene (Cavalla and McGhie, *J.*, 1951, 834) gave *lanostenediol* in hard translucent plates, m. p. 213—214°, $[\alpha]_D^{20}$ +94·0° (*c*, 3·1) (Found : C, 81·2; H, 11·4. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%). The diol (1 g.) in glacial acetic acid (100 ml.) was treated at room temperature with a solution of chromic acid (1·5 g.) in 90% acetic acid (15 ml.). The solution was shaken at this temperature for 1 hour, then poured into water, and the excess of oxidant destroyed by sulphurous acid. Working up in the usual manner gave a yellow oil, which was adsorbed on a column of alumina (12 × 1·3 cm.) from light petroleum (100 ml.). Elution with light petroleum–benzene (1 : 1) (500 ml.) gave a white solid (0·5 g.) which crystallized from methanol in felting plates, m. p. 147—149°, $[\alpha]_D^{20}$ +17·8° (*c*, 1·80) (Found : C, 81·9; H, 11·1. Calc. for $C_{30}H_{48}O_2$: C, 81·8; H, 11·0%). Absorption : Max., 254 mμ. (log ε, 4·03). This was identical with the diketolanostene prepared from lanostenol by the method of Wieland and Joost (*Annalen*, 1941 **546** 103). Further elution of the column with benzene (350 ml.) gave a yellow oil (0·3 g.); three recrystallizations from aqueous methanol gave yellow needles of lanostenetrione m. p. 108—109° $[\alpha]_D^{20}$ +169·0° (*c*, 3·7) (Found : C, 79·7; H, 10·5. Calc. for $C_{30}H_{46}O_3$: C, 79·2; H, 10·2%). Absorption : Max., 271 mμ. (log ε, 4·02).

The authors are indebted to Dr. D. H. R. Barton for very helpful discussions and suggestions, to Mr. P. Barker for the specific rotations, and to Professor H. Burton for facilities for the determination of absorption data. One of us (J. F. C.) acknowledges the award of a maintenance grant from the Department of Scientific and Industrial Research.

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[*Received, May* 30*th*, 1951.]