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#### Terpenoids. Part LI.\* The Isolation of Some New Cyclopropane-789. containing Triterpenes from Spanish Moss (Tillandsia usneoides, L.).

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The constitution and stereochemistry of four new triterpenoids from extracts of Spanish moss have been elucidated. They are cycloart-23-ene- $3\beta$ , 25-diol, cycloart-25-ene- $3\beta$ , 24( $\alpha$  or  $\beta$ )-diol, 25-methoxycycloart-23-en- $3\beta$ -ol, and  $3\beta$ -hydroxycycloart-25-en-24-one, the last two being isolated as 3-acetates. In addition, the extracts have yielded cycloartenone, cycloartenol, friedelin,  $\beta$ -sitosterol, and a mixture of the straight-chain paraffins from  $C_{14}H_{30}$  to  $C_{27}H_{56}$ .

RECENTLY we reported <sup>1</sup> the isolation of four new triterpenoids from *Tillandsia usneoides* and assigned the structure cycloart-23-ene-39,25-diol (I) to one of them. This assignment is now expanded and in addition we present evidence for the structures of the remaining three compounds.

Chromatography of the ether-soluble neutral fraction of a methanolic extract of T. usneoides afforded cycloartenone (XIV), friedelin, cycloartenol (III),  $\beta$ -sitosterol, and two of the four new triterpenes, cycloart-25-ene- $3\beta$ ,24( $\alpha$  or  $\beta$ )-diol (IV) and cycloart-23ene- $3\beta$ , 25-diol (I). When the similar fraction of a chloroform extract of the plant was chromatographed, the above compounds were obtained and, in addition, a mixture of straight-chain paraffins from C14H30 to C27H56. Acetylation of the more polar oily fractions from this chromatogram and rechromatography then afforded the other two new cycloartane derivatives,  $3\beta$ -hydroxycycloart-25-en-24-one (VI) and 25-methoxycycloart-23-en-33-ol (II), as their 3-acetates.

The structural relationship of the four new compounds was evident from a common spectroscopic property, namely, a pair of doublets in their nuclear magnetic resonance spectra centred at 9.67 and 9.42  $\tau$ , indicative of a cyclopropane ring bearing two nonequivalent hydrogen atoms. Cycloartenol (III) has similarly spaced doublets at the same positions. The diol (I)  $[\nu_{max}$  (in CHCl<sub>3</sub>) 3600 cm.<sup>-1</sup> (OH)] had the molecular formula  $C_{30}H_{50}O_2$  and revealed its unsaturated nature in its ultraviolet absorption ( $\varepsilon_{200 \text{ m}\mu}$  3300;  $\varepsilon_{210 \text{ m}\mu}$  330), characteristic of a disubstituted ethylenic linkage.<sup>2</sup> Treatment with acetic anhydride-pyridine yielded a monoacetate (Ia) † which still showed infrared absorption (in CHCl<sub>2</sub>) at 3600 cm.<sup>-1</sup> (OH). The position of the hindered hydroxyl group (on C-25) was indicated by the nuclear magnetic resonance spectra of the diol and its monoacetate, both showing a singlet (six protons) at  $8.69 \tau$ , as expected <sup>3</sup> for a substituted propan-2-ol. Catalytic hydrogenation of the diol (I) in acetic acid with platinum oxide led to the saturated dihydro-diol (VII), which showed no selective absorption between 200 and 300 mµ. A minor product in this hydrogenation proved to be cycloartanol (VIII), the formation of which not only provided evidence for the carbon skeleton but also suggested the close proximity of the olefinic bond to the non-acetylatable hydroxyl group. Indeed dehydration of the monoacetate (Ia) with phosphoryl chloride and pyridine yielded an oily diene ( $\lambda_{max}$ , 225, 230, and 237 mµ;  $\varepsilon$  19,000, 23,000, and 16,000). The dihydro-diol also formed a monoacetate (VIIa), dehydration of which gave cycloartenyl acetate (IIIa), thus confirming the position of the hindered 25-hydroxyl group. The ease of formation of cycloartanol (VIII), apparently by hydrogenolysis of the tertiary hydroxyl group and reduction of the olefinic bond, made it probable that the hydroxyl group was in an allylic

McCrindle and Djerassi, Chem. and Ind., 1961, 1311.

<sup>\*</sup> The note by McCrindle and Djerassi (*Chem. and Ind.*, 1961, 1311) is considered to be Part L. † A letter "a" following a Roman numeral denotes the derived 3-acetate throughout this paper.

<sup>&</sup>lt;sup>2</sup> Halsall, Chem. and Ind., 1951, 867; Bladon, Henbest, and Wood, J., 1952, 2737.

<sup>&</sup>lt;sup>3</sup> Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

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position, and hence the double bond would necessarily link C-23 and C-24. However, an alternative explanation for the loss of the inert hydroxyl group, namely, dehydration and subsequent reduction of the resulting double bond, could not be excluded. The position of the olefinic bond was rigidly defined in the following manner. The monoacetate (Ia), on hydroxylation with osmium tetroxide, gave a mixture of the two isomeric triols (IXa) which were cleaved by lead tetra-acetate to the aldehyde (Xa) and acetone (identified as the 2,4-dinitrophenylhydrazone). Oxidation of this aldehyde with silver oxide in the presence of base produced the hydroxy-acid (XI), isolated as the crystalline methyl ester (XII), the composition of which was established by mass-spectrometric molecular-weight determination. On this basis the original diol could be confidently formulated as cycloart-23-ene-3 $\beta$ ,25-diol (I).

The nuclear magnetic resonance spectrum of  $3\beta$ -acetoxycycloart-23-en-25-ol (Ia) was practically identical with that of the acetate (IIa) of another of the new triterpenes, except for a singlet (3 protons) at 6.85  $\tau$  attributable<sup>3</sup> to a methyl ether. The compound was, therefore, assumed to be  $3\beta$ -acetoxy-25-methoxycycloart-23-ene and this was substantiated by its separation on a preparative-scale thin-layer chromatogram (silica gel) from the mixture obtained by treatment of the monoacetate (Ia) with methanolic hydrochloric acid. The question arises whether this methyl ether is in fact present in the plant or whether it is an artifact of the isolation procedure. We tend to favour the former assumption since the substance was isolated by chloroform extraction of the plant and was in contact with methanol only during the alumina chromatography. Furthermore, in the absence of acid, the monoacetate (Ia) was stable to prolonged boiling with methanol.



A letter "a" following a Roman numeral denotes the derived 3-acetate.

The other new diol (IV) was isomeric with (I) but in contrast it readily formed a diacetate (Va) with acetic anhydride-pyridine. Oxidation with chromic acid in acetone afforded a dione (XV) which had  $\nu_{max}$  (in CHCl<sub>3</sub>) 1700 (6-membered ketone) and 1680 cm.<sup>-1</sup> ( $\alpha\beta$ -unsaturated ketone), the presence of an  $\alpha\beta$ -unsaturated ketone grouping being confirmed by its ultraviolet absorption [ $\lambda_{max}$ . (in MeOH) 216 m $\mu$ ;  $\varepsilon$  8000]. The nuclear magnetic resonance spectrum of the diol diacetate (Va), apart from revealing the presence of two cyclopropyl protons, gave further valuable information in that there were no signals attributable to two methyl groups attached to C-25 as in cycloartenol (III) [at 8·39 (3 protons) and 8·32  $\tau$  (3 protons)] or in cycloart-23-ene-3 $\beta$ ,25-diol (I) [at 8·69  $\tau$  (6 protons)]. It did have a peak at 8·27  $\tau$  corresponding to one methyl group located on an olefinic bond. The assumption was made that the two diols had arisen biogenetically by oxidative attack at one or other end of the olefinic linkage in a cycloartenol-type precursor (with a shift of the double bond) and that this new diol was therefore cycloart-25-ene-3 $\beta$ ,24( $\alpha$  or  $\beta$ )-diol

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(IV), a formulation which was verified as follows. The diol, when stirred in chloroform with manganese dioxide, formed the unsaturated keto-alcohol (VI) which with acetic anhydride-pyridine yielded a compound identical (mixed m. p., [2]<sub>p</sub>, infrared and ultraviolet absorption and identical thin-layer chromatographic mobility) with the fourth new triterpene of natural provenance (VIa)  $[\nu_{max}]$  (in CHCl<sub>3</sub>) 1720 (OAc) and 1680 cm.<sup>-1</sup> ( $\alpha\beta$ -unsaturated ketone);  $\lambda_{max}$  218 m $\mu$  ( $\epsilon$  10,000)]. This was hydrogenated in ethyl acetate in the presence of palladium-charcoal to the keto-acetate (XIIIa), identified by direct comparison (mixed m. p.,  $[\alpha]_p$ , infrared absorption, thin-layer chromatography) with authentic 3β-acetoxycycloartan-23-one <sup>4</sup> kindly supplied by Dr. M. Shimizu (Tokyo).

These newly described compounds increase the number of known naturally occurring cycloartane derivatives to nine, the others being cycloartenone,<sup>5</sup> cycloartenol,<sup>6</sup> cyclolaudenol,<sup>7</sup> cycloeucalenol,<sup>8</sup> and 24-methylenecycloartenol.<sup>4</sup> The side-chain substitution pattern of our compound (I) is particularly interesting, since the only other triterpenoids (based on a cholestane-type skeleton) possessing a 23-en-25-ol grouping are the cucurbitacins<sup>9</sup> with additional oxygen groups at positions 20 and 22.

#### EXPERIMENTAL

Ultraviolet absorption spectra were determined with the Carey model 14 spectrophotometer and are for solutions in ethanol unless specified otherwise. Infrared spectra were determined with the Perkin-Elmer Infracord or model 21 spectrometer. The light petroleum used was of b. p. 40-60°. Chromatographic alumina was Merck Standardised, deactivated if required according to Brockmann.<sup>10</sup> Merck silica gel G. was used for thin-layer chromatography on glass (chromatoplate technique). Microanalyses were carried out by Mr. E. Meier, nuclear magnetic resonance spectra were determined with a Varian AR-60 instrument by Dr. Lois J. Durham, and mass spectra were measured by Dr. H. Budzikiewicz using a Consolidated Electrodynamics Corporation model 21-103C mass spectrometer.

Extraction of Spanish Moss.—(i) With methanol. The methanol extractives (470 g.) (from 7 kg. of plant collected in the outskirts of Mexico City) were triturated with acetone  $(4 \times 750 \text{ ml.})$ , the residual pale green solid (182 g.) being set aside. Extraction of the acetonesoluble brown oil with ether (5  $\times$  100 ml.) left a tarry cake (80 g.). The combined ethereal extracts were washed with dilute alkali, acid, and water (2  $\times$  300 ml. in each case), dried and The resulting green viscous oil (54 g.) was placed on alumina (activity I; 2 kg.) evaporated. in benzene. Elution with light petroleum-ether (7:3) afforded, first, cycloartenone (XIV) (2.55 g.) (plates from ether-ethanol), m. p. 108–109°,  $[\alpha]_{\rm p}$  +24° (c 1.00 in CHCl<sub>3</sub>), and then friedelin (200 mg.) (needles from hexane), m. p. 259-264° (both identified by comparison with authentic specimens). Ether-methanol (49:1) eluted cycloart-23-ene-33,25-diol (I) (720 mg.) (prisms from benzene), m. p. 198-203°. Recrystallised from ethyl acetate it had m. p. 200-204°, [a]<sub>D</sub><sup>27</sup> +38° (c 0.85 in CHCl<sub>3</sub>) (Found: C, 81.2; H, 11.15. C<sub>30</sub>H<sub>50</sub>O<sub>2</sub> requires C, 81.4; H, 11.4%),  $\varepsilon_{200 \text{ m}\mu}$  3300,  $\varepsilon_{210 \text{ m}\mu}$  330. The fractions (17.7 g.) immediately preceding the above diol were readsorbed from benzene on alumina (activity III; 700 g.). Light petroleum-ether (7:3) eluted cycloartenol (III) (900 mg.) (leaflets from ether-methanol), m. p. 111-112° (after prolonged drying) (comparison with authentic specimen). Elution with light petroleumether (3:2) afforded  $\beta$ -sitosterol (1.3 g.) (plates from methanol), m. p. 139-141° (identity established by comparison with an authentic sample and by oxidation to the known<sup>11</sup> 4-ene-3,6-dione). Light petroleum-ether (1:1) eluted cycloart-25-ene-3 $\beta$ ,24( $\alpha$  or  $\beta$ )-diol (IV) (182 mg.) (plates from ethyl acetate), m. p. 184–188°, [a]<sub>n</sub><sup>35</sup> +48° (c 1.00 in CHCl<sub>3</sub>) (Found: C, 81.35;

<sup>4</sup> Ohta and Shimizu, Chem. and Pharm. Bull. (Japan), 1958, 6, 325; Ohta, ibid., 1960, 8, 5, 9.

<sup>5</sup> Barton, J., 1951, 1444.
<sup>6</sup> Barton, Page, and Warnhoff, J., 1954, 2715; Bentley, Henry, Irvine, and Spring, J., 1953, 3673; Irvine, Henry, and Spring, J., 1955, 1316.
<sup>7</sup> Bentley, Henry, Irvine, Mukerji, and Spring, J., 1955, 596; Henry, Irvine, and Spring, J., 1955, 1305.

<sup>1607.</sup> 

<sup>&</sup>lt;sup>8</sup> Cox, King, and King, J., 1956, 1384; 1959, 514.

<sup>&</sup>lt;sup>9</sup> For leading references see Lavie, Shvo, Gottlieb, and Glotter, Tetrahedron Letters, 1961, 615.
<sup>10</sup> Brockmann, Ber., 1941, 74, 73.

<sup>&</sup>lt;sup>11</sup> Crabbe, Azpeitia, and Djerassi, Bull. Soc. chim. belges, 1961, 70, 168.

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H, 11·3.  $C_{30}H_{50}O_2$  requires C, 81·4; H, 11·4%). The derived *diacetate* (Va) formed needles (from methanol), m. p. 146–148°,  $[\alpha]_{D}^{27}$  +40° (c 1·00 in CHCl<sub>3</sub>),  $\nu_{max}$  (in CHCl<sub>3</sub>) 1725 cm.<sup>-1</sup> (OAc) (Found: C, 77·65; H, 10·25.  $C_{34}H_{54}O_4$  requires C, 77·5; H, 10·35%).

(ii) With chloroform. The waxy extract (208 g.) obtained with chloroform from the plant (2.3 kg.) was triturated with ether (6  $\times$  250 ml.), and the insoluble pale green solid (36.5 g.) reserved. The combined ethereal extracts were washed with dilute alkali, acid, and water  $(2 \times 250 \text{ ml. in each case})$ , dried, and evaporated. The residual oil (106.5 g.) in ether (750 ml.)was mixed with alumina (500 g.), the ether evaporated, and the resulting mixture packed on top of a column of activated alumina (Grade I; 2.8 kg.). Elution with light petroleum afforded oily needles (2.5 g.). Gas-liquid chromatography (Aerograph; SE 30 column) of this material coupled with mass spectrometry showed it to be a series of straight-chain saturated hydrocarbons from  $C_{14}$  to  $C_{27}$ , with the typical pattern of such naturally occurring series, *i.e.*, increasing abundance with increasing molecular weight and greater relative abundance of odd than of even members. Light petroleum-ether (7:3) eluted friedelin (70 mg.). Elution with ether-methanol (99:1) afforded a green oil (24.5 g) which was readsorbed on alumina (activity II; 1 kg.) from benzene. The column was eluted by a gradient technique [ether flowing into light petroleum–ether (9:1)] and yielded cycloartenol (1·1 g.),  $\beta$ -sitosterol (1·2 g.), cycloart-25ene-36,24-diol (250 mg.), and cycloart-23-ene-36,25-diol (650 mg.). The non-crystalline material from the column was acetylated and chromatographed over activated alumina (Grade II; 1.5 kg.) by a gradient elution technique (ether flowing into ligroin), affording successively 3β-acetoxy-25-methoxycycloart-23-ene (IIa) (232 mg.) (needles from methanol-ether), m. p. 152—154°,  $[\alpha]_{\rm p}^{28}$  +48° (c 0.75 in CHCl<sub>3</sub>),  $\nu_{\rm max}$  (in CHCl<sub>3</sub>) 1725 cm.<sup>-1</sup> (Found: C, 79.75; H, 10.6. C<sub>33</sub>H<sub>54</sub>O<sub>3</sub> requires C, 79.45; H, 10.9%), 3β-acetoxycycloart-25-en-24-one (VIa) (540 mg.) (plates from methanol), m. p. 133—136°,  $[\alpha]_{\rm p}^{27}$  +58° (c 1.00 in CHCl<sub>3</sub>),  $\lambda_{\rm max}$  218 mµ (ε 10,000),  $v_{max}$  (in CHCl<sub>3</sub>) 1710 (OAc) and 1680 cm.<sup>-1</sup> ( $\alpha\beta$ -unsaturated ketone) (Found: C, 79.85; H, 10.35.  $C_{32}H_{50}O_3$  requires C, 79.6; H, 10.45%), and 3 $\beta$ ,24-diacetoxycycloart-25-ene (90 mg.), m. p. 146—148° [identical with acetylation product from the diol (IV) (see above)].

Reactions of Cycloart-23-ene-3 $\beta$ ,25-diol.—Monacetate (Ia). The diol (158 mg.) was kept in acetic anhydride-dry pyridine (1:1) (5 ml.) for 16 hr. The product obtained as usual was chromatographed over alumina (grade III; 8 g.) and then afforded the monoacetate (151 mg.) (prisms from hexane), m. p. 148—150°,  $[\alpha]_D^{22} + 43°$  (c 0.75 in CHCl<sub>3</sub>),  $\nu_{max}$  (in CHCl<sub>3</sub>) 3600 (OH) and 1725 cm.<sup>-1</sup> (OAc) (Found: C, 79.35; H, 10.75. C<sub>32</sub>H<sub>52</sub>O<sub>3</sub> requires C, 79.3; H, 10.8%).

The monoacetate (71 mg.) in pyridine (5 ml.) was treated with pure phosphoryl chloride (0.5 ml.). After 1 hr. ice and then water (20 ml.) were added and the mixture was extracted with ether (2  $\times$  20 ml.). The combined ethereal extracts were washed with water (2  $\times$  20 ml.), dried, and evaporated. The product (45 mg.) was eluted from alumina (activity I; 4 g.) with ligroin-ether (10:1), giving a colourless sticky solid (26 mg.),  $\lambda_{max}$  225 ( $\varepsilon$  19,000), 230 ( $\varepsilon$  23,000), and 237 m $\mu$  ( $\varepsilon$  16,000), which from chromatoplate analysis appeared homogeneous but did not crystallise.

*Hydrogenation.* The diol (I) (184 mg.) in acetic acid (15 ml.) was hydrogenated over platinum oxide (100 mg.) (a microhydrogenation showed a hydrogen uptake of 1.3 mol.). The product (189 mg.), freed from catalyst and solvent, was chromatographed over activated alumina (grade I; 20 g.). Elution with ligroin-ether (1:1) afforded cycloartanol (27 mg.) (plates from methanol), m. p. (after careful drying) 106—108° (comparison with an authentic sample by mixed m. p.,  $[\alpha]_{\rm p}$ , chromatoplate, and infrared spectra). Elution with ethermethanol (10:1) afforded 25-hydroxycycloartanol (VII) (151 mg.) (prisms from benzene), m. p. 187—188°,  $[\alpha]_{\rm p}^{30} + 45°$  (c 0.72 in CHCl<sub>3</sub>) (Found [after very thorough drying]: C, 80.6; H, 11.7. C<sub>30</sub>H<sub>52</sub>O<sub>2</sub> requires C, 81.0; H, 11.8%).

This product (85 mg.) was dissolved in acetic anhydride-pyridine (1:1) (2 ml.) and kept at room temperature for 20 hr. The *product* (91 mg.) (plates from methanol), isolated as usual, had m. p. 126—128°,  $[\alpha]_D^{29} + 53^\circ$  (c 1.05 in CHCl<sub>3</sub>),  $\nu_{max}$ . (in CHCl<sub>3</sub>) 3600 (OH) and 1725 cm.<sup>-1</sup> (OAc). After very careful drying (80°/0.2 mm. for 6 days) the m. p. was 139—141° (Found: C, 78.8; H, 11.1. C<sub>32</sub>H<sub>54</sub>O<sub>3</sub> requires C, 78.95; H, 11.2%).

Dehydration of the Monoacetate (VIIa).—The monoacetate (61 mg.) was kept with pyridine (3 ml.) and phosphoryl chloride (0.5 ml.). After 1 hr. at room temperature the product (43 mg.) was isolated by extraction with ether as usual and after ten recrystallisations gave cycloartenyl acetate (plates from ether-methanol), m. p. 118—122° (after thorough drying)

(comparison with an authentic sample by mixed m. p.,  $[\alpha]_p$ , chromatoplate, and infrared spectra).

The Tetrol Monoacetate (IXa).—The diol monoacetate (Ia) (113 mg.) in ether (10 ml.) was added to a solution of osmium tetroxide (120 mg.) in the same solvent and kept in the dark for 5 days. Methanol (15 ml.) was added and the osmate decomposed with hydrogen sulphide. Anhydrous magnesium sulphate (2 g.) was added (to facilitate filtration), the solid collected, and the solvent evaporated. The residue (134 mg.) was adsorbed on alumina (activity V; 10 g.) from benzene. Elution with light petroleum–ether (1 : 1) afforded  $3\beta$ -acetoxycycloartane-23,24,25-triol (IXa) (124 mg.) (prisms from ether–hexane), m. p. 184—188° (partial melting from 166°) (Found: C, 73·8; H, 10·6. C<sub>32</sub>H<sub>54</sub>O<sub>5</sub> requires C, 74·1; H, 10·5%) (chromatoplate analysis showed two spots very close together).

Cleavage of the Acetoxy-triol (IXa) by Lead Tetra-acetate.—The acetoxy-triol (108 mg.) in "AnalaR" acetic acid (15 ml.) and lead tetra-acetate in the same solvent (10 ml.) were mixed, kept at 20° in the dark for 12 hr., diluted with water (15 ml.), and concentrated. Acetone dinitrophenylhydrazone (14 mg.) was obtained from the distillate. (A control determination afforded 2 mg.) The non-volatile fraction was oxidised with silver oxide,<sup>12</sup> and the methyl ester (15 mg.) obtained with diazomethane was chromatographed over activated alumina (grade II; 1 g.); elution with ether afforded methyl 3 $\beta$ -hydroxy-24,25,26,27-tetranorcycloartan-23-oate (XII) (14 mg.) (needles from methanol), m. p. 134—138° (Found: C, 78.35; H, 10.75. C<sub>27</sub>H<sub>44</sub>O<sub>3</sub> requires C, 77.85; H, 10.65%). Mass spectroscopy established the molecular weight of 416.

 $3\beta$ -Acetoxy-25-methoxycycloart-23-ene (IIa).—The diol (I) (120 mg.) in methanol (10 ml.) was kept with concentrated hydrochloric acid (1 drop) at 20° for 20 hr., and the product acetylated in the usual way. Chromatoplate analysis of the resulting solid (122 mg.) indicated at least four components, one of which corresponded to the methoxy-acetate previously isolated (see above). The mixture (60 mg.) was placed on a preparative-scale chromatoplate, development of which with ethyl acetate-light petroleum (1 : 19) gave three strong bands (strips stained with potassium permanganate), which were collected separately. The organic material was recovered from the silica with ether and the fraction containing the expected methoxy-acetate (IIa) afforded needles (14 mg.) (from methanol), m. p. 148—151°,  $[\alpha]_D^{28} + 50°$ , identical (mixed m. p. and infrared absorption) with the methoxy-acetate of natural provenance (see above).

Reactions of Cycloart-25-ene-3 $\beta$ ,24( $\alpha$  or  $\beta$ )-diol (IV).—(a) Dione (XV). The diol (IV) (175 mg.) in acetone (20 ml.) was treated with an excess of chromium trioxide reagent <sup>13</sup> at 0° under nitrogen. Working up in the usual way after 5 min. afforded the dione (XV) (128 mg.) (prisms from methanol), m. p. 126—130°,  $[\alpha]_p^{27} + 21°$  (c 1.00 in CHCl<sub>3</sub>),  $\nu_{max}$  (in CHCl<sub>3</sub>) 1700 (6-membered ketone) and 1680 cm.<sup>-1</sup> ( $\alpha\beta$ -unsaturated ketone),  $\lambda_{max}$  (in MeOH) 216 m $\mu$  ( $\epsilon$  8000) (Found: C, 81.85; H, 10.4. C<sub>30</sub>H<sub>46</sub>O<sub>2</sub> requires C, 82.15; H, 10.55%). The derived di(ethylene ketal) (prisms from ether-methanol) had m. p. 149—151° (Found: C, 77.75; H, 10.15. C<sub>34</sub>H<sub>54</sub>O<sub>4</sub> requires C, 77.5; H, 10.35%).

(b) Oxidation with manganese dioxide. The diol (110 mg.) was stirred in chloroform with manganese dioxide <sup>14</sup> (5 g.). Removal of the inorganic precipitate and solvent yielded an oil (40 mg.), a further quantity (40 mg.) of which was obtained by Soxhlet-extraction of the precipitate with chloroform. The combined oils had strong carbonyl absorption at 1680 cm.<sup>-1</sup> but chromatoplate analysis indicated a mixture of products. This mixture was acetylated and afforded an oil (87 mg.) which contained the expected enone acetate (VIa) (chromatoplate). Preparative-scale thin-layer chromatography [development with ethyl acetate-light petroleum (1:9)] afforded  $3\beta$ -acetoxycycloart-25-en-24-one (VIa) (18 mg.), m. p. 130—132°,  $[\alpha]_p^{29} + 58^\circ$ , indistinguishable from material of natural origin (see above) by infrared and ultraviolet absorption, mixed m. p., and chromatoplate behaviour.

Hydrogenation of  $3\beta$ -Acetoxycycloart-25-en-24-one (VIa).—The ketone (23 mg.) in ethyl acetate (20 ml.) was hydrogenated over 10% palladium-charcoal (100 mg.). After 1 hr. (uptake, 1·1 mol. of H<sub>2</sub>), the catalyst was collected and the solvent evaporated. The crystalline product (23 mg.) was  $3\beta$ -acetoxycycloartan-24-one (plates from hexane),  $[\alpha]_D^{27} + 56^\circ$ , m. p. 120—123° (undepressed when mixed with an authentic sample <sup>4</sup> and indistinguishable in infrared and chromatoplate behaviour).

<sup>12</sup> Kuhn, Badstubner, and Grundmann, Ber., 1936, 69, 106.

<sup>13</sup> Bowden, Heilbron, Jones, and Weedon, J., 1946, 39.

<sup>14</sup> Sondheimer, Amendolla, and Rosenkranz, J. Amer. Chem. Soc., 1953, 75, 5930.

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