738. *Triterpene Resinols and Related Acids. Part XXVIII.* The Non-saponifiable Fraction from* Strychnos nux-vomica *Seed Fat: The Structure of* cyclo*Artenol.*

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The non-saponifiable fraction from the seed fat of *Strychnos nux-vomica L.* contains α-amyrin, *cyclo*artenol, and stigmasterol. *cyclo*Artenol is shown to be a *cyclo*lanost-24-enol containing a *cyclo*propane bridge extending from $C_{(9)}$ (cf. *Chem. and Ind.*, 1953, 217).

After preliminary work by Schröder (*Arch. Pharm.*, 1905, **243**, 633), the non-saponifiable fraction of *Strychnos nux-vomica* seed fat was investigated in some detail by Heiduschka and Wallenreuter (*ibid.*, 1912, **250**, 398; 1915, **253**, 202) who isolated three crystalline alcohols. One of these, m. p. 158°, was described as a phytosterol, analysis of which corresponded to the formula $C_{27}H_{46}O,H_2O$; a second alcohol, m. p. 115°, was formulated as $C_{32}H_{54}O$, and a third, m. p. 186°, as $C_{35}H_{58-60}O$. Several esters of the alcohol, m. p. 186°, were prepared and it was observed that oxidation of the acetate, m. p. 223°, with chromic oxide gave a product resembling " oxy-amyrin acetate." Through the courtesy of the Directors of Messrs. T. & H. Smith, Limited, Edinburgh, we have re-examined *S. nux-vomica* seed fat and have isolated and identified these three alcohols.

The fat contains a high proportion (12—15%) of non-saponifiable matter. Acetylation and chromatography of this gave four well-defined fractions. The first, a colourless volatile oil, has not been examined in detail. Purification of the second readily gave α-amyrin acetate, characterised by hydrolysis to α-amyrin, m. p. 185°. Purification of the final fraction gave an acetate, m. p. 142·5—143°, which after hydrolysis gave stigmasterol, m. p. 165·5—167·5°. The third fraction readily gave an acetate, m. p. 122—124°, hydrolysis of which yielded *cyclo*artenol, $C_{30}H_{50}O$, m. p. 99°, raised to 115° after rigorous drying. This identification follows from a comparison of the constants of the alcohol and its derivatives with those of corresponding derivatives described by Barton (*J.*, 1951, 1444); the identities of the alcohol and its acetate have been confirmed by mixed m. p. determinations kindly made by Dr. D. H. R. Barton.

	From *S. nux-vomica*		From *A. integrifolia*		
	M. p.	$[\alpha]_D$	M. p.	$[\alpha]_D$	Mixed m. p.
*cyclo*Artenol	115° (99° solvated)	+54°	85—92°	+48°	112—113·5° (sinters 110°)
Acetate	122—124	+59·5	122·5—123·5	+58	121·5—122·5
Benzoate	130	+76	129—130	+65	—
*cyclo*Artenone	105—106	+22	109	+24	—
*cyclo*Artanol	99	+50	99—101	+45	—
Acetate	130—132	+59	132—133	+45	—

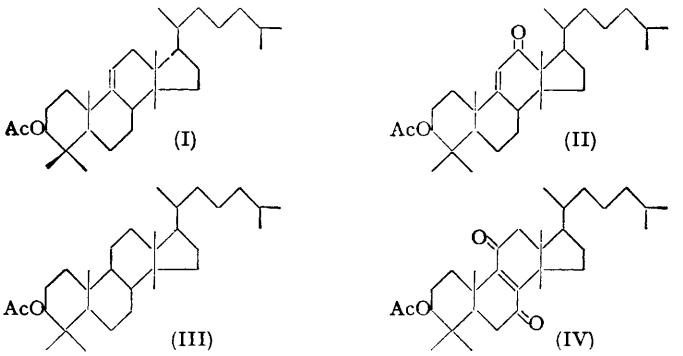
Barton isolated *cyclo*artenol together with the corresponding ketone *cyclo*artenone, $C_{30}H_{48}O$, from the latex of the fruit of *Artocarpus integrifolia*. *cyclo*Artenol has since been recognised as a minor constituent of the latex of *Euphorbia balsamifera* (Chapon and David, *Bull. Soc. chim.*, 1952, 456) and is probably identical with handianol from *Euphorbia handiensis* (Gonzalez, Calero, and Calero, *Anal. Fís. Quím.*, 1949, **45**, *B*, 1441; Gonzalez and Calero, *ibid.*, **46**, *B*, 175).

The presence of an *iso*propylidene group in a side chain, and of a *cyclo*propane ring, in *cyclo*artenol has been established by Barton (*loc. cit.*). These observations have been confirmed and extended by us. Ozonolysis of *cyclo*artenyl acetate yields acetone and oxidation with chromic acid in acetic acid gives an acid, $C_{29}H_{46}O_4$ (trisnor*cyclo*artanoloic acid acetate), characterised as its methyl ester.

Hydrogenation of *cyclo*artenyl acetate readily gave *cyclo*artanyl acetate, treatment of which with hydrogen chloride in chloroform gives a mixture, m. p. 137—157°, $[\alpha]_D$ +68°.

* Part XXVII, preceding paper.

In contrast to the parent *cyclo*artanyl acetate, this mixture gave a strong yellow colour with tetranitromethane and showed selective absorption between 1950 and 2200 Å characteristic of unsaturation. Attempted purification of the mixture by crystallisation and chromatography, and by chromatography of the derived benzoate, alcohol, and ketone mixtures failed to give a homogeneous product. A homogeneous component was isolated from the acetate mixture by treatment with chromic acid in acetic acid (cf. Marker, Wittle, and Mixon, *J. Amer. Chem. Soc.*, 1937, **59**, 1368). The component which escaped oxidation was readily separated and proved to be lanost-9(11)-enyl acetate (I) (Voser, Montavon, Günthard, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 1893; McGhie,

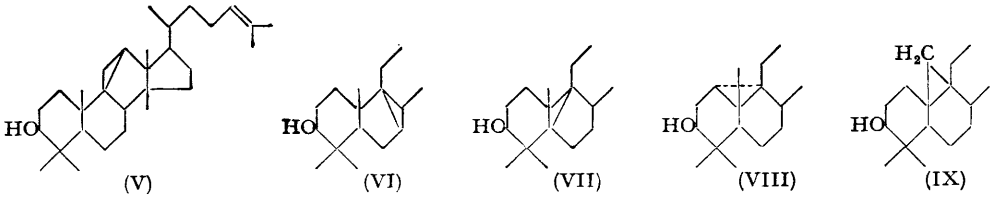


Pradhan, and Cavalla, *J.*, 1952, 3176). The artenyl acetate described by Barton is probably largely lanost-9(11)-enyl acetate. 7 : 11-Dioxolanost-8-enyl acetate was not isolated from the oxidation mixture; chromatography gave small fractions which, although they could not be adequately purified, showed the characteristic ultra-violet absorption spectrum of 7 : 11-dioxolanost-8-enyl acetate.

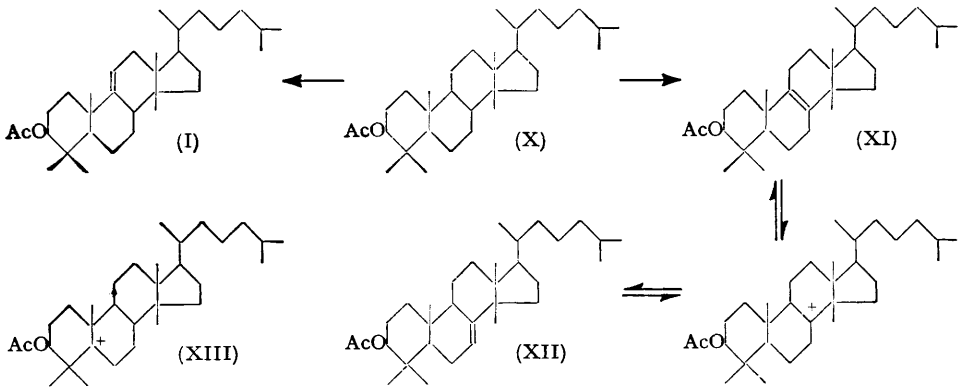
Hydrogenation of the hydrogen chloride isomerisation product from *cyclo*artanyl acetate under conditions known to ensure complete hydrogenation of lanost-9(11)-enyl acetate (Voser *et al.*, *loc. cit.*) yielded a product which still gives a yellow colour with tetranitromethane and shows selective absorption at 2070 Å. Treatment of this mixture with chromic acid followed by chromatography gave lanostanyl acetate (III) in 50—60% yield together with 10% of 7 : 11-dioxolanost-8-enyl acetate (IV). The last compound is formed by the oxidation of lanost-8-enyl acetate (XI) or lanost-7-enyl acetate (XII) with chromic acid (Ruzicka, Rey, and Muhr, *Helv. Chim. Acta*, 1944, **27**, 472; Dorée and McGhie, *Nature*, 1944, **153**, 148; Voser *et al.*, *loc. cit.*; Cavalla, McGhie, and Pradhan, *J.*, 1951, 3142), but not by oxidation of lanost-9(11)-enyl acetate with chromic acid. The last reaction yields 12-oxolanost-9(11)-enyl acetate (II) which is also obtained by relatively vigorous oxidation of the acetate mixture, m. p. 137—157°, with the same reagent. These results imply that the acetate mixture contains a relatively large proportion of lanost-9(11)-enyl acetate and a smaller quantity of lanost-7- and/or -8-enyl acetate.

Lanost-9(11)-enyl acetate is recovered unchanged in quantitative yield after treatment with hydrogen chloride in chloroform and it is not obtained by similar treatment of lanost-8- or -7-enyl acetate. Similar treatment of lanost-8-enyl acetate gives a mixture from which lanost-7-enyl acetate has been isolated (Marker, Wittle, and Mixon, *loc. cit.*; Cavalla, McGhie, and Pradhan, *loc. cit.*; Barton, Fawcett, and Thomas, *J.*, 1951, 3147). The initial product obtained from the last reaction is probably an equilibrium mixture of the 7- and 8-enyl acetates; it does not contain any appreciable amount of the 9(11)-isomer since oxidation of the equilibrium mixture with chromic anhydride gives 7 : 11-dioxolanost-8-enyl acetate in high yield, and chromatography of the product failed to disclose the presence of 12-oxolanost-9(11)-enyl acetate. Although we have only accounted for approximately 60—70% of the acetate mixture, m. p. 137—157°, as lanost-9(11)-enyl acetate (50—60%) and lanost-7- and -8-enyl acetate (approx. 10%) we believe that the mixture contains only these three components. Crystallisation of a mixture of lanost-9(11)enyl acetate (60%)

and the equilibrium mixture of lanost-7- and -8-enyl acetates (40%) gave an acetate mixture which closely resembled the acetate mixture, m. p. 137—157°.



The simplest explanation of the formation of lanost-9(11)-enyl acetate in high yield by the action of mineral acid on *cyclo*artanyl acetate is that the *cyclo*propane ring in *cyclo*artenol extends from $C_{(9)}$. The evidence at present available does not allow a satisfactory choice to be made from the structures (V)—(IX) for *cyclo*artenol, the acetyl dihydro-derivative from each of which may yield with mineral acid the carbonium intermediate (X), the subsequent fate of which is depicted below :



Structure (VII) appears improbable since the mixed acetates, m. p. 137—157°, do not contain any appreciable quantity of rearrangement products derived from the carbonium ion (XIII).

Experimental

Rotations were measured in chloroform solution at approx. 15°, and ultra-violet absorption spectra were measured in ethanol solutions using a Unicam SP. 500 spectrophotometer. Grade II alumina and a light petroleum fraction of b. p. 60—80° were used for chromatography unless otherwise specified.

α-Amyrin Acetate.—A solution of sodium hydroxide (160 g.) in water (200 ml.) was added to one of *S. nux-vomica* fat (1 kg.) in ethanol (3 l.), and the mixture was boiled under reflux for 4 hr., concentrated, and mixed with hot water (12 l.), The dry non-saponifiable matter (125 g.), isolated by means of ether, in acetic anhydride (100 ml.) and dry pyridine (250 ml.) was kept for 24 hr. at room temperature and the product isolated by means of ether. The acetylated product formed an orange-coloured waxy solid (130 g.). A solution of the solid in light petroleum (1 l.) was percolated through a column (132 × 5·5 cm.) of alumina (3 kg.), and the chromatogram eluted with (*a*) light petroleum (5 l.), (*b*) light petroleum–benzene (1 : 1 ; ·7 l.), (*c*) benzene (2 l.), (*d*) benzene–ether (9 : 1 ; 5 l.), and (*e*) acetone (6 l.). Evaporation of fraction (*a*) gave a colourless oil (6·5 g.) which has not been examined. Fraction (*b*) gave a solid (44·0 g.) which, after crystallisation from chloroform–methanol, yielded α-amyrin acetate as plates, m. p. and mixed m. p. 223—225°, $[\alpha]_D$ +79·5° (*c*, 1·6) (Found : C, 81·8; H, 11·2. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%). Alkaline hydrolysis of the acetate yielded α-amyrin which separated from aqueous methanol as needles, m. p. and mixed m. p. 185°, $[\alpha]_D$ +82° (*c*, 2·0). Fraction (*c*) gave a clear gum (3·5 g.) which was not examined.

cyclo*Artenyl Acetate.*—Fraction (*d*) (above) gave a crystalline solid (26·4 g.), repeated

crystallisation of which from chloroform–methanol gave *cyclo*artenyl acetate (12·1 g.) as plates (Found: C, 81·9; H, 11·4. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%). For this and other *cyclo*artenol derivatives see also the Table (p.).

cyclo*Artenol*.—Hydrolysis of the acetate with methanolic potassium hydroxide gave *cyclo*artenol which separated from methanol as needles, m. p. 99° raised to 115° after drying for 12 hr. at 65° *in vacuo*, $[\alpha]_D$ +54° (c, 1·25) (Found: C, 84·5; H, 11·8. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%). The formation of solvated crystals by crystallisation of *cyclo*artenol from methanol is a characteristic property. On drying in high vacuum at 65° the m. p. of the crystals gradually rises to 115°.

*cyclo*Artenyl benzoate separated from methanol as needles (Found: C, 83·5; H, 10·25. Calc. for $C_{37}H_{54}O_2$: C, 83·7; H, 10·25%).

cyclo*Artenone*.—Oxidation of *cyclo*artenol (600 mg.) with chromic acid (104 mg.) in acetic acid (60 ml.) for 12 hr. at room temperature and isolation of the product in the usual way gave *cyclo*artenone, plates from methanol (Found: C, 85·0; H, 11·35. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4%).

cyclo*Artanyl Acetate*.—Hydrogenation of *cyclo*artenyl acetate in presence of a platinum catalyst in acetic acid gave *cyclo*artanyl acetate, needles from methanol–chloroform (Found: C, 81·8; H, 11·8. Calc. for $C_{32}H_{54}O_2$: C, 81·6; H, 11·6%), hydrolysed by alkali to *cyclo*artanol, plates from methanol (Found: C, 84·1; H, 12·3. Calc. for $C_{30}H_{52}O$: C, 84·0; H, 12·2%).

cyclo*Artanone*.—A solution of chromic acid (125 mg.) in acetic acid (10 ml.) was added dropwise with stirring during 1 hr. to a solution of *cyclo*artanol (660 mg.) in acetic acid (70 ml.). After 16 hr. methanol (5·0 ml.) was added, the solution was diluted with water (500 ml.), and the neutral product isolated in the usual manner. Crystallisation of this from methanol gave cyclo*artanone* (510 mg.) as plates, m. p. 110°, $[\alpha]_D$ +24° (*c*, 2·9) (Found: C, 84·4; H, 11·9. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%). The *semicarbazone* formed needles, m. p. 215°, from methanol (Found: C, 76·9; H, 10·6. $C_{31}H_{53}ON_3$ requires C, 77·0; H, 11·0%)].

Ozonolysis of cyclo*Artenyl Acetate*.—An ice-cold solution of *cyclo*artenyl acetate (2·0 g.) in dry carbon tetrachloride (50 ml.) was treated with ozonised oxygen (5—7%) until a sample of the solution no longer absorbed bromine (4 hr.). The residue obtained after evaporation was decomposed by boiling it under reflux for 40 min. with water (250 ml.). The mixture was distilled and the distillate (100 c.c.) treated with 2 : 4-dinitrophenylhydrazine in hydrochloric acid, which gave acetone 2 : 4-dinitrophenylhydrazone (120 mg.), yellow needles (from ethanol), m. p. and mixed m. p. 128° (Found: N, 23·4. Calc. for $C_9H_{10}O_4N_4$: N, 23·5%). Extraction of the non-volatile solid with ether, separation into acidic and neutral fractions, and attempted chromatographic purification of these did not yield homogeneous products.

*Trisnor*cyclo*artanoloic Acid*.—Chromic acid (2·8 g.) in water (3 ml.) and acetic acid (85 ml.) was added dropwise during 90 min. to a boiling solution of *cyclo*artenyl acetate (2·0 g.) in acetic acid (100 ml.). The mixture was evaporated and the dry residue shaken with sulphuric acid (2%; 250 ml.) and ether. The ethereal solution was washed with water (100 ml.) and with sodium hydroxide solution (3%; 3 × 100 ml.); a sodium salt separated at the solvent interface. The salt was collected and suspended in water (100 ml.), the mixture acidified (methyl-red) with hydrochloric acid, and the solid collected by means of ether. *Trisnor*cyclo*artanoloic acid acetate* (104 mg.) separated from aqueous acetone as short prismatic needles, m. p. 221·5—223°, $[\alpha]_D$ +62° (*c*, 0·9) (Found: C, 76·2; H, 10·3. $C_{29}H_{46}O_4$ requires C, 75·95; H, 10·1%). With ethereal diazomethane this gave the *methyl ester acetate*, needles, m. p. 121—123° (from methanol) $[\alpha]_D$ +56° (*c*, 1·6) (Found: C, 76·0; H, 10·2. $C_{30}H_{48}O_4$ requires C, 76·2; H, 10·2%). Neither the alkali-soluble acidic nor the neutral fraction obtained from the oxidation mixture yielded homogeneous products.

Isomerisation of cyclo*Artanyl Acetate*.—Treatment of *cyclo*artanyl acetate with hydrogen chloride in chloroform as described by Barton (*loc. cit.*) gave a product which crystallised from methanol–chloroform as plates, m. p. 137—157°, $[\alpha]_D$ +68° (*c*, 2·4). Light absorption: Max. at 2070 Å (ε = 3600). Repeated crystallisation from the same solvent was accompanied by a gradual and continuous increase in m. p. and considerable loss of material. After five recrystallisations, the product had m. p. 157—159°, $[\alpha]_D$ +76° (*c*, 1·7). Alkaline hydrolysis of the acetate mixture, m. p. 137—157°, gave an alcohol mixture, m. p. 152—154°, $[\alpha]_D$ +60° (*c*, 1·5) (benzoate, m. p. 197—198°), acetylation of which gave an acetate, m. p. 137—160°. These observations confirm those of Barton (*loc. cit.*) who also noted the sharp m. p. of the alcohol and benzoate mixtures. The equilibrium mixture of lanost-7- and -8-enyl acetates (40 mg.) (Cavalla, McGhie, and Pradhan, *loc. cit.*) was mixed with lanost-9(11)-enyl acetate (60 mg.) and crystallised from methanol–chloroform, in plates, m. p. 138—158°, $[\alpha]_D$ +73° (*c*, 2·1), which

melted over the same range when mixed with a sample of the acetate, m. p. 137—157°. Hydrolysis gave an alcohol mixture, $[\alpha]_D$ +63° (*c*, 1·8), m. p. 153—154° alone or mixed with a specimen of the alcohol, m. p. 152—154°.

Lanost-9(11)-*enyl Acetate*.—Chromic acid (0·3 g.) in 90% acetic acid (25 ml.) was added during 5 min. with stirring to a solution of the acetate mixture (m. p. 137—157°; 1·0 g.) in acetic acid (75 ml.) heated on the steam-bath. Heating was continued for 10 min., the mixture was poured into water (500 ml.), and the solid collected by means of ether. A solution of the dry solid (1·1 g.) in light petroleum (100 ml.) was filtered through a column (23 × 2 cm.) containing alumina (60 g.), and the chromatogram developed by elution with light petroleum and light petroleum–benzene (9 : 1; then 4 : 1). The last solvent eluted a fraction (m. p. 167—170°; 448 mg.) which on crystallisation from chloroform–methanol gave lanost-9(11)-enyl acetate as hexagonal plates, m. p. 170—172°, $[\alpha]_D$ +85° (*c*, 1·63) (Found: C, 81·5; H, 11·8. Calc. for $C_{32}H_{54}O_2$: C, 81·6; H, 11·6%). When mixed with a specimen (m. p. 173°, $[\alpha]_D$ +84°) prepared from lanost-8-enyl acetate (Voser *et al.*, and McGhie, Pradhan, and Cavalla, *locc. cit.*) the m. p. was undepressed. Lanost-9(11)-enyl acetate was recovered in high yield after treatment with dry hyrogen chloride in chloroform for 3 hr.

Lanost-9(11)-*enol*.—A solution of lanost-9(11)-enyl acetate (0·2 g.) in ethanolic potassium hydroxide (3%; 25 ml.) was heated under reflux for 3 hr. The product, isolated by means of ether and crystallised from methanol, gave *lanost*-9(11)-*enol* (0·16 g.) as matted needles, m. p. 167°, $[\alpha]_D$ +76°(*c*, 0·84) (Found: C, 83·8; H, 12·4. $C_{30}H_{52}O$ requires C, 84·0; H, 12·2%).

12-*Oxolanost*-9(11)-*enyl Acetate*.—Chromic acid (0·22 g.) in acetic acid (50 ml.) was added during 1 hr. to a refluxing solution of lanost-9(11)-enyl acetate (0·5 g.) in acetic acid (50 ml.). The solution was heated under reflux for 2 hr., kept overnight at room temperature, and mixed with water (300 ml.), and the solid collected by means of ether. A solution of the yellow crystalline product (0·53 g.) in light petroleum (100 ml.) was filtered through a column (1·5 × 13 cm.) of alumina (20 g.), and the chromatogram eluted with light petroleum, light petroleum–benzene (4 : 1), benzene, and benzene–ether (9 : 1). The fraction (0·16 g.) eluted by light petroleum–benzene was lanost-9(11)-enyl acetate, m. p. 170—171°, $[\alpha]_D$ +84° (*c*, 1·5). The fractions eluted with benzene and benzene–ether (0·2 g.) were combined and crystallised from methanol, to yield 12-*oxolanost*-9(11)-*enyl acetate* as needles, m. p. 184—185°, $[\alpha]_D$ +91° (*c*, 0·62) (Found: C, 78·3; H, 10·9. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). Light absorption in ethanol: Max. at 2420 Å (ε = 9800). The αβ-unsaturated ketone was also obtained (in low yield) by vigorous oxidation of the mixed acetates, m. p. 137—157°, with chromic acid.

Lanostanyl Acetate.—(*a*) A solution of the acetate mixture, m. p. 137—157° (0·84 g.), in acetic acid (150 ml.) was shaken with hydrogen and platinum (500 mg.) for 24 hr. at 80°. The solution was filtered and evaporated, to give a crystalline solid (0·84 g.) which gave a yellow colour with tetranitromethane and showed light absorption at 2070 Å (ε = 2600). Chromic acid (0·32 g.) in acetic acid (25 ml.) was added during 30 min. with stirring to a solution of the hydrogenation product (0·84 g.) in acetic acid (100 ml.) heated on the steam-bath, and heating was continued for 90 min. The cooled solution was mixed with methanol (25 ml.) and evaporated to dryness, and the residue diluted with water (200 ml.). The neutral product (0·82 g.), isolated by means of ether, in light petroleum (50 ml.) was filtered through a column (2 × 12 cm.) of alumina (25 g.). Elution with light petroleum–benzene (4 : 1; 375 ml.) gave a solid (0·48 g.) which on crystallisation from chloroform–methanol gave lanostanyl acetate as needles, m. p. 155—156°, $[\alpha]_D$ +41° (*c*, 1·6) (Found: C, 81·3; H, 12·0. Calc. for $C_{32}H_{56}O_2$: C, 81·3; H, 11·9%), identified by direct comparison with an authentic specimen, m. p. 155—156°, $[\alpha]_D$ +41° (*c*, 1·16), prepared as described by Voser *et al.* (*loc. cit.*). Elution with light petroleum–benzene (1 · 4; 100 ml.) and with benzene (150 ml.) gave a partly crystalline product (83 mg.) which on crystallisation from methanol gave 7 : 11-dioxolanost-8-enyl acetate as pale yellow plates, m. p. and mixed m. p. 155—156°, $[\alpha]_D$ +91° (*c*, 0·57) (Found: C, 77·2; H, 10·4. Calc. for $C_{32}H_{50}O_4$: C, 77·1; H, 10·1%). Light absorption in ethanol: Max. at 2060 (ε = 3800) and 2700 Å (ε = 7600).

(*b*) A solution of 12-oxolanost-9(11)-enyl acetate (100 mg.) in acetic acid (100 ml.) was shaken with hydrogen and platinum catalyst (200 mg.) for 24 hr. at 80°. The filtered solution was evaporated and the residue dissolved in light petroleum (b. p. 40—60°; 40 ml.) and purified by absorption on alumina (10 g.) and elution with light petroleum–benzene (7 : 3) which gave lanostanyl acetate (80 mg.) as needles (from chloroform–methanol), m. p. and mixed m. p. 156°, $[\alpha]_D$ +40·5° (*c*, 0·67) (Found: C, 81·51; H, 12·05%).

9 : 11-*Epoxylanostanyl Acetate*.—A mixture of lanost-9(11)-enyl acetate (100 mg.) and perhydrol (0·5 ml.) in acetic acid (100 ml.) was heated on the steam-bath for 2 hr. The cooled solution was diluted with water, and the crystalline product collected, washed with water,

dried, and recrystallised from methanol, giving 9 : 11-*epoxylanostanyl acetate* (60 mg.) as plates, m. p. 181—182°, $[\alpha]_D$ +29° (*c*, 0·73) (Found: C, 79·2; H, 11·4. $C_{32}H_{54}O_3$ requires C, 79·0; H, 11·2%). The compound gives no colour with tetranitromethane and shows no selective light absorption in the ultra-violet region; it is probably identical with the " artenyl acetate oxide " described by Barton (*loc. cit.*).

Wolff–Kishner Reduction of 7 : 11-*Dioxolanostanyl Acetate*.—By using the Huang-Minlon modification described by McGhie, Pradhan, and Cavalla (*loc. cit.*) 7 : 11-dioxolanostanyl acetate readily gave 11-oxolanostanyl acetate, m. p. 143—144°, $[\alpha]_D$ +64° (*c*, 1·07). When the normal Wolff–Kishner method was used, however, the reduction proceeded in a different direction.

A mixture of 7 : 11-dioxolanostanyl acetate (5·0 g.) and hydrazine hydrate (100%; 11·0 ml.) in dry ethanol (130 ml.) was boiled under reflux for 2 hr., a solution of sodium (12·0 g.) in ethanol (150 ml.) was added and the mixture heated at 200° in an autoclave for 16 hr. The cooled mixture was diluted with water (1 l.), and the product (4·9 g.) collected by means of ether and acetylated on the steam-bath for 45 min. with acetic anhydride (20 ml.) and pyridine (30 ml.). A solution of the acetylated product (5·1 g.) in light petroleum (b. p. 40—60°)–benzene (4 : 1) was filtered through a column (3·8 × 24 cm.) of alumina (210 g.). The combined, partly crystalline fractions (4·1 g.) eluted by light petroleum–benzene (1 : 4), benzene, and benzene–ether (9 : 1), when recrystallised from methanol, yielded 3 : 7-diacetoxylanostan-11-ol as fine needles, m. p. 236—237°, $[\alpha]_D$ +58° (*c*, 1·0) (Found: C, 74·8; H, 10·8. Calc. for $C_{34}H_{58}O_5$: C, 74·7; H, 10·7%). A specimen prepared by the method of Voser *et al.* (*loc. cit.*) had m. p. and mixed m. p. 236—237°, $[\alpha]_D$ +57° (*c*, 0·95) (Voser *et al.* give m. p. 235—236°, $[\alpha]_D$ +73°).

Stigmasterol (with M. B. E. Fayez).—Evaporation of fraction (*e*) from the original chromatogram gave a brown resin (25 g.) which was combined with similar fractions from three experiments. Acetylation of the resin (*ca.* 100 g.) with pyridine and acetic anhydride yielded a resinous acetate (108 g.). A solution of this in light petroleum (b. p. 40—60°) was filtered through a column (5·5 × 120 cm.) of alumina (4000 g.). Crystallisation of a series of fractions eluted by light petroleum–benzene (1 : 1) gave (in decreasing ease of elution), α-amyrin acetate (40 g.), m. p. and mixed m. p. 223°, *cyclo*artenyl acetate (15 g.), m. p. and mixed m. p. 122°, and a steroid acetate (*ca.* 5 g.), m. p. 135°. Repeated recrystallisation from chloroform–methanol of the steroid fractions, which gave a green Liebermann–Burchard reaction, yielded stigmasteryl acetate (1·5 g.) as flat needles, m. p. 142·5—143°, $[\alpha]_D$ −51° (Found: C, 81·9; H, 11·1. Calc. for $C_{31}H_{50}O_2$: C, 81·9; H, 11·1%), identified by comparison with an authentic specimen, m. p. 142—143°, $[\alpha]_D$ −51°, kindly supplied by Dr. D. H. R. Barton. Hydrolysis gave stigmasterol as needles (from chloroform–methanol), m. p. 165·5—167·5°, $[\alpha]_D$ −49° (Found: C, 83·8; H, 11·9. Calc. for $C_{29}H_{48}O$: C, 84·5; H, 11·7%), and bromination in ether–acetic acid gave stigmasteryl acetate tetrabromide which forms small needles, m. p. 203°, $[\alpha]_D$ −39°, from ethanol–chloroform (Found: C, 48·1; H, 6·6; Br, 40·6. Calc. for $C_{31}H_{50}O_2Br_4$: C, 48·1; H, 6·5; Br, 41·3%).

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