Triterpenoids. Part XXXVII. The Constitution of Taraxerol.*

By J. M. Beaton, F. S. Spring, Robert Stevenson, and J. L. Stewart.

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Considerations based on the reactions of taraxerol, a widely occurring triterpenoid alcohol, lead to the view that it has the structure (XVIII; R = H). This has been confirmed by the partial synthesis of taraxerol from β-amyrin (cf. *Chem. and Ind.*, 1954, 1454; 1955, 35).

In 1923, Zellner and Röglsperger (*Sitzungsber. Akad. Wiss. Wien*, 1923, **132**, 258) isolated an alcohol, alnulin, from the bark of the grey alder (*Alnus incana* L.) (cf. Fröschl and Zellner, *ibid.*, 1930, **139**, 476) and later it was obtained from the bark of the black alder (*Alnus glutinosa* L.) (Zellner and Weiss, *ibid.*, 1925, **134**, 312). Jeger and his collaborators (Koller, Hiestand, Dietrich, and Jeger, *Helv. Chim. Acta*, 1950, **33**, 1050) demonstrated the identity of alnulin and taraxerol, isolated by Burrows and Simpson (*J.*, 1938, 2042) from the root of the dandelion (*Taraxacum officinale*) and by Dunstan, Hughes, and Smithson (*Nature*, 1947, **160**, 577; *Austral. J. Chem.*, 1953, **6**, 321) from the bark of *Litsea dealbata* (*Lauraceae*). Meanwhile, Takeda (*J. Pharm. Soc. Japan*, 1941, **61**, 117; 1942, **62**, 390; 1943, **63**, 193, 197; Takeda and Yosiki, *ibid.*, 1941, **61**, 506) isolated an alcohol, skimmiol, from *Skimmia* (*Rutaceae*) species and suggested that it was identical with taraxerol. The identity of these alcohols has been established by Brooks (*Chem. and Ind.*, 1953, 1178). We suggest that the names alnulin and skimmiol be abandoned and that, in conformity with majority practice, the alcohol from these sources should be called taraxerol.†

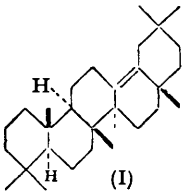
When our study of taraxerol started, a relation between this alcohol and the oleanane group of triterpenoids had been established. Takeda (*loc. cit.*) found that Clemmensen reduction of the derived ketone, taraxerone, gives olean-13(18)-ene (I) and this was confirmed by Koller *et al.* (*loc. cit.*). The excellent work of Takeda, some of which is mentioned below, led him to conclude that taraxerol is olean-18-en-3β-ol (II; R = H).‡ This opinion became untenable when germanicol, which differs from taraxerol, was shown to have this structure (Barton and Brooks, *J.*, 1951, 257). Koller *et al.* (*loc. cit.*) found that the double bond in taraxerol is of the type >C:CH· and that the hydroxyl group is present in a six-membered, or larger, ring. The Swiss workers did not construe the formation of olean-13(18)-ene from taraxerol as proof that the latter compound is an oleanane derivative.

* Part XXXVI, preceding paper.

† Tiliadin, isolated from the bark of *Tilia cordata* and *T. platyphyllos* (Brāutigam, *Arch. Pharm.*, 1900, **238**, 555; Thoms and Michaelis, *Ber. deut. pharm. Ges.*, 1916, **26**, 185; Zellner and Pelikant, *Sitzungsber. Akad. Wiss. Wien*, 1925, **134**, 616; Gerloff, *Planta*, 1936, **25**, 667), may be identical with taraxerol, but direct proof appears to be lacking.

‡ In the formulæ (II)—(XXV), R = Ac unless otherwise stated.

A considerable advance in the chemistry of taraxerol was marked by a preliminary report by Brooks (*loc. cit.*) on the treatment of taraxeryl acetate with selenium dioxide. This oxidation gives oleana-11 : 13(18)-dien-3β-yl acetate (III) and 12 : 19-dioxo-oleana-9(11) : 13(18)-dien-3β-yl acetate (IV). Brooks suggested that taraxerol is 13α-germanicol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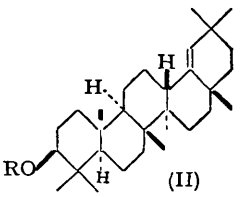
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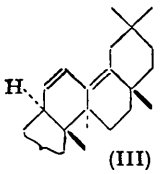
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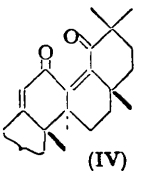
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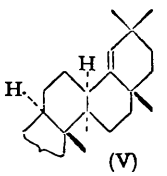
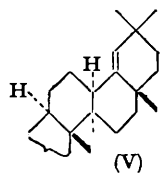

(V)

(V; R = H) with the proviso that rearrangement of the carbon skeleton does not occur during the oxidation.

For a number of reasons, we doubted the correctness of the structure (V; R = H) for taraxerol and, as our doubt transpired to be well founded, we believe they merit discussion. Takeda (*loc. cit.*) prepared taraxeryl acetate oxide, treatment of which with mineral acid yielded an unsaturated diol monoacetate, which on oxidation gave an unsaturated keto-acetate and on acetylation gave a diacetate. If taraxeryl acetate is (V), the oxide is (VI), the diol monoacetate (VII) and the keto-acetate (VIII) [19-oxo-olean-13(18)-en-3β-yl acetate]. By analogy, 19-oxo-olean-13(18)-en-3β-yl acetate (VIII) will be strongly lævorotatory as is methyl 3β-acetoxy-19-oxo-olean-13(18)-enoate ($[\alpha]_D$ −203°) and its relatives (Bilham, Kon, and Ross, *J.*, 1952, 540; Ruzicka, Grob, Egli, and Jeger, *Helv. Chim. Acta*, **1943**, **26**, 1218); Takeda found that the unsaturated keto-acetate from taraxeryl acetate is dextrorotatory ($[\alpha]_D$ +4°). The reaction sequence (V) ⟶ (VII), in our view, could not represent the conversion of taraxeryl acetate into the diol monoacetate since the last compound is formulated as an allylic alcohol which is unlikely to survive the acid condition used in its preparation.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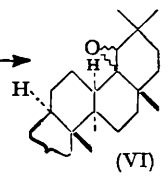
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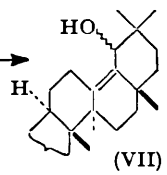
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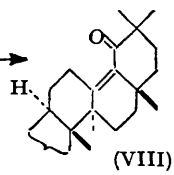
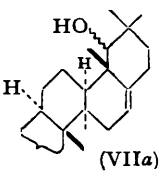
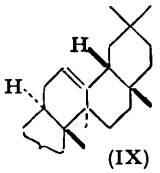
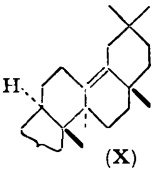

(VIII)


(VIIa)

These views were not considered to be more than reasons for testing the validity of the structure (V; R = H) for taraxerol, since alternative formulæ (*e.g.*, VII*a*) for the unsaturated diol monoacetate circumvent the criticisms outlined above. Two other facts, however, were difficult to reconcile with the structure (V; R = H) for taraxerol. First, dry distillation of taraxeryl benzoate gives a small yield of oleana-2 : 12-diene (Takeda, *loc. cit.*). Secondly, Clemmensen reduction of taraxerone for 24 hours gives olean-13(18)-ene, whereas similar reduction for 8 hours gives a hydrocarbon, the constants of which (m. p. 164—165°, $[\alpha]_D$ +25°) (Koller *et al.*, *loc. cit.*) correspond closely with those of a mixture of olean-12-ene and olean-13(18)-ene (Davy, Halsall, and Jones, *J.*, 1951, 458). If the hydrocarbon, m. p. 164—165°, is a mixture of the 12- and the 13(18)-ene, its conversion into pure olean-13(18)-ene by continued acid treatment is adequately explained, and, what is more important, during the Clemmensen reduction, the double bond originally present in taraxerone is moving to the 13(18)- *via* the 12 : 13-position. A simple experiment supported this view. A suspension of taraxeryl acetate in acetic acid at 90° was

treated with hydrochloric acid. The solid rapidly dissolved and after 10 minutes an excellent yield of β-amyrin acetate (olean-12-en-3β-yl acetate) (IX) was isolated. This shows that taraxerol cannot be (V; R = H), since the conversion of (V) into β-amyrin acetate (IX) would, in our view, require the conversion of the intermediate olean-13(18)-en-3β-yl acetate (X) into the thermodynamically less stable β-amyrin acetate (IX).


(IX)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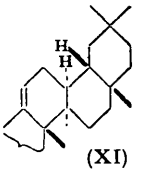
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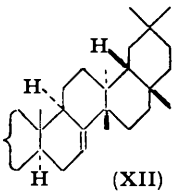

(XII)

At this stage we concluded that, if the conversion of taraxeryl acetate into β-amyrin acetate consists in a simple double-bond movement (without molecular rearrangement), the former compound must be 13α-olean-9(11)-en-3β-yl acetate (XI), the conversion of which into β-amyrin acetate (IX) must be due to the configuration at $C_{(13)}$; it is known that the 13β-isomer of (XI), olean-9(11)-en-3β-yl acetate, is stable to mineral acid (Budziarek, Johnston, Manson, and Spring, *J.*, 1951, 3019).

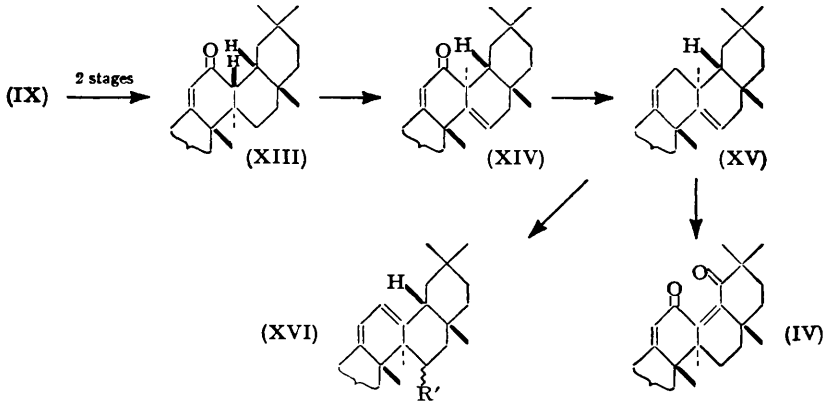
A re-examination of Takeda's oxide, unsaturated diol monoacetate, and unsaturated keto-acetate supplied a vital clue in the determination of the structure of taraxerol. The unsaturated keto-acetate does not contain an αβ-unsaturated ketone chromophore and consequently the fission of taraxeryl acetate oxide involves a molecular rearrangement. Dehydration of the diol monoacetate with phosphorus oxychloride in pyridine gives a non-conjugated dienyl acetate, catalytic hydrogenation of which yields β-amyrin acetate (IX). Hence the molecular rearrangement has *led* to an oleanane derivative and taraxerol cannot be an oleanane derivative, and more specifically, it cannot have the constitution represented by (XI; R = H).

The diol monoacetate is a hydroxy-β-amyrin acetate, the hydroxyl group in which marks the position of the double bond in taraxeryl acetate. The experiments and arguments outlined above led to consideration of the structures (XII; R = H) and (XVIII; R = H) for taraxerol. The acid-catalysed rearrangement of (XII) into β-amyrin acetate may be adequately represented as initiated by the approach of a proton to the double bond with synchronous movement of the methyl groups from $C_{(14)}$ (β) and $C_{(13)}$ (α) to $C_{(8)}$ and $C_{(14)}$ respectively, with final stabilisation by elimination of a proton from $C_{(12)}$. In its main features, this closely follows the pattern of the mechanism responsible for the conversion of euphenyl acetate into *iso*euphenyl acetate (Barton, McGhie, Pradhan, and Knight, *Chem. and Ind.*, 1954, 1325).

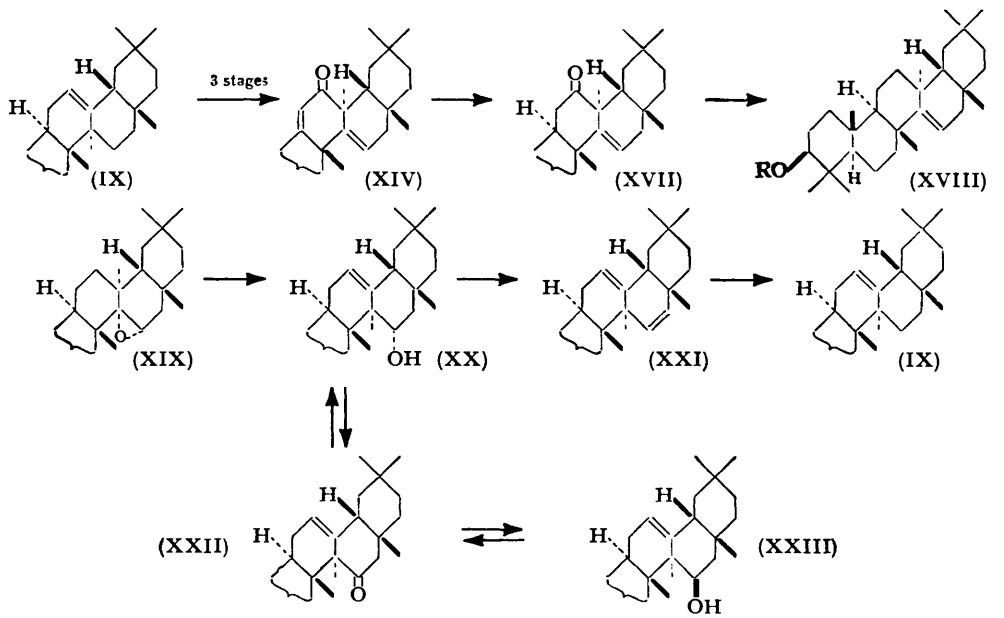
The alternative constitution (XVIII) for taraxeryl acetate was preferred because of a close analogy between the reactions of this acetate and those of *iso*oleana-9(11) : 14-dienyl acetate (XV) (Allan, Johnston, and Spring, *J.*, 1954, 1546). The latter compound was prepared by Wolff–Kishner reduction of 12-oxo*iso*oleana-9(11) : 14-dien-3β-yl acetate (XIV), itself obtained from 12-oxo-olean-9(11)-en-3β-yl acetate (XIII) by oxidation with selenium dioxide or bromine (Green, Mower, Picard, and Spring, *J.*, 1944, 527; Budziarek, Johnson, Manson, and Spring, *loc. cit.*). Treatment of the acetate (XV) with mineral acid gives oleana-9(11) : 12-dien-3β-yl acetate (XVI; R′ = H), a reaction bearing a striking resemblance to the conversion of taraxeryl acetate into β-amyrin acetate. When the acetate (XV) is treated with selenium dioxide, oxidation is accompanied by molecular rearrangement to give 12 : 19-dioxo-oleana-9(11) : 13(18)-dien-3β-yl acetate (IV), behaviour which again resembles that of taraxeryl acetate. Oxidation of the acetate (XV) with perbenzoic acid yields 15-hydroxyoleana-9(11) : 12-dienyl acetate (XVI; R′ = OH), presumably by rearrangement of an unstable oxide, a reaction to be compared with the conversion of taraxeryl acetate into the diol monoacetate.

A decision between the formulæ (XII) and (XVIII) for taraxeryl acetate was made in favour of the latter by partial synthesis. Reduction of 12-oxo*iso*oleana-9(11) : 14-dien-3β-yl acetate (XIV) with lithium in liquid ammonia yielded 12-oxo*iso*olean-14-en-3β-yl

acetate (XVII). By a modified (forcing) variant of the Wolff–Kishner technique (Barton, Ives, and Thomas, *J.*, 1955, 2056), the conditions for which were described to us, before their publication, by Professor D. H. R. Barton, F.R.S., to whom we express our best thanks, reduction of the ketone (XVII), followed by acetylation, yielded *iso*olean-14-en-3β-yl acetate



(XVIII) which is identical with taraxeryl acetate (taraxer-14-en-3β-yl acetate).* Since the ketone (XIV) is obtained from β-amyrin (IX), these reactions constitute a partial synthesis of taraxerol from β-amyrin. Taraxeryl acetate oxide is (XIX), the diol mono-acetate is olean-12-en-3β : 15α-diol 3-acetate (XX), the non-conjugated dienyl acetate is

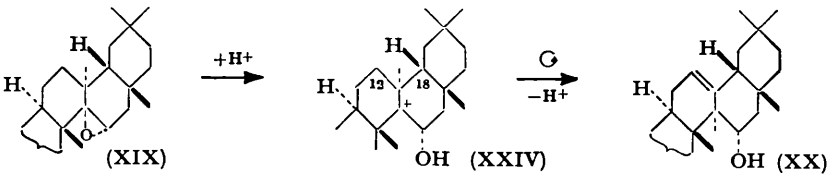


oleana-12 : 15-dien-3β-yl acetate (XXI), and the unsaturated keto-acetate is 15-oxo-olean-12-en-3β-yl acetate (XXII).

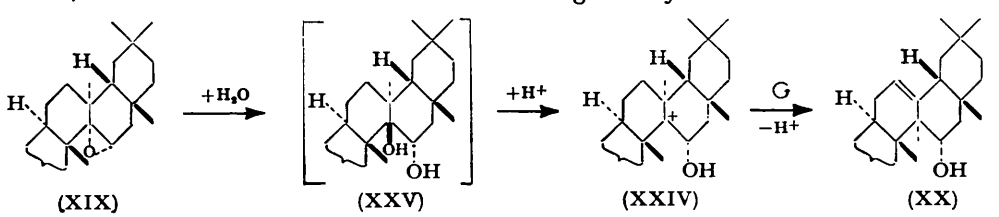
* The use of the name *iso*oleanane for the parent hydrocarbon of a naturally occurring triterpenoid is confusing because of the prior, frequent, and indiscriminate use of the prefix *iso* in the oleanane group of triterpenoids. We propose to change this name to taraxerane, and the derivatives of this hydrocarbon (in which the orientation of the hydrogen attached to $C_{(14)}$ is arbitrarily defined as α) described in the Experimental section are named accordingly. The saturated hydrocarbon obtained from dihydrotaraxerone by Clemmensen reduction (Takeda, *loc. cit.*) is almost certainly 13ε-taraxerane. Taraxer-14-ene has recently been isolated from a lichen (*Cladonia deformis* Hoffm.) by Bruun (*Acta Chem. Scand.*, 1954, **8**, 1291).

The configuration of the hydroxyl group in (XX) was deduced as follows: Reduction of 15-oxo-olean-12-en-3β-yl acetate (XXII) with lithium aluminium hydride gives olean-12-ene-3β : 15β-diol (XXIII; R = H). This diol gives a monoacetate (XXIII) only and in this respect it differs from its isomer (XX; R = H) which, under the same conditions, gives a diacetate. The relation of the diol monoacetates (XX) and (XXIII) as epimers at $C_{(15)}$ was confirmed by oxidation of (XXIII) to 15-oxo-olean-12-en-3β-yl acetate (XXII). It follows that the hydroxyl group in the diol monoacetate obtained by acid fission of taraxeryl acetate oxide is equatorially bound (α); support for this decision is afforded by reduction of 15-oxo-olean-12-en-3β-yl acetate with sodium and *iso*amyl alcohol to a diol identical with that obtained by hydrolysis of (XX) (Takeda, *loc. cit.*). The isomer (XXIII) obtained as described above is the axial (15β) epimer. The formation of the axial alcohol (XXIII; R = H) conforms to the rule that reduction of a heavily hindered ketone with lithium aluminium hydride gives an axial alcohol. The hindrance to the ketone group in (XXII) is demonstrated by the fact that this compound was recovered unchanged after an attempted Wolff–Kishner reduction under normal conditions.

In our opinion the demonstration of α-configuration for the hydroxyl group in (XX) proves that the epoxide ring in taraxeryl acetate oxide likewise has the α-configuration and that the conversion of the epoxide (XIX) into (XX) is to be represented, not as a group of fully synchronous events, but rather as follows:



The degeneration of the cation (XXIV) to (XX) consists in the movement of a methyl group and the elimination of a proton from $C_{(12)}$ and these are probably synchronous. It is noteworthy that proton elimination takes place from $C_{(12)}$, and not from $C_{(18)}$, to give the thermodynamically less stable Δ^{12}-compound rather than the more stable $\Delta^{13(18)}$-isomer; the reason for this is believed to lie in the geometry of the molecule.



Fission of the oxide ring in (XIX) appears to follow the usual rule of axial opening (Barton, *J.*, 1953, 1027). This is more evident if the assumption is made that an intermediate (*trans*-)glycol (XXV) is formed; both hydroxyl groups in (XXV) are ***axially*** bound with respect to ring D. The change from a taraxeran-15α-ol derivative (XXV) (in which the 15-hydroxyl group is ***axial***) to an oleanan-15α-ol derivative (XX) (in which the hydroxyl group is ***equatorial***) and a change in the conformation of ring D are concomitant.

Experimental

Rotations were measured in $CHCl_3$ at room temperature. Absorption spectra were measured in EtOH (unless otherwise stated) with a Unicam SP.500 spectrophotometer. For chromatography, Grade II alumina and a light petroleum fraction, b. p. 60—80°, were used.

Taraxerol.—This was obtained by lithium aluminium hydride reduction of taraxerone (isolated from *Alnus glutinosa* L.); it separates as plates from chloroform–methanol and as needles from benzene, and has m. p. 282—285°, $[\alpha]_D$ ±0° (*c*, 0·6). Koller *et al.* (*loc. cit.*) give m. p. 282—283°, $[\alpha]_D$ ±0°, and Takeda (*loc. cit.*) gives m. p. 279—281°, $[\alpha]_D$ +3°. Acetylation with pyridine and acetic anhydride gave taraxeryl acetate as plates (from chloroform–methanol),

m. p. 303—305°, $[\alpha]_D$ +10·5° (*c*, 1·8). Koller *et al.* (*loc. cit.*) give m. p. 304—305°, $[\alpha]_D$ +9°, and Takeda (*loc. cit.*) gives m. p. 298—299°, $[\alpha]_D$ +13·8°. In the later stages of this work, we used taraxerol isolated from *Skimmia* by Dr. K. Takeda; we thank Dr. C. J. W. Brooks for his generosity in giving us this material.

14α : 15α-*Epoxytaraxeran*-3β-*yl Acetate*.—A solution of taraxeryl acetate (150 mg.) in chloroform (50 c.c.) was treated at 0° with a freshly prepared solution of perbenzoic acid (1·2 mol.) in chloroform, and the solution kept at 0° for 18 hr. The solution was washed with sodium hydrogen carbonate solution and water, and dried (Na_2SO_4), and the solvent removed below 15°. Crystallisation of the residue from chloroform–methanol gave 14α : 15α-epoxytaraxeran-3β-yl acetate as plates (110 mg.), m. p. 257—260°, $[\alpha]_D$ +43° (*c*, 1·0), no selective light absorption above 2000 Å. The oxide does not give a colour with tetranitromethane. Takeda (*loc. cit.*) gives m. p. 257—260°, $[\alpha]_D$ +47°.

It is essential that the per-acid solution should be freshly prepared. Thus, part of a freshly made solution of perbenzoic acid in chloroform was successfully used for the preparation of the epoxide. Use of the remaining part of the same solution after storage at 0° in the dark for 2 days gave olean-12-ene-3β : 15α-diol 3-acetate and not the epoxide. The constants (m. p. 287°, $[\alpha]_D$ +73°) given by Koller *et al.* (*loc. cit.*) for " taraxeryl acetate oxide " show that their product is olean-12-ene-3β : 15α-diol 3-acetate (see below).

Olean-12-*ene*-3β : 15α-*diol* 3-*Acetate*.—(*a*) 2N-Sulphuric acid (5 c.c.) was added to a solution of 14α : 15α-epoxytaraxeran-3β-yl acetate (80 mg.) in glacial acetic acid (100 c.c.), and the mixture heated on the steam-bath for 1 hr. A solution of the product in benzene–light petroleum (2 : 1; 25 c.c.) was chromatographed on alumina. Elution with benzene gave a solid (35 mg.), which, after crystallisation from chloroform–methanol, gave olean-12-ene-3β : 15α-diol 3-acetate as needles, m. p. 284—288°, $[\alpha]_D$ +73°, +72° (*c*, 0·9, 1·5), ε at 2060 Å = 4500 (Found: C, 79·1; H, 10·6. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%). It gives a pale yellow colour with tetranitromethane. Takeda (*loc. cit.*) gives m. p. 283—286°, $[\alpha]_D$ +78·7°.

(*b*) Concentrated hydrochloric acid (4 c.c.) and water (4 c.c.) were added to a solution of 14α : 15α-epoxytaraxeran-3β-yl acetate (135 mg.) in methanol (100 c.c.) and chloroform (25 c.c.). The mixture was kept at room temperature for 18 hr., and the product isolated in the usual manner. Crystallisation from chloroform–methanol gave olean-12-ene-3β : 15α-diol 3-acetate as needles (80 mg.), m. p. and mixed m. p. 284—288°, $[\alpha]_D$ +74° (*c*, 1·3).

3β : 15α-*Diacetoxyolean*-12-*ene*.—Olean-12-ene-3β : 15α-diol 3-acetate (70 mg.) was treated at 100° with pyridine and acetic anhydride for 1 hr. The product, isolated in the usual way, crystallised from chloroform–methanol, to give 3β : 15α-diacetoxyolean-12-ene as needles (40 mg.), m. p. 203—205°, $[\alpha]_D$ +51°, +50° (*c*, 0·8, 1·3) (Found: C, 77·3; H, 9·85. Calc for $C_{34}H_{54}O_4$: C, 77·5; H, 10·3%). Takeda (*loc. cit.*) gives m. p. 207—208·5°.

Hydrolysis of the diacetate with 5% methanolic potassium hydroxide solution, and crystallisation of the product from aqueous acetone gave olean-12-ene-3β : 15α-diol as needles, m. p. 244—246°, $[\alpha]_D$ +82°, +83° (*c*, 0·95, 1·0) (Found: C, 81·1; H, 11·4. Calc. for $C_{30}H_{50}O_2$: C, 81·4; H, 11·4%). It gives a pale yellow colour with tetranitromethane. Takeda (*loc. cit.*) gives m. p. 246—247°, $[\alpha]_D$ +85°.

15-*Oxo-olean*-12-*en*-3β-*yl-Acetate*.—A solution of olean-12-ene-3β : 15α-diol 3-acetate (100 mg.) in benzene (10 c.c.) and acetic acid (100 c.c.) was treated at room temperature with a solution of chromium trioxide (15·3 mg.) in acetic acid (3 c.c.), added with stirring during 15 min. The mixture, after being kept overnight, was worked up in the usual way. Crystallisation of the product from chloroform–methanol gave 15-oxo-olean-12-en-3β-yl acetate as needles (70 mg.), m. p. 278—280°, $[\alpha]_D$ +27°, +27° (*c*, 1·2, 1·0), ε at 2040 Å = 4800, with no high-intensity selective absorption above 2200 Å (Found: C, 79·7; H, 10·4. Calc. for $C_{32}H_{50}O_3$: C, 79·6; H, 10·4%). It gives a pale yellow colour with tetranitromethane. Takeda (*loc. cit.*) gives m. p. 278—279°, $[\alpha]_D$ +4·1°. The ketone was recovered unchanged after being exposed to normal Wolff–Kishner reduction, followed by acetylation.

Olean-12-*ene*-3β : 15β-*diol*.—A solution of 15-oxo-olean-12-en-3β-yl acetate (207 mg.) in dry ether (130 c.c.) was refluxed for 1 hr. with lithium aluminium hydride (210 mg.), and kept overnight at room temperature. The *product*, isolated in the usual way, crystallised from aqueous acetone, to yield olean-12-ene-3β : 15β-diol (150 mg.) as needles, m. p. 194—196°, $[\alpha]_D$ +68° (*c*, 1·1, 0·9) (Found: C, 81·35; H, 11·3. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). It gives a pale yellow colour with tetranitromethane.

Olean-12-*ene*-3β : 15β-*diol* 3-*Acetate*.—(*a*) The 3β : 15β-diol (100 mg.) in pyridine and acetic anhydride was kept at room temperature overnight. The product, obtained in the usual way, crystallised from chloroform–methanol to furnish *olean*-12-*ene*-3β : 15β-*diol* 3-*acetate* (70 mg.) as

plates, m. p. 273—276°, $[\alpha]_D$ +65°, +64° (*c*, 0·9, 1·1) Found: C, 79·25; H, 11·0. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%).

(*b*) The diol (45 mg.) was treated with pyridine and acetic anhydride at 100° for 1 hr. Crystallisation of the product from chloroform–methanol gave the diol monoacetate as plates (20 mg.), m. p. and mixed m. p. 273—276°, $[\alpha]_D$ +64° (*c*, 0·45). A mixture of the 3β : 15β-diol 3-acetate with the isomeric 3β : 15α-diol 3-acetate (m. p. 284—288°) had m. p. 277—282°.

Chromic Acid Oxidation of Olean-12-ene-3β : 15β-diol 3-Acetate.—A solution of the 3β : 15β-diol monoacetate (75 mg.) in glacial acetic acid (60 c.c.) was treated with a solution of chromium trioxide (1·2 mol.) in acetic acid (2·7 c.c.), added dropwise with stirring during 15 min., and kept at room temperature overnight. The product, isolated in the usual way, crystallised from chloroform–methanol to give 15-oxo-olean-12-en-3β-yl acetate as needles (30 mg.), m. p. and mixed m. p. 277—279°, $[\alpha]_D$ +25° (*c*, 1·0).

Conversion of Taraxeryl Acetate into β-Amyrin Acetate.—To a suspension of taraxer-14-en-3β-yl acetate (150 mg.) in glacial acetic acid (35 c.c.) at 90°, was added concentrated hydrochloric acid (1 c.c.). After the mixture had been heated on the steam-bath for 10 min., during which the suspended solid dissolved, the solvent was rapidly removed under reduced pressure. Crystallisation of the solid from chloroform–methanol gave β-amyrin acetate as prismatic needles (80 mg.), m. p. and mixed m. p. 241—242°, $[\alpha]_D$ +82° (*c*, 0·9). Concentration of the mother-liquors gave a second crop of β-amyrin acetate (60 mg.), m. p. and mixed m. p. 238—240°.

Dehydration of Olean-12-ene-3β : 15α-diol 3-Acetate.—The diol monoacetate (100 mg.), pyridine (5 c.c.), and phosphorus oxychloride (0·5 c.c.) were heated under reflux for 2 hr. The product was isolated in the usual manner. It crystallised from methanol as needles, m. p. 153—185°. Five recrystallisations from chloroform–methanol gave *oleana-12 : 15-dien-3β-yl acetate* as needles, m. p. 207—208°, $[\alpha]_D$ +42° (*c*, 0·8), ε at 2050 Å = 8200 (Found: C, 81·8; H, 10·8. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%).

Hydrogenation of Oleana-12 : 15-dien-3β-yl Acetate.—A solution of the dienyl acetate (39 mg.) in glacial acetic acid (100 c.c.) was shaken in hydrogen with platinum (from 100 mg. of PtO_2) for 14 hr. Crystallisation of the product from chloroform–methanol gave β-amyrin acetate as needles (32 mg.), m. p. and mixed m. p. 238—240°, $[\alpha]_D$ +78° (*c*, 1·4).

12-Oxotaraxer-14-en-3β-yl Acetate.—A solution of 12-oxotaraxera-9(11) : 14-dien-3β-yl acetate [12-oxo*iso*oleana-9(11) : 14-dien-3β-yl acetate] (2·0 g.) in ether (75 c.c.) was added during 2 min. with stirring to a solution of lithium (600 mg.) in liquid ammonia (400 c.c.). After 3 minutes' stirring, acetone was added, and the ammonia allowed to evaporate. The product was heated for 1 hr. with acetic anhydride and pyridine, and the acetylated product purified by chromatography of its solution in light petroleum–benzene (5 : 1) on alumina. Elution of the column with light petroleum–benzene (1 : 1) yielded a solid which recrystallised from chloroform–methanol to give *12-oxotaraxer-14-en-3β-yl acetate* as needles (700 mg.), m. p. 298—300°, $[\alpha]_D$ −30°, −29° (*c*, 1·2, 1·1), absorption max. at 2060 Å (ε 4300) in EtOH, 2850 Å (ε 50) in $CHCl_3$ (Found: C, 79·9; H, 10·45. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). It gives a pale yellow colour with tetranitromethane.

Hydrolysis of the acetate for 1 hr. by refluxing 5% methanolic potassium hydroxide solution and working up in the usual way gave *12-oxotaraxer-14-en-3β-ol* as needles (from methanol), m. p. 276—278°, $[\alpha]_D$ −45°, −43° (*c*, 1·1, 0·9) (Found: C, 80·95; H, 10·9. $C_{30}H_{48}O_2,\frac{1}{2}CH_3{\cdot}OH$ requires C, 81·0; H, 10·9%).

Reduction of 12-Oxotaraxer-14-en-3β-yl Acetate to Taraxeryl Acetate.—12-Oxotaraxer-14-en-3β-yl acetate (200 mg.) was added to a solution obtained by the addition of sodium (500 mg.) to freshly distilled diethylene glycol (25 c.c.), and the mixture heated to 180°. Anhydrous hydrazine was distilled into the mixture until the solution refluxed gently at 180°. After refluxing at this temperature for 18 hr., the mixture was distilled until the temperature rose to 210°, whereafter refluxing was continued for 24 hr. The product, isolated by means of benzene, was acetylated on the steam-bath with pyridine and acetic anhydride. Crystallisation from chloroform–methanol gave taraxer-14-en-3β-yl acetate as plates (110 mg.), m. p. 302—304°, $[\alpha]_D$ +10·5° (*c*, 1·8), undepressed in m. p. on mixing with an authentic specimen of taraxeryl acetate, m. p. 302—305°, isolated from alder bark.

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