737. *Triterpene Resinols and Related Acids. Part XXVII.* Oleana-9(11) : 13(18)-dienol and Oleana-9(11) : 18-dienol. The Conversion of β-Amyrin into Germanicol.*

By J. M. Beaton, J. D. Johnston, L. C. McKean, and F. S. Spring.

Oleana-9(11) : 13(18)-dienyl acetate (II; R = Ac) has been obtained by catalytic hydrogenolysis or stepwise reduction of dioxo-β-amyradienyl acetate (I; R = Ac). Lithium aluminium hydride reduces (I; R = Ac) to oleana-9(11) : 13(18)-diene-3 : 19-diol † (V; R = H), the mono- and di-acetates of which yield (II; R = Ac) on catalytic hydrogenolysis. By a stepwise series of reductions (I; R = Ac) has been converted into olean-9(11)-ene-3 : 19α-diol (XVII; R = H) and 18α-olean-9(11)-ene-3 : 19β-diol (XIX; R = H), the monoacetates of which give oleana-9(11) : 18-dienyl acetate (XVIII; R = Ac) on dehydration. Oleana-9(11) : 13(18)- and -9(11) : 18-dienyl acetates are isomerised by mineral acid to oleana-11 : 13(18)-dienyl acetate (III; R = Ac).

The conversion of β-amyrin into germanicol is described. Oxidation of the β-amyrin derivative 18α-olean-9(11)-ene-3 : 19β-diol 3-acetate (XIX; R = Ac) with hydrogen peroxide, followed by Wolff–Kishner reduction of the intermediate 11-oxo-18α-oleanane-3 : 19β-diol 3-acetate (XX; R = Ac), gives 18α-oleanane-3 : 19β-diol (XXI; R = H) previously obtained from lupeol by Ames, Davy, Halsall, and Jones (*J.*, 1952, 2868). Dehydration of the monoacetate (XXI; R = Ac) yields germanicyl acetate (XXII; R = Ac).

The formation of dioxo-β-amyradienyl acetate from derivatives of β-amyrin acetate by selenium dioxide oxidation is discussed.

The experiments described below were undertaken with the object of preparing the non-conjugated dienyl acetates, oleana-9(11) : 13(18)-, 9(11) : 18-, and -11 : 18-dienyl acetates † which are required for comparison with a non-conjugated dienyl acetate obtained from oxo-*iso*-β-amyradienyl acetate to be described in a later part of this Series. A method for the preparation of oleana-11 : 18-dienyl acetate has not yet been discovered but alternative methods for the preparation of the 9(11) : 18- and 9(11) : 13(18)-dienyl acetates are described below.

As a first approach to oleana-9(11) : 13(18)-dienyl acetate, the hydrogenolysis of dioxo-β-amyradienyl acetate (I) ‡ was examined. When platinum was used as catalyst and acetic acid as solvent two products, $C_{32}H_{50}O_2$ and $C_{32}H_{50}O_3$, were isolated. The former gives a deep yellow colour with tetranitromethane in chloroform, and shows an apparent absorption maximum at 2100 Å (ε = 10,000) but does not selectively absorb in the ultra-violet region above 2200 Å. When treated with hydrochloric–acetic acid, it is isomerised to oleana-11 : 13(18)-dienyl acetate (III) (Barton and Brooks, *J.*, 1951, 257) in high yield. The compound $C_{32}H_{50}O_2$ is therefore one of the three non-conjugated oleanadienyl acetates named in the first paragraph; its intense absorption of light between 2100 and 2250 Å (Bladon, Henbest, and Wood, *J.*, 1952, 2737; Halsall, *Chem. and Ind.*, 1951, 867), together with its method of preparation, suggests that one of the double bonds is between $C_{(13)}$ and $C_{(18)}$. Consequently we conclude that the compound is oleana-9(11) : 13(18)-dienyl acetate (II), a decision confirmed by its formation by another route to be described.

The second product of the catalytic hydrogenolysis of dioxo-β-amyradienyl acetate is 19-oxo-olean-9(11)-enyl acetate (XI) : it gives a yellow colour with tetranitromethane and its ultra-violet absorption spectrum indicates the presence of a triply substituted double bond and an isolated carbonyl group. 19-Oxo-olean-9(11)-enyl acetate has been obtained from dioxo-β-amyradienyl acetate by an unambiguous stepwise method described below.

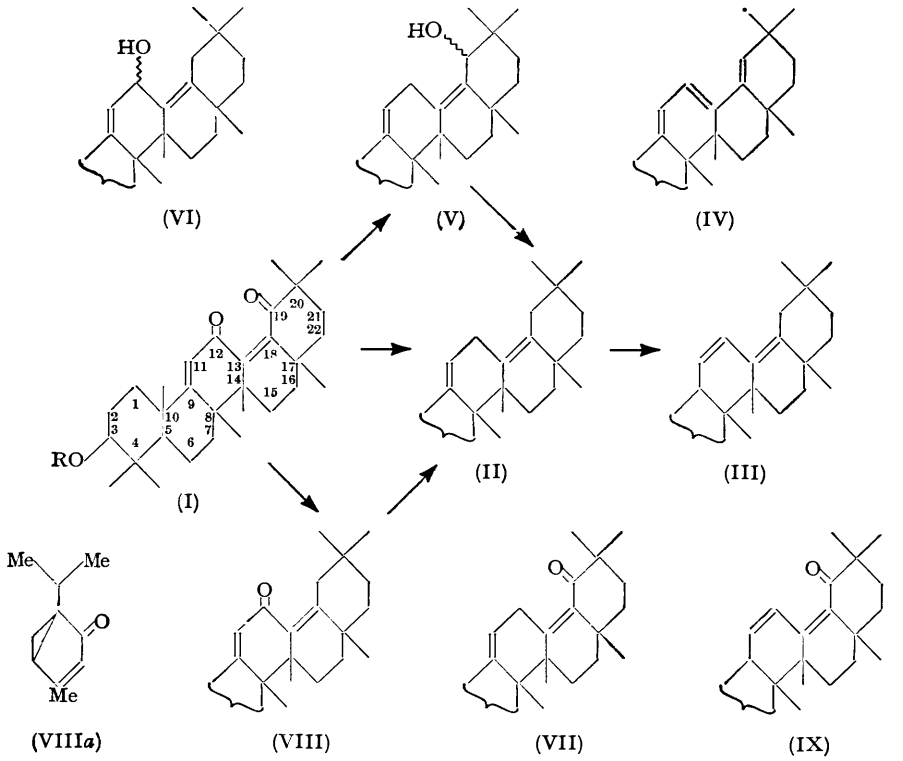
Oleana-9(11) : 13(18)-dienyl acetate has also been prepared from dioxo-β-amyradienyl acetate by a two-stage reduction process. Treatment of the dioxodienyl acetate with

* Part XXVI, *J.*, 1953, 943.

† For numbering [cf. (I)] see *J.*, 1953, 3024.

‡ Unless specified to the contrary, R = Ac in all the formulæ.

lithium aluminium hydride gives an oleanadienediol, $C_{30}H_{48}O_2$. This remarkable reaction has involved the reduction of one of the two carbonyl groups of the parent dioxodienyl acetate to a methylene group and the normal reduction of the second carbonyl to a secondary hydroxyl group. Partial acetylation of the diol yields a monoacetate, $C_{32}H_{50}O_3$, which gives a yellow colour with the tetranitromethane reagent. The monoacetate does not exhibit selective absorption in the ultra-violet region above 2200 Å but shows strong absorption between 2100 and 2250 Å similar to that of oleana-9(11) : 13(18)-dienyl acetate.

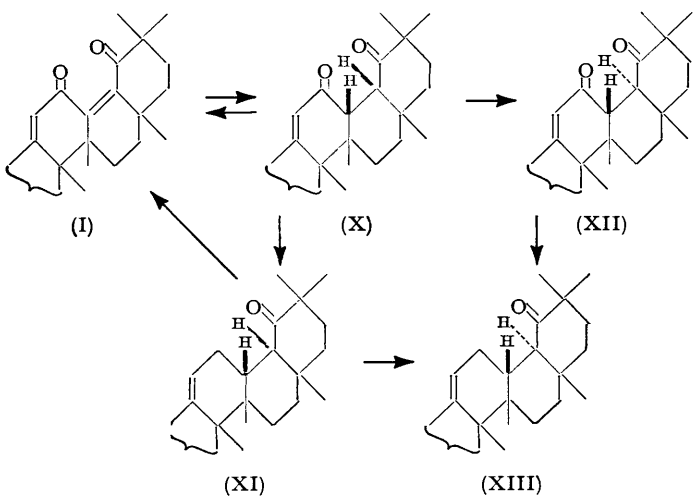


Prolonged acetylation of the monoacetate yields a diacetate, $C_{34}H_{52}O_4$, and catalytic hydrogenolysis of either the monoacetate or the diacetate yields oleana-9(11) : 13(18)-dienyl acetate. In order to decide between the two possible structures, (V) and (VI), for the monoacetate an attempt was made to oxidise it to the ketone; a decision between the alternative formulæ (VII) and (VIII) for the latter should be readily made. The ketone was not obtained; oxidation of the diol monoacetate with chromic acid equivalent to one oxygen atom at room temperature yielded a mixture from which dioxo-β-amyradienyl acetate (I) and unchanged diol monoacetate were separated; on use of an excess of oxidising agent, again at room temperature, the dioxodienyl acetate was isolated as sole product in excellent yield. Treatment of the diol diacetate with chromic acid at room temperature also gave the dioxodienyl acetate. Treatment of the monoacetate with mineral acid converts it in high yield into oleana-9(11) : 12 : 18-trienyl acetate (IV) (Ruzicka, Jeger, and Redel, *Helv. Chim. Acta*, 1943, **26**, 1235) presumably by anionotropic rearrangement and dehydration. It is probable that the oxidation of the monoacetate (and diacetate) is preceded by a similar conversion into the trienyl acetate, oxidation of which with chromic acid gives the dioxodienyl acetate (Newbold and Spring, *J.*, 1944, 532). An attempt to oxidise the diol monoacetate with manganese dioxide also led to the trienyl acetate.

Attention was next directed to the preparation of oleana-9(11) : 18-dienyl acetate.

Barton, Holness, Overton, and Rosenfelder (*J.*, 1952, 3751) observed that methyl 12 : 19-dioxo-oleana-9(11) : 13(18)-dienolate acetate * is reduced smoothly by zinc and acetic acid to methyl 12 : 19-dioxo-olean-9(11)-enolate acetate. Using their conditions we find that reduction of the related 12 : 19-dioxo-oleana-9(11) : 13(18)-dienyl acetate (dioxo-β-amyradienyl acetate) is a complex reaction, giving a mixture separated by chromatography into (*a*) oleana-9(11) : 13(18)-dienyl acetate (II) identical with the dienyl acetate obtained from dioxo-β-amyradienyl acetate by the two methods described above, (*b*) an acetate, $C_{32}H_{48}O_3$, and (*c*) an acetate, $C_{32}H_{48}O_4$.

Reduction of dioxo-β-amyradienyl acetate with zinc dust in ethanol gives the acetate, $C_{32}H_{48}O_4$, as sole product in excellent yield; it is probably identical with an acetate, $C_{32}H_{48}O_4$, obtained by Ruzicka and Jeger (*Helv. Chim. Acta*, 1941, **24**, 1236) by the catalytic hydrogenation of dioxo-β-amyradienyl acetate for which the structure 12 : 19-dioxo-olean-13(18)-enyl acetate was considered and rejected. Ruzicka and Jeger suggested that the acetate may have been produced from dioxo-β-amyradienyl acetate by reduction of one of the carbonyl groups to a secondary hydroxyl group. Barton *et al.* (*loc. cit.*, 1952), however, preferred to regard the reduction product as 12 : 19-dioxo-olean-9(11)-enyl acetate (X) and this opinion is, in our view, undoubtedly correct for the following reasons. The acetate, $C_{32}H_{48}O_4$, does not contain a secondary hydroxyl group since it is recovered unchanged after treatment with acetic anhydride and is stable to chromic anhydride at room temperature. The presence of an αβ-unsaturated carbonyl group is established by the ultra-violet absorption spectrum (max. at 2460 Å, $\varepsilon = 12{,}500$), and the presence of a second (isolated) carbonyl group by conversion of the acetate into 19-oxo-olean-9(11)-enyl acetate by hydrogenolysis as described below. Consequently the formation of the acetate $C_{32}H_{48}O_4$ from dioxo-β-amyradienyl acetate has involved the reduction of the 13 : 18-double bond as in the analogous reduction of methyl 12 : 19-dioxo-olean-9(11) : 13(18)-dienolate acetate and as expected from mechanistic considerations (Barton *et al.*, *loc. cit.*, 1952). Treatment of 12 : 19-dioxo-olean-9(11)-enyl acetate with alkali, followed by reacetylation, gave the isomeric 12 : 19-dioxo-18α-olean-9(11)-enyl acetate (XII).



The differences between the products obtained from our catalytic reduction of dioxo-β-amyradienyl acetate and those obtained by Ruzicka and Jeger are to be attributed either to a difference in the activity of the platinum catalysts or to the incompleteness of the latter reaction since hydrogenolysis of 12 : 19-dioxo-olean-9(11)-enyl acetate using a platinum catalyst in acetic acid at room temperature yields 19-oxo-olean-9(11)-enyl acetate (XI) identical with the product obtained by direct hydrogenolysis of dioxo-β-amyradienyl acetate under the same conditions. The latter reaction, as shown above,

* Numbering as in this paper, not that of *J.*, 1952, 3751.

yields a mixture of oleana-9(11) : 13(18)-dienyl acetate (II) and 19-oxo-olean-9(11)-enyl acetate (XI). These two products are presumably formed by concurrent reactions, the latter as a result of saturation of the 13 : 18-double bond followed by hydrogenolysis of the 12-carbonyl group, and the former as a result of initial hydrogenolysis of one of the carbonyl groups to give 19- and/or 12-oxo-oleana-9(11) : 13(18)-dienyl acetate, further hydrogenolysis of which yields the 9(11) : 13(18)-dienyl acetate.

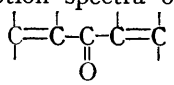
The acetate, $C_{32}H_{48}O_3$, obtained by zinc and acetic acid reduction of dioxo-β-amyradienyl acetate, gives a pale yellow colour with tetranitromethane, and its ultra-violet absorption spectrum shows intense maxima at 2080 ($\varepsilon = 9000$), 2600 ($\varepsilon = 9250$), and 2950 Å ($\varepsilon = 8450$). On catalytic hydrogenolysis it is converted in high yield into oleana-9(11) : 13(18)-dienyl acetate and on oxidation with selenium dioxide is converted into dioxo-β-amyradienyl acetate. Furthermore, during an attempt to convert it into an enol acetate by prolonged refluxing with acetic anhydride and sodium acetate, it was oxidised to dioxo-β-amyradienyl acetate. Because of its remarkable ultra-violet absorption spectrum, considerable pains were taken to ensure its homogeneity; on alkaline hydrolysis it gives a well-defined alcohol $C_{30}H_{46}O_2$, showing essentially the same ultra-violet absorption spectrum as the parent acetate. Reacetylation of the alcohol yields the acetate, $C_{32}H_{48}O_3$, with unaltered physical characteristics. This acetate is an intermediate in the conversion of dioxo-β-amyradienyl acetate into oleana-9(11) : 13(18)-dienyl acetate by means of zinc and acetic acid since further treatment of the acetate $C_{32}H_{48}O_3$ with these reagents converts it into the dienyl acetate.

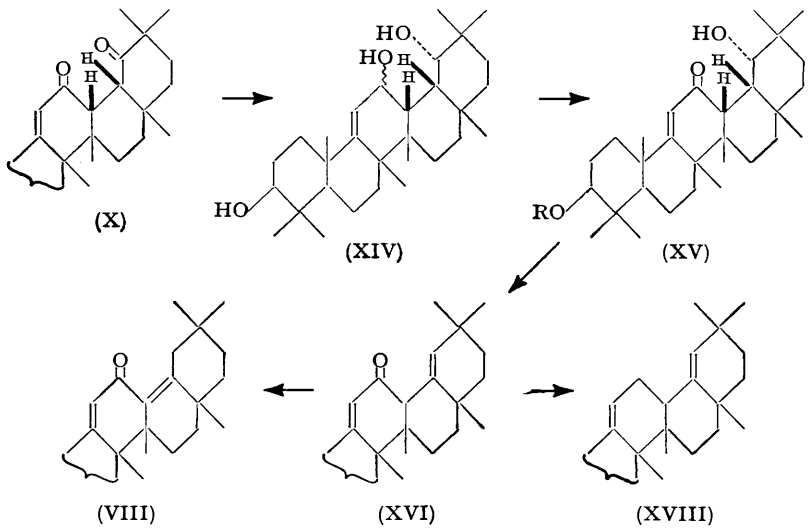
The acetate $C_{32}H_{48}O_3$ is formed from dioxo-β-amyradienyl acetate by the reduction of one of the carbonyl groups to a methylene group and is consequently to be formulated as either (VII) or (VIII). It was realised, however, that the nature of its ultra-violet absorption spectrum is roughly consistent with the view that the acetate is an inseparable mixture of (VII) and the conjugated dienone (IX), in which case the absorption maximum at 2600 Å is due to the αβ-unsaturated ketone chromophore of (VII) and the maximum at 2950 Å is attributable to the dienone chromophore of (IX). This view became improbable when the acetate was shown to be stable to strong mineral acid, and in particular when the ultra-violet absorption spectrum of the acetate was found to be unchanged after such treatment; if the mixed-crystal view is correct, mineral acid treatment of the acetate would be expected to yield the homogeneous conjugated dienone (IX) with a consequent change in the ultra-violet absorption spectrum. These considerations suggested that the acetate $C_{32}H_{48}O_3$ is 12-oxo-oleana-9(11) : 13(18)-dienyl acetate (VIII) and this has been confirmed by its partial synthesis by an unambiguous method.

Reduction of 12 : 19-dioxo-olean-9(11)-enyl acetate (X) with lithium aluminium hydride gives the unstable olean-9(11)-ene-3 : 12 : 19-triol (XIV) which may be a mixture of the 3 : 12α : 19α- and the 3 : 12β : 19α-triol. A differential oxidation of this triol was achieved by the use of manganese dioxide in acetone (Goodwin and Morton, *Biochem. J.*, 1948, **42**, 516) which oxidises αβ-unsaturated alcohols to the corresponding αβ-unsaturated carbonyl derivative (Attenburrow, Cameron, Chapman, Evans, Hems, Johnson, and Walker, *J.*, 1952, 1094) and is without effect, at room temperature, on saturated alcohols (Sondheimer and Rosenkranz, *Experientia*, 1953, **9**, 62). The triol (XIV) thus gave, on subsequent partial acetylation, 12-oxo-olean-9(11)-ene-3 : 19α-diol 3-acetate (XV), characterised as an αβ-unsaturated ketone by its ultra-violet absorption maximum at 2460 Å ($\varepsilon = 11{,}400$). Dehydration of 12-oxo-olean-9(11)-ene-3 : 19α-diol 3-acetate gave 12-oxo-oleana-9(11) : 18-dienyl acetate (XVI) which shows an ultra-violet absorption maximum at 2500 Å ($\varepsilon = 11{,}000$) and, unlike the parent 12-oxo-olean-9(11)-ene-3 : 19α-diol 3-acetate, gives a yellow colour with tetranitromethane. Treatment of 12-oxo-oleana-9(11) : 18-dienyl acetate with mineral acid readily gave 12-oxo-oleana-9(11) : 13(18)-dienyl acetate (VIII) * identical with the acetate $C_{32}H_{48}O_3$ obtained by treatment of dioxo-β-amyradienyl acetate with zinc and acetic acid.

Our initial reluctance to accept the now established structure (VIII) for the acetate

* Unsuccessful attempts to isomerise methyl 12-oxo-olean-18-enolate acetate to methyl 12-oxo-olean-13(18)-enolate acetate have been reported (Barton *et al.*, *loc. cit.*, 1952).

$C_{32}H_{48}O_3$ was due to its remarkable ultra-violet absorption spectrum. The ultra-violet absorption spectra of a number of conjugated dienones containing the chromophoric group  have been recorded (see, for example, the discussion by Ruzicka, Cohen, Furter, and Sluys-Veer, *Helv. Chim. Acta*, 1938, **21**, 1735). The acyclic phorone shows a single absorption maximum at 2650 Å in alcohol whilst cyclic dienones of this type

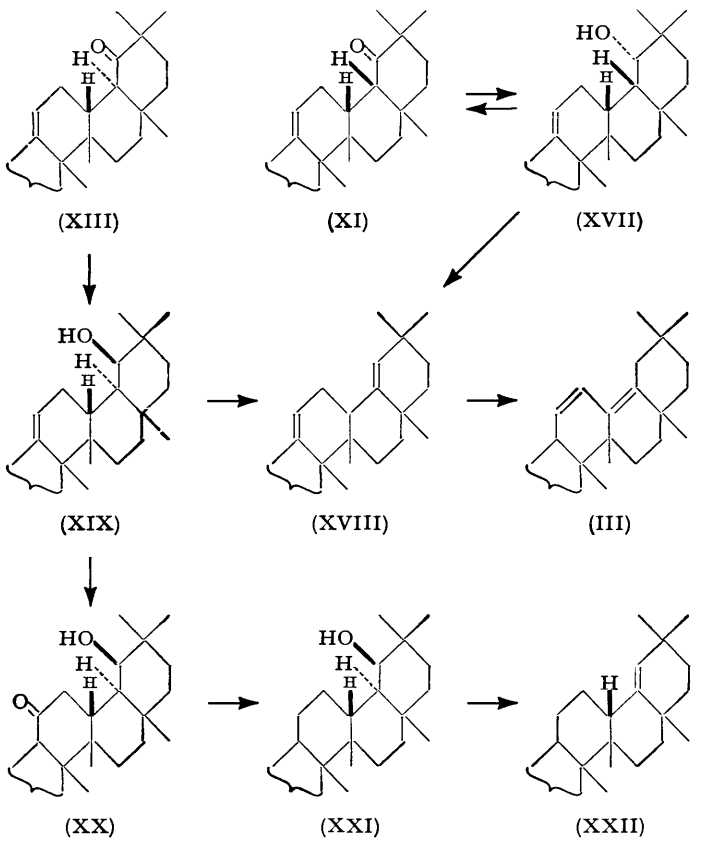


which contain the chromophore in a single six-membered ring (*e.g.*, steroid 1 : 4-dien-3-ones) show an intense absorption maximum at approx. 2400 Å. A dienone strictly analogous to 12-oxo-oleana-9(11) : 13(18)-dienyl acetate in which the chromophore is spread over two rings does not appear to have been described in either the steroid or the triterpenoid groups. It is probable that the abnormal absorption spectrum of 12-oxo-oleana-9(11) : 13(18)-dienyl acetate is to be associated with the distorted geometry of the chromophoric group. A resemblance in the shape of the absorption spectra curves for this acetate and for umbellulone (VIII*a*) is worthy of comment : the latter is also anomalous, with two maxima at 2200 ($\varepsilon = 5000$) and 2650 Å ($\varepsilon = 2900$) (Gillam and West, *J.*, 1945, 97), and this has been attributed to the distorted geometry of the total chromophore.

The establishment of the structure of the acetate $C_{32}H_{48}O_3$ as 12-oxo-oleana-9(11) : 13(18)-dienyl acetate has permitted a decision to be made between the alternative formulæ (V) and (VI) for the oleana-9(11) : 13(18)-diol monoacetate obtained from dioxo-β-amyradienyl acetate by lithium aluminium hydride reduction followed by partial acetylation. Reduction of 12-oxo-oleana-9(11) : 13(18)-dienyl acetate with lithium aluminium hydride (followed by acetylation) gives oleana-9(11) : 13(18)-dienyl acetate, reduction of the 12-carbonyl to a methylene group having occurred. This is similar to the reduction of dioxo-β-amyradienyl acetate with the same reagent and it is probable that the same carbonyl group has been involved in each case. If this is true, the diol monoacetate obtained from dioxo-β-amyradienyl acetate is oleana-9(11) : 13(18)-diene-3 : 19-diol 3-acetate (V).

Treatment of 19-oxo-olean-9(11)-enyl acetate (XI) with alkali followed by acetylation gives 19-oxo-18α-olean-9(11)-enyl acetate (XIII), also obtained, but not without difficulty, by hydrogenolysis of 12 : 19-dioxo-18α-olean-9(11)-enyl acetate (XII). These reactions prove that 19-oxo-olean-9(11)-enyl acetate and its alkali-stable isomer have the same configuration at $C_{(13)}$, that they differ solely in orientation around $C_{(18)}$, and that a similar relation obtains for the two isomeric 12 : 19-dioxo-olean-9(11)-enyl acetates.

Reduction of 19-oxo-18α-olean-9(11)-enyl acetate (XIII) with lithium aluminium hydride yields 18α-olean-9(11)-en-3 : 19β-diol, readily converted into the 3-monoacetate (XIX) by partial acetylation. Dehydration of the diol monoacetate with phosphorus oxychloride in pyridine yielded the required oleana-9(11) : 18-dienyl acetate (XVIII)



which does not show selective absorption in the ultra-violet region above 2200 Å. Treatment of the 9(11) : 18-dienyl acetate with hydrochloric–acetic acid converted it into oleana-11 : 13(18)-dienyl acetate (III). Reduction of 19-oxo-olean-9(11)-enyl acetate (XI) with lithium aluminium hydride gave olean-9(11)-ene-3 : 19α-diol, characterised as its 3-monoacetate (XVII) oxidation of which with chromic anhydride yielded the parent 19-ketone (XI). Dehydration of the diol monoacetate (XVII) with phosphorus oxychloride in pyridine again gave oleana-9(11) : 18-dienyl acetate (XVIII). Oleana-9(11) : 18-dienyl acetate (XVIII) is also obtained by catalytic hydrogenolysis of 12-oxo-oleana-9(11) : 18-dienyl acetate (XVI).

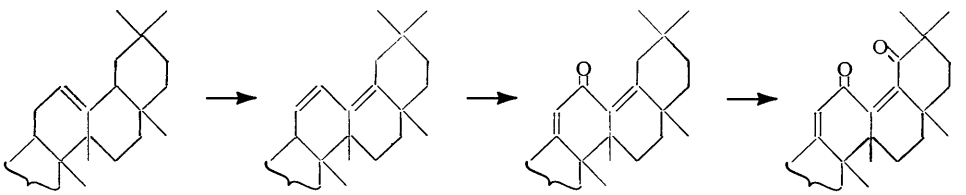
The conversion of 19-oxo-olean-9(11)-enyl acetate and its alkali-stable isomer into oleana-9(11) : 18-dienyl acetate again proves that the ketones have the same configuration at $C_{(13)}$. The configurations assigned to the 19-hydroxyl group in olean-9(11)-ene-3 : 19-diol 3-acetate and the 18α-isomer follow from the ease of dehydration with phosphorus oxychloride which requires a *trans*-arrangement of the hydrogen attached to $C_{(18)}$ and the $C_{(19)}$-hydroxyl group in each case.

The conversion of dioxo-β-amyradienyl acetate (readily available from β-amyrin) into olean-9(11)-ene-3 : 19α-diol 3-acetate (XVII) and 18α-olean-9(11)-ene-3 : 19β-diol 3-acetate (XIX) suggested a method for the direct inter-relation of the two naturally occurring triterpenoid alcohols, β-amyrin and germanicol, and this has been achieved starting from

(XIX); the 18α-isomer was chosen since this leads at an earlier stage to a known intermediate.

Oxidation of the unsaturated diol monoacetate (XIX) with hydrogen peroxide in acetic acid gave the expected 11-oxo-18α-oleanane-3 : 19β-diol 3-acetate (XX), Wolff–Kishner reduction of which gave 18α-oleanane-3 : 19β-diol (XXI; R = H) identical with a specimen prepared from lupeol as described by Ames, Davy, Halsall, and Jones (*J.*, 1952, 2868); identity was confirmed by a mixed melting point determination kindly effected by Professor E. R. H. Jones, F.R.S. The monoacetate (XXI) of the diol was converted smoothly into germanicyl acetate (XXII) as described by Ames *et al.*, thus completing the conversion of β-amyrin into germanicol.

The conversion of 19-oxo-18α-olean-9(11)-enyl acetate into 18α-oleanane-3 : 19β-diol proves that the configuration at $C_{(13)}$ in 19-oxo-olean-9(11)-enyl acetate, 12 : 19-dioxo-olean-9(11)-enyl acetate and its alkali-stable isomer is the same (β) as that in morolic acid (Barton and Brooks, *J.*, 1951, 257; Barton and Holness, *J.*, 1952, 78). It follows that 12 : 19-dioxo-olean-9(11)-enyl acetate has the 13β : 18β-configuration shown in (X) and that the alkali-stable isomer has the 13β : 18α-configuration shown in (XII). Thus the zinc dust reduction of dioxo-β-amyradienyl acetate involves *cis*-addition of hydrogen to the 13 : 18-double bond, as assumed by Barton, Holness, Overton, and Rosenfelder (*loc. cit.*) for the reduction of the analogous methyl 12 : 19-dioxo-oleana-9(11) : 13(18)-dienolate acetate. The first case of such a *cis*-addition of hydrogen to an ene-1 : 4-dione was reported by Barton, Holness, Overton, and Rosenfelder (*loc. cit.*) who showed that reduction of methyl 12 : 19-dioxo-olean-13(18)-enolate acetate gives 12 : 19-dioxo-oleananolate acetate, and a similar *cis*-addition of hydrogen to a steroid ene-1 : 4-dione has subsequently been reported (Budziarek and Spring, *J.*, 1953, 956). Recently, the elegant experiments of Barnes and Barton (*J.*, 1953, 1419) have led to the generalisation that selenium dioxide oxidation of anediones of the type $-CO\cdot\underset{|}{C}H\cdot\underset{|}{C}H\cdot CO-$ to the enedione $-CO\cdot\underset{|}{C}{:}\underset{|}{C}\cdot CO$ requires a *cis*-arrangement of the hydrogen atoms in the former. We are grateful to Dr. D. H. R. Barton for informing us of these observations before their publication. In agreement with this generalisation and with the stereochemical relations deduced above, 12 : 19-dioxo-olean-9(11)-enyl acetate (X) is readily oxidised with selenium dioxide to dioxo-β-amyradienyl acetate (I) whereas the 18α-isomer (XII) is recovered unchanged after the same treatment. It is pertinent at this juncture to comment on the formation of dioxo-β-amyradienyl acetate from a number of the β-amyrin derivatives described above. This acetate is obtained, among other methods, by the oxidation of 19-oxo-olean-9(11)-enyl acetate (XI), 12-oxo-oleana-9(11) : 13(18)-dienyl acetate (VIII), and 12 : 19-dioxo-olean-9(11)-enyl acetate (X) with selenium dioxide. In a recent discussion, Barton, Holness, Overton, and Rosenfelder (*loc. cit.*) observed that the dioxodienyl acetate is never produced if substituents containing oxygen are already present even at $C_{(12)}$ and/or $C_{(19)}$. This view must now be abandoned although the corollary that selenium dioxide oxidations of -enes and -dienes (in which the double bonds are in the fragment $C_{(10)}$–$C_{(19)}$) to the dienedione system proceed *via* the 9(11) : 12 : 18-triene may still be true. An alternative hypothesis is that at least some of these oxidations proceed *via* the 12-oxo-9(11) : 13(18)-diene without the intervention of the 9(11) : 12 : 18-triene, as exemplified below for β-amyrin acetate.



The fact that the 12-oxo-9(11) : 13(18)-diene has not been isolated as an intermediate oxidation product is explained as in the case of the 9(11) : 12 : 18-triene hypothesis, by its relative ease of oxidation to the dioxodienyl acetate.

Experimental

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

Catalytic Hydrogenolysis of Dioxo-β-amyradienyl Acetate.—A solution of dioxo-β-amyradienyl acetate (1·27 g.) in glacial acetic acid (120 c.c.) was shaken with hydrogen and platinum (from 0·5 g. of PtO_2) for 48 hr. Hydrogen absorption (approx. 4 mols.) had then ceased and crystalline solid had separated. The product was isolated in the usual way, and chromatographed in light petroleum (100 c.c.) on alumina (12 × 2 cm.). Light petroleum (60 c.c.) and light petroleum–benzene (1 : 1; 100 c.c.) eluted a solid (400 mg.) which after four crystallisations from methanol–chloroform gave *oleana*-9(11) : 13(18)-*dienyl acetate* as plates, m. p. 198·5—200·5°, $[\alpha]_D$ +60°, +59·5° (*c*, 1·3, 1·0) (Found: C, 82·6; H, 11·1. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%). Light absorption: ε_{2100} = 10,000, ε_{2150} = 9000, ε_{2220} = 5600. *Oleana*-9(11) : 13(18)-*dienol*, obtained by hydrolysis of the acetate with 4% ethanolic potassium hydroxide, separates from methanol as needles, m. p. 204·5—206·5°, $[\alpha]_D$ +53·5°, +52° (*c*, 0·5, 0·9) (Found: C, 84·9; H, 11·5. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%).

Continued elution of the alumina with benzene (300 c.c.) gave a crystalline solid (250 mg.) which after five crystallisations from methanol–chloroform gave 19-*oxo-olean*-9(11)-*enyl acetate* as plates, m. p. 254—256°, $[\alpha]_D$ +117·5°, +116° (*c*, 1·15, 1·0) (Found: C, 79·9; H, 10·4. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). It gives a pale yellow colour with tetranitromethane in chloroform. Light absorption: Max. at 3020 Å (ε = 44); ε_{2060} = 3400, ε_{2100} = 2400, ε_{2150} = 920.

Further elution of the alumina column gave fractions which could not be adequately purified but which did not show intense selective absorption in the ultra-violet above 2200 Å.

Conversion of Oleana-9(11) : 13(18)-*dienyl Acetate into Oleana*-11 : 13(18)-*dienyl Acetate.*—A solution of oleana-9(11) : 13(18)-dienyl acetate (87 mg.) in acetic acid (15 c.c.) containing concentrated hydrochloric acid (1·5 c.c.) was heated for 3 hr. on the steam-bath. The product, isolated by means of ether, was treated with acetic anhydride (1 c.c.) and pyridine (1 c.c.). Crystallisation of the acetylated product from methanol–chloroform gave oleana-11 : 13(18)-dienyl acetate (50 mg.) as plates, m. p. and mixed m. p. 223—226°, $[\alpha]_D$ −63° (*c*, 1·2). Light absorption: Max. at 2420 (ε = 23,500), 2500 (ε = 27,000), and 2600 Å (ε = 17,600).

Reduction of Dioxo-β-amyradienyl Acetate with Lithium Aluminium Hydride.—A solution of dioxo-β-amyradienyl acetate (2 g.) in dry ether (250 c.c.) was added to a suspension of lithium aluminium hydride (3 g.) in ether (400 c.c.), and the mixture heated under reflux for 4 hr. The product was isolated in the usual manner, mineral acid being avoided. A solution of the product in pyridine (50 c.c.) and acetic anhydride (25 c.c.) was kept overnight at room temperature and then heated on the water-bath for 1 hr. The crude product is probably contaminated with β-amyratrienyl acetate since it gives a red-brown colour with tetranitromethane and a broad absorption maximum at 3110 Å (ε = 1100). Seven crystallisations of the acetylated product from methanol gave *oleana*-9(11) : 13(18)-*diene*-3 : 19-*diol* 3-*acetate* as needles, m. p. 223—224°; the $[\alpha]_D$, +75° (*c*, 0·7), did not change during the last three crystallisations (Found: C, 79·35; H, 10·4. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). It gives a yellow colour with tetranitromethane in chloroform and does not selectively absorb in the ultra-violet region above 2200 Å.

A solution of the monoacetate (300 mg.) in pyridine (10 c.c.) and acetic anhydride (10 c.c.) was kept at room temperature for 6 days. Crystallisation of the product from methanol gave *oleana*-9(11) : 13(18)-*diene*-3 : 19-*diol diacetate* as needles, m. p. 231—231·5°, $[\alpha]_D$ +60° (*c*, 0·8) (Found: C, 77·6; H, 10·1. $C_{34}H_{52}O_4$ requires C, 77·8; H, 10·0%). Light absorption: ε_{2100} = 11,800, ε_{2150} = 8900, ε_{2200} = 6000, ε_{2250} = 3200, ε_{2300} = 1100. The diacetate gives a yellow colour with tetranitromethane.

Oleana-9(11) : 13(18)-*diene*-3 : 19-*diol.*—A solution of the diol diacetate (200 mg.) in dry ether (200 c.c.) was treated with lithium aluminium hydride (200 mg.). After 1 hr. the product was isolated (the use of mineral acid being avoided) and crystallised from aqueous methanol from which *oleana*-9(11) : 13(18)-*diene*-3 : 19-*diol* separated as plates, m. p. 240—243°. Purification by recrystallisation from the same solvent was accompanied by a drop in m. p. to 230—231°, unaltered by further recrystallisation or by drying in a vacuum, $[\alpha]_D$ +58° (*c*, 0·5, 0·6) (Found: C, 81·5; H, 11·2. $C_{30}H_{48}O_2$ requires C, 81·8; H, 11·0%). Light absorption: ε_{2090} = 12,500, ε_{2150} = 10,000, ε_{2200} = 6300, ε_{2300} = 1200.

Oleana-9(11) : 12 : 18-*trienyl Acetate from Oleana*-9(11) : 13(18)-*diene*-3 : 19-*diol* 3-*Acetate.*—(*a*) A solution of the monoacetate (210 mg.) in acetic acid (25 c.c.) was treated with 3 drops of concentrated hydrochloric acid, and the solution kept at room temperature for 16 hr. It was

then heated on a steam-bath for 30 min. The product was isolated by means of ether and crystallised from chloroform–methanol, to yield oleana-9(11) : 12 : 18-trienyl acetate (175 mg.) as plates, m. p. 180—181°, $[\alpha]_D$ +570° (*c*, 1·0); it gives a deep brown colour with tetranitromethane in chloroform. Light absorption: Max. at 3100 Å (ε = 14,800). Ruzicka *et al.* (*loc. cit.*, 1943) give m. p. 185° (corr.), $[\alpha]_D$ +527°, max. at 3080 Å (log ε = 4·1), for β-amyratrienyl acetate; Newbold and Spring (*J.*, 1944, 532) give m. p. 184—185°, $[\alpha]_D$ +560°.

(*b*) The monoacetate (310 mg.) in acetone (100 c.c.) was shaken with freshly prepared manganese dioxide (10 g.) for 9 hr. The product isolated in the usual manner was crystallised from methanol, to give oleana-9(11) : 12 : 18-trienyl acetate (198 mg.), m. p. 179—183° and 180—181·5° after recrystallisation from the same solvent; $[\alpha]_D$ +545° (*c*, 1·5); Max. at 3100 Å (ε = 14,000); a mixture with an authentic specimen was undepressed in m. p.

Catalytic Hydrogenolysis of Oleana-9(11) : 13(18)-diene-3 : 19-diol Diacetate.—A solution of the diacetate (150 mg.) in glacial acetic acid (50 c.c.) was added to a suspension of platinum (from 100 mg. of PtO_2) in glacial acetic acid (20 c.c.), and the mixture shaken with hydrogen for 18 hr. The product crystallised from chloroform–methanol, to yield oleana-9(11) : 13(18)-dienyl acetate (100 mg.) as plates, m. p. 199—200°, $[\alpha]_D$ +58°, +59° (*c*, 0·8, 0·5) (Found: C, 82·2; H, 10·9. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%). Light absorption: ε_{2160} = 6200, ε_{2200} = 5600, ε_{2250} = 3300, ε_{2300} = 950. A mixture with a specimen prepared by the hydrogenolysis of dioxo-β-amyradienyl acetate was undepressed in m. p.

Similar hydrogenolysis of oleana-9(11) : 13(18)-diene-3 : 19-diol 3-acetate gave oleana-9(11) : 13(18)-dienyl acetate as plates (from chloroform–methanol), m. p. and mixed m. p. 198—200°, $[\alpha]_D$ +59° (*c*, 1·2).

Oxidation of Oleana-9(11) : 13(18)-diene-3 : 19-diol 3-Acetate with Chromic Acid.—(*a*) The diol monoacetate (500 mg.) in glacial acetic acid (100 c.c.) was treated with chromic acid (77 mg.) in water (1 c.c.) and acetic acid (24 c.c.) at room temperature, and the solution kept for 16 hr. It was heated on the water-bath for 15 min. and the product isolated in the usual manner. Crystallisation from methanol gave a less soluble fraction (210 mg.) as needles, m. p. 215—218°, recrystallisation of which gave the diol monoacetate, m. p. 221—223°, $[\alpha]_D$ +70° (*c*, 1·3), undepressed in m. p. when mixed with starting material. A more soluble fraction (160 mg.) separated as plates, m. p. 222—225°, $[\alpha]_D$ −62°, recrystallisation of which gave dioxo-β-amyradienyl acetate, m. p. 234—236°, undepressed when mixed with an authentic specimen and showing an absorption maximum at 2800 Å (ε = 10,000).

(*b*) Repetition of the experiment, but with chromic anhydride equivalent to 4O, gave dioxo-β-amyradienyl acetate, m. p. 239—240°, $[\alpha]_D$ −86° (*c*, 1·8), max. at 2780 Å (ε = 12,000), in nearly quantitative yield.

A similar oxidation of oleana-9(11) : 13(18)-diene-3 : 19-diol diacetate (325 mg.) with chromic acid equivalent to 2O in acetic acid at room temperature gave a mixture which was separated by chromatography on alumina into unchanged diol diacetate (23 mg.), needles (from methanol), m. p. 218—224° undepressed when mixed with starting material, and the more strongly absorbed dioxo-β-amyradienyl acetate (250 mg.) which separated from aqueous methanol as plates, m. p. and mixed m. p. 236—238°, $[\alpha]_D$ −87° (*c*, 0·9). Light absorption: Max. at 2760 Å (ε = 12,600).

Reduction of Dioxo-β-amyradienyl Acetate with Zinc and Acetic Acid.—A solution of dioxo-β-amyradienyl acetate (0·95 g.) in glacial acetic acid (100 c.c.) was gently refluxed for 4 hr. with zinc dust (1·8 g.). A solution of the product, isolated by means of ether, in light petroleum (100 c.c.) and benzene (40 c.c.) was chromatographed on alumina (15 × 1·5 cm.). The fraction (229 mg.; m. p. 190°) eluted with light petroleum–benzene (2 : 1, 200 c.c.; then 1 : 1, 300 c.c.) was crystallised thrice from methanol–chloroform, to give oleana-9(11) : 13(18)-dienyl acetate as plates, $[\alpha]_D$ +60° (*c*, 1·0), m. p. 195—197° alone or mixed with the specimen described above.

A fraction (28 mg.) obtained by continued washing of the alumina column with benzene–light petroleum (3 : 2; 100 c.c.) was not examined. The fractions obtained by washing the column with benzene (300 c.c.), benzene–ether (9 : 1, 200 c.c.; then 4 : 1, 50 c.c.) were combined (314 mg.; m. p.s 204° to 207°) and crystallised from aqueous methanol from which the *12-oxo-oleana-9(11) : 13(18)-dienyl acetate* separated as plates from concentrated solution and as prisms from dilute solution; these had m. p. 205—207°, $[\alpha]_D$ −79°, −78° (*c*, 1·0, 0·9) (Found: C, 79·95; H, 10·3. $C_{32}H_{48}O_2$ requires C, 79·95; H, 10·1%). Light absorption: Max. at 2080 (ε = 9000), 2600 (ε = 9250), and 2950 Å (ε = 8450).

A fraction (157 mg.; m. p. 280—287°) obtained by washing the alumina column with benzene–ether (3 : 2, 50 c.c.; then 1 : 1, 100 c.c.; then 2 : 3, 50 c.c.) and ether (200 c.c.) crystallised from aqueous methanol, to yield *12 : 19-dioxo-olean-9(11)-enyl acetate* as plates, m. p. 285—

287°, $[\alpha]_D$ +132° (*c*, 1·0) (Found: C, 77·6; H, 9·9. $C_{32}H_{48}O_4$ requires C, 77·4; H, 9·7%). Light absorption: Max. at 2460 Å (ε = 12,400). Ruzicka and Jeger (*loc. cit.*) give m. p. 290—292° (corr.), $\lambda_{max.}$ at 2400 Å (log ε = 4·05), for a compound $C_{32}H_{48}O_4$ obtained by catalytic reduction of dioxo-β-amyradienyl acetate.

12-*Oxo-oleana*-9(11) : 13(18)-*dienol* was obtained when the corresponding acetate was heated with 3% alcoholic potassium hydroxide for 3 hr. It separated from aqueous methanol as needles, m. p. 267—269°, $[\alpha]_D$ −99·5°, −100°, −99° (*c*, 1·1, 0·75, 0·8) (Found: C, 82·3; H, 10·7. $C_{30}H_{46}O_2$ requires C, 82·1; H, 10·6%). Light absorption: Max. at 2100 (ε = 7600), 2620 (ε = 8600), and 2950 Å (ε = 7900). Reacetylation (pyridine–acetic anhydride) of the alcohol gave 12-oxo-oleana-9(11) : 13(18)-dienyl acetate as prisms or plates (from aqueous methanol), m. p. 205—206°, $[\alpha]_D$ −78° (*c*, 1·35). The acetate (125 mg.) was recovered unchanged [m. p. 204—205°, $[\alpha]_D$ −78° (*c*, 1·1). Light absorption: Max. at 2080 (ε = 7250), 2600 (ε = 8950) and 2950 Å (ε = 8100)] after being heated on a steam-bath for 3 hr. with acetic acid (25 c.c.) and concentrated hydrochloric acid (3 c.c.).

Reduction of 12-*Oxo-oleana*-9(11) : 13(18)-*dienyl Acetate.*—(a) *Catalytic.* A solution of the acetate (0·3 g.) in acetic acid (50 c.c.) was shaken with platinum (from 0·2 g. of PtO_2) and hydrogen for 7 hr. Towards the end of the reaction the product separated from the solution. Oleana-9(11) : 13(18)-dienyl acetate, isolated by means of ether, crystallised from methanol–chloroform as plates (250 mg.), m. p. 197—199°, $[\alpha]_D$ +59° (*c*, 0·9); the m. p. of a mixture with the specimen described above was undepressed.

(b) *With zinc and acetic acid.* A solution of the acetate (250 mg.) in glacial acetic acid (50 c.c.) was refluxed with zinc (0·5 g.) for 4 hr. The product was isolated by means of ether and crystallised from chloroform–methanol to yield the relatively insoluble oleana-9(11) : 13(18)-dienyl acetate (50 mg.) as plates, m. p. 190—191°. The mother-liquor was evaporated to dryness, the residue dissolved in glacial acetic acid, and the solution again refluxed with zinc (0·5 g.) for 4 hr. The product was isolated by means of ether and crystallised from chloroform–methanol, to yield oleana-9(11) : 13(18)-dienyl acetate (58 mg.) as plates, m. p. 188—190°. Recrystallisation of the combined crops from chloroform–methanol yielded the dienyl acetate as plates, m. p. and mixed m. p. 196—198°.

(c) *With lithium aluminium hydride.* A solution of the acetate (1·0 g.) in dry ether (250 c.c.) containing lithium aluminium hydride (1·0 g.) was refluxed for 3 hr. The product was isolated, the use of mineral acid being avoided, and acetylated with pyridine and acetic anhydride at room temperature. The acetylated product crystallised from methanol–chloroform to give a mixture (approx. 500 mg.), m. p. 192—194°. This gives a brown colour with tetranitromethane and shows an absorption maximum at 2950 Å (ε = 440) probably due to the presence of oleana-9(11) : 12 : 18-trienyl acetate. Recrystallisation of this solid from chloroform–methanol, which was accompanied by large losses, gave oleana-9(11) : 13(18)-dienyl acetate (50 mg.) as plates, m. p. and mixed m. p. 199—200°, giving a yellow colour with tetranitromethane; $[\alpha]_D$ was +59° (*c*, 0·9, 1·0). Light absorption: Max. at 2100 Å (ε = 8000).

Dioxo-β-amyradienyl Acetate from 12-*Oxo-oleana*-9(11) : 13(18)-*dienyl Acetate.*—(*a*) The acetate (86 mg.) was refluxed for 72 hr. with acetic anhydride (10 c.c.) containing freshly fused potassium acetate (0·1 g.). The product was isolated in the usual manner and crystallised from methanol, to yield dioxo-β-amyradienyl acetate (50 mg.) as plates, m. p. and mixed m. p. 241—242°, $[\alpha]_D$ −89° (*c*, 0·6). Light absorption: Max. at 2780 Å (ε = 11,000).

(*b*) The acetate (250 mg.) in glacial acetic acid (50 c.c.) was refluxed with selenium dioxide (250 mg.) for 6 hr. Crystallisation of the product from aqueous methanol yielded dioxo-β-amyradienyl acetate (130 mg.) as large plates, m. p. and mixed m. p. 240—241°, $[\alpha]_D$ −91° (*c*, 1·3). Light absorption: Max. at 2760 Å (ε = 12,500).

Reduction of Dioxo-β-amyradienyl Acetate with Zinc Dust in Ethanol.—A solution of the dioxodienyl acetate (5 g.) in boiling ethanol (500 c.c.) was refluxed with freshly activated zinc dust (25 g.) for 5 hr. The product was crystallised from methanol–chloroform, to yield 12 : 19-dioxo-olean-9(11)-enyl acetate (4·5 g.) as blades, m. p. 287—290°, (decomp.), $[\alpha]_D$ +135°, +132° (*c*, 1·4, 1·3), undepressed in m. p. when mixed with the specimen described above. 12 : 19-Dioxo-olean-9(11)-enyl acetate was recovered unchanged after 1 hr.' heating on the water-bath with acetic anhydride and pyridine, also after being kept overnight in glacial acetic acid containing chromic acid (equiv. to 1O).

12-*Oxo-olean*-9(11)-*ene*-3 : 19α-*diol* 3-*Acetate from* 12 : 19-*Dioxo-olean*-9(11)-*enyl Acetate.*—A solution of 12 : 19-dioxo-olean-9(11)-enyl acetate (2·0 g.) in benzene (150 c.c.) was added to a suspension of lithium aluminium hydride (2·0 g.) in ether (1 l.). After the mixture had been shaken for 1 hr. at room temperature the excess of hydride was decomposed by the addition of

ice. The solution was washed with water, dried, and concentrated to 40 c.c. Crude olean-9(11)-ene-3 : 12 : 19-triol separated as needles, m. p. 210—230°. A second experiment gave a product which separated from acetone–light petroleum as fine matted needles, m. p. 220—224°. Attempted purification by crystallisation was not successful, the m. p. falling to 183—185°. In a third experiment the product was not obtained crystalline. Each of these specimens, however, was essentially the required triol since each was successfully converted in high yield into 12-oxo-olean-9(11)-ene-3 : 19α-diol 3-acetate as described below. The crude triol did not show appreciable selective absorption above 2200 Å.

A solution of the crude triol (1·8 g.) in acetone (150 c.c.) was shaken with freshly precipitated, dry manganese dioxide (20 g.) for 17 hr. The product recovered in the usual manner showed an absorption maximum at 2480 Å (ε = 7200). It was again dissolved in acetone and shaken with manganese dioxide (20 g.) for 17 hr.; the absorption spectrum of the product then showed a maximum at 2480 Å (ε = 8500). The crude product was partially acetylated by treatment in acetic anhydride (25 c.c.) and pyridine (50 c.c.) at room temperature. After 13 hr. the acetylated product was isolated in the usual manner and crystallised from aqueous methanol from which 12-*oxo-olean*-9(11)-*ene*-3 : 19α-*diol* 3-*acetate* (0·72 g.) separated as prismatic needles, m. p. 266—267°, $[\alpha]_D$ +97° (*c*, 1·45) (Found: C, 77·4; H, 10·2. $C_{32}H_{50}O_4$ requires C, 77·1; H, 10·1%). Light absorption: Max. at 2460 Å (ε = 11,400). Chromatography of solid recovered from the aqueous-methanolic mother-liquors gave a further quantity (0·22 g.) of this acetate, m. p. 266—267°.

Dehydration of 12-*Oxo-olean*-9(11)-*ene*-3 : 19α-*diol* 3-*Acetate*.—A solution of the diol monoacetate (450 mg.) in pyridine (50 c.c.) was treated with phosphorus pentachloride (2 g.) and kept in nitrogen for 17 hr. at room temperature. The mixture was diluted with water, the solid collected and washed with water, and its solution in chloroform dried. Concentration of the chloroform solution and dilution with methanol, followed by recrystallisations from the same solvent, yielded 12-*oxo-oleana*-9(11) : 18-*dienyl acetate* (130 mg.) as plates, m. p. 268—269°, $[\alpha]_D$ +27° (*c*, 0·87) (Found: C, 79·7; H, 10·4. $C_{32}H_{48}O_3$ requires C, 79·95; H, 10·1%). Light absorption: Max. at 2500 Å (ε = 10,900); ε_{2040} = 3900. The methanol–chloroform mother-liquors gave a more soluble component identified as dioxo-β-amyradienyl acetate. Initial attempts to dehydrate the diol 3-monacetate by pyridine and phosphorus oxychloride (in air) were unsuccessful, oxidation intervening with the formation of dioxo-β-amyradienyl acetate.

12-*Oxo-oleana*-9(11) : 13(18)-*dienyl Acetate from* 12-*Oxo-oleana*-9(11) : 18-*dienyl Acetate*.—A solution of the 12-oxo-9(11) : 18-dienyl acetate (120 mg.) in acetic acid (25 c.c.) containing concentrated hydrochloric acid (3 c.c.) was heated on the steam-bath for 2 hr. The product was isolated by means of ether and treated with acetic anhydride (5 c.c.) and pyridine (10 c.c.) at room temperature overnight. 12-Oxo-oleana-9(11) : 13(18)-dienyl acetate (42 mg.) crystallised from methanol as prisms, m. p. 208—209°, $[\alpha]_D$ −81° (*c*, 1·15). Light absorption: Max. at 2060 (ε = 9300), 2640 (ε = 9500), and 2920 Å (ε = 8600). A mixture with the specimen described above was undepressed in m. p.

Hydrogenolysis of 12 : 19-*Dioxo-olean*-9(11)-*enyl Acetate*.—A solution of 12 : 19-dioxo-olean-9(11)-enyl acetate (537 mg.) in acetic acid (200 c.c.) was shaken with hydrogen and platinum (from 190 mg. of PtO_2). Absorption of hydrogen was slow and ceased after 21 hr. 19-Oxo-olean-9(11)-enyl acetate (413 mg.) crystallised from chloroform–methanol as plates, m. p. 256—258°, $[\alpha]_D$ +117°, +116° (*c*, 1·4, 0·8) (Found: C, 79·6; H, 10·4. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). It gives a yellow colour with tetranitromethane and a mixture with the specimen described above was undepressed in m. p. Light absorption: ε_{2060} = 2900, ε_{2100} = 2200, ε_{2150} = 1100, ε_{2200} = 280.

Oxidation of 19-*Oxo-olean*-9(11)-*enyl Acetate with Selenium Dioxide*.—The acetate (83 mg.) in glacial acetic acid was refluxed with selenium dioxide (83 mg.) for 8 hr. The product was isolated by means of ether and treated with methanol. A relatively insoluble fraction (12 mg.), m. p. 283—286°, $[\alpha]_D$ +97° (*c*, 0·4), was not investigated further. The mother-liquor was evaporated to dryness and the residue crystallised from light petroleum from which dioxo-β-amyradienyl acetate (30 mg.) separated as prisms, m. p. 232—234°. Recrystallised from aqueous methanol, it separated as plates, m. p. and mixed m. p. 236—238°, $[\alpha]_D$ −91° (*c*, 0·5). Light absorption: Max. at 2780 Å (ε = 11,000).

12 : 19-*Dioxo*-18α-*olean*-9(11)-*enyl Acetate*.—A solution of 12 : 19-dioxo-olean-9(11)-enyl acetate (400 mg.) in 10% methanolic potassium hydroxide was refluxed for 3 hr. The product was acetylated (acetic anhydride–pyridine) and the acetate crystallised from methanol, to yield 12 : 19-*dioxo*-18α-*olean*-9(11)-*enyl acetate* as plates, m. p. 279—281°, $[\alpha]_D$ +91°, +92°, +89·5° (*c*, 0·5, 1·2, 1·3) (Found: C, 77·6; H, 9·7. $C_{32}H_{48}O_4$ requires C, 77·4; H, 9·7%). Light absorption: Max. at 2430 Å (ε = 11,700).

19-*Oxo*-18α-*olean*-9(11)-*enyl Acetate*.—(*a*) A solution of 19-oxo-olean-9(11)-enyl acetate (1·3 g.) in 10% ethanolic potassium hydroxide (500 c.c.) was heated under reflux for 3 hr. The product was isolated by means of ether and acetylated (pyridine–acetic anhydride). Crystallisation from methanol–chloroform gave 19-*oxo*-18α-*olean*-9(11)-*enyl acetate* (1·14 g.) as blades or needles, m. p. 254—256°, $[\alpha]_D$ +139° (*c*, 1·2) (Found: C, 79·8; H, 10·4. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%).

(*b*) Catalytic hydrogenolysis of 12 : 19-dioxo-18α-olean-9(11)-enyl acetate was more difficult than that of the corresponding 18β-isomer. A solution of the 18α-diketone (1 g.) in glacial acetic acid (150 c.c.) was shaken with hydrogen and platinum (from 0·5 g. of PtO_2) for 48 hr. The filtered solution was added to freshly prepared platinum (from 0·25 g. of PtO_2) in glacial acetic acid (20 c.c.) and shaken with hydrogen for 24 hr. The product obtained by filtration and evaporation gave a pale yellow colour with tetranitromethane in chloroform and showed absorption maxima at 2070 (ε = 2100) and 2400 Å (ε = 3700). A solution of the product in light petroleum–benzene (2 : 1, 150 c.c.) was chromatographed on alumina (Grade II/III; 15 × 2 cm.). The same solvent mixture (250 c.c.) eluted a solid (260 mg.), crystallisation of which from chloroform–methanol yielded 19-oxo-18α-olean-9(11)-enyl acetate as blades, m. p. 257—259° [undepressed when mixed with the specimen described under (*a*)], $[\alpha]_D$ +136° (*c*, 1·2). Light absorption: $\varepsilon_{2060} = 3300$, $\varepsilon_{2100} = 2200$, $\varepsilon_{2150} = 670$. It gives a yellow colour with the tetranitromethane reagent. Continued washing of the alumina with the same solvent mixture (200 c.c.) gave intermediate fractions (total, 250 mg.) of 19-oxo-18α-olean-9(11)-enyl acetate of decreasing purity, whereafter benzene–ether (1 : 1; 100 c.c.) eluted a fraction (360 mg.), crystallisation of which from chloroform–methanol yielded 12 : 19-dioxo-18α-olean-9(11)-enyl acetate as plates, m. p. and mixed m. p. 282—284°, $[\alpha]_D$ +86° (*c*, 2·2) showing an absorption maximum at 2440 Å (ε = 9800).

Reduction of 19-*Oxo*-18α-*olean*-9(11)-*enyl Acetate with Lithium Aluminium Hydride*—A solution of 19-oxo-18α-olean-9(11)-enyl acetate (1·04 g.) in dry ether (100 c.c.) was treated with lithium aluminium hydride (0·5 g.) and refluxed for 1½ hr. The cold mixture was treated with water, and the product isolated in the usual manner. Crystallisation from methanol gave three crops, m. p.s 239—241°, 240—243°, and 240—244°, which were combined (0·89 g.) and recrystallised from the same solvent, to give 18α-*olean*-9(11)-*ene*-3 : 19β-*diol* as prismatic needles, m. p. 243—245°, $[\alpha]_D$ +108° (*c*, 1·1) (Found: C, 81·25; H, 11·5. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Light absorption: $\varepsilon_{2080} = 2400$, $\varepsilon_{2150} = 940$, $\varepsilon_{2210} = 100$. The diol gives a pale yellow colour with tetranitromethane.

Treatment of the diol (0·81 g.) with acetic anhydride (10 c.c.) and pyridine (20 c.c.) at room temperature for 16 hr. followed by chromatography of a solution of the product (0·79 g.; m. p. 258—260°) in benzene on alumina gave 18α-*olean*-9(11)-*ene*-3 : 19β-*diol* 3-*acetate* (0·77 g.) which separates from chloroform–methanol as needles, m. p. 262—265°, $[\alpha]_D$ +112° (*c*, 1·1) (Found: C, 79·3; H, 10·8. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%).

Reduction of 19-*Oxo-olean*-9(11)-*enyl Acetate with Lithium Aluminium Hydride*.—The ketone (0·5 g.) in dry ether (200 c.c.) was treated with lithium aluminium hydride (0·5 g.) in ether (200 c.c.), and the mixture kept at room temperature for 4 hr. The product was isolated (mineral acid being avoided) and crystallised from aqueous methanol from which *olean*-9(11)-*ene*-3 : 19α-*diol* separated as prismatic needles or plates (according to the concentration), m. p. 204—205°, $[\alpha]_D$ +78°, +79° (*c*, 0·7, 1·3) (Found: C, 81·3; H, 11·5. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Light absorption: $\varepsilon_{2100} = 2000$, $\varepsilon_{2150} = 1400$, $\varepsilon_{2200} = 470$. It gives a pale yellow colour with tetranitromethane.

Partial acetylation of the diol, with acetic anhydride and pyridine at room temperature as described for the isomeric 18α-diol, gave *olean*-9(11)-*ene*-3 : 19α-*diol* 3-*acetate*, prismatic needles (from chloroform–methanol), m. p. 262—263°, $[\alpha]_D$ +88°, +89° (*c*, 1·5, 0·9) (Found: C, 79·1; H, 10·9. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). Light absorption: $\varepsilon_{2090} = 2000$ $\varepsilon_{2150} = 820$, $\varepsilon_{2200} = 200$; it gives a pale yellow colour with tetranitromethane. A mixture of the monoacetate with the isomeric 18α-olean-9(11)-ene-3 : 19β-diol 3-acetate did not show a depression in m. p.

Olean-9(11)-ene-3 : 19α-diol 3-acetate (150 mg.) in glacial acetic acid (50 c.c.) was treated at room temperature with chromic anhydride (≡1·2O) in acetic acid (11·5 c.c.) added dropwise during 30 min., and the solution was kept at room temperature for 20 hr. 19-Oxo-olean-9(11)-enyl acetate was isolated in the usual manner and crystallised from chloroform–methanol as plates, m. p. and mixed m. p. 253—255°, $[\alpha]_D$ +118° (*c*, 0·8); a mixture with 19-oxo-18α-olean-9(11)-enyl acetate, m. p. 254—256°, $[\alpha]_D$ +139°, had m. p. 232—238°.

Oleana-9(11) · 18-*dienyl Acetate*.—(*a*) A solution of 18α-olean-9(11)-ene-3 : 19β-diol 3-acetate (280 mg.) in dry pyridine (30 c.c.) and phosphorus oxychloride (10 c.c.) was refluxed for 8 hr.

The product, isolated by the addition of water and filtration, was dried, and chromatographed in light petroleum (50 c.c.) on alumina. Light petroleum–benzene (20 : 1, 360 c.c.; then 1 : 1, 220 c.c.) eluted fractions (243 mg.; m. p.s between 251° and 258°) which were combined and crystallised from methanol–chloroform, to yield *oleana*-9(11) : 18-*dienyl acetate* as plates, m. p. 259—260°, $[\alpha]_D$ +101° (*c*, 1·1) (Found: C, 82·5; H, 10·9. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%). Light absorption: $\varepsilon_{2070} = 3500$, $\varepsilon_{2100} = 3100$, $\varepsilon_{2150} = 1000$, $\varepsilon_{2220} = 100$. It gives a yellow colour with tetranitromethane in chloroform.

(*b*) A solution of olean-9(11)-ene-3 : 19α-diol 3-acetate in pyridine (75 c.c.) and phosphorus oxychloride (25 c.c.) was heated on the steam-bath for 7 hr. The product, crystallised from chloroform–methanol, yielded oleana-9(11) : 18-dienyl acetate as plates, m. p. 256—257°, $[\alpha]_D$ +99° (*c*, 2·2) (Found: C, 82·6; H, 11·0%), undepressed in m. p. when mixed with the specimen described above.

(*c*) A solution of 12-oxo-oleana-9(11) : 18-dienyl acetate (44 mg.) in glacial acetic acid was shaken with a platinum catalyst (from 100 mg. of PtO_2) and hydrogen for 18 hr. Isolation in the usual manner and two crystallisations from chloroform–methanol yielded oleana-9(11) : 18-dienyl acetate (21 mg.), plates, m. p. 257—258°, $[\alpha]_D$ +99° (*c*, 0·9). Light absorption: $\varepsilon_{2060} = 3300$. The m. p. of a mixture with a specimen prepared by method (*a*) was not depressed.

Hydrolysis of oleana-9(11) : 18-dienyl acetate using lithium aluminium hydride gave *oleana*-9(11) : 18-*dienol* which separated from *n*-hexane as fine matted needles, m. p. 158—159°, $[\alpha]_D$ +87° (*c*, 1·2) (Found: C, 84·5; H, 11·5. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%). Light absorption: $\varepsilon_{2070} = 4100$, $\varepsilon_{2100} = 3450$, $\varepsilon_{2200} = 280$. Acetylation as above gave the acetate, plates (from chloroform–methanol), m. p. 257—258°, $[\alpha]_D$ +100° (*c*, 1·5).

Conversion of Oleana-9(11) : 18-*dienyl Acetate into Oleana*-11 : 13(18)-*dienyl Acetate*.—A solution of oleana-9(11) : 18-dienyl acetate (208 mg.) in acetic acid (100 c.c.) and concentrated hydrochloric acid (3 c.c.) was heated on a steam-bath for 20 hr. The product, after treatment with acetic anhydride and pyridine, was crystallised from methanol–chloroform to yield oleana-11 : 13(18)-dienyl acetate as plates, m. p. 228—229° (undepressed when mixed with an authentic specimen, m. p. 227—228°), $[\alpha]_D$ −63° (*c*, 1·2). Light absorption: Max. at 2420 (ε = 27,500), 2510 (ε = 31,000) and 2600 Å (ε = 20,100).

Oxidation of 18α-*Olean*-9(11)-*ene*-3 : 19β-*diol* 3-*Acetate with Hydrogen Peroxide*.—A refluxing solution of this acetate (2·9 g.) in glacial acetic acid (400 c.c.) was treated during 10 min. with hydrogen peroxide (100-vol; 30 c.c.) in acetic acid (30 c.c.), then refluxed for 1 hr. and again treated during 10 min. with hydrogen peroxide (100-vol.; 20 c.c.) in acetic acid (20 c.c.), whereafter the mixture was refluxed for 2 hr. The hot solution was treated with water until a crystalline solid (1·4 g.; m. p. 318—327°) separated. After cooling, the solid was collected and crystallised from methanol–chloroform, to yield 11-*oxo*-18α-*oleanane*-3 : 19β-*diol* 3-*acetate* (1·1 g.) as prismatic needles, m. p. 334—336°, $[\alpha]_D$ +36° (*c*, 1·3) (Found: C, 77·1; H, 10·6. $C_{32}H_{52}O_4$ requires C, 76·75; H, 10·5%).

18α-*Oleanane*-3 : 19β-*diol* 3-*Acetate*.—A mixture of 11-oxo-18α-oleanane-3 : 19β-diol 3-acetate (0·7 g.), methanolic sodium methoxide (from 1·75 g. of sodium and 22 c.c. of methanol), and hydrazine hydrate (100%; 7 ml.) was heated at 200—210° for 19 hr. A portion of the product (90 mg.), isolated in the usual manner, was crystallised from aqueous methanol, to yield 18α-oleanane-3 : 19β-diol as prismatic needles, m. p. 267—268°, $[\alpha]_D$ +26° (*c*, 0·7), undepressed in m. p. when mixed with a specimen, m. p. 265·6—267°, prepared from lupeol. The remainder of the product was kept with acetic anhydride–pyridine at room temperature overnight. The acetylated product (560 mg.) was purified by chromatography on alumina, to yield 18α-oleanane-3 : 19β-diol 3-monoacetate as long blades, m. p. 289—293°, $[\alpha]_D$ +35° (*c*, 0·7). Ames *et al.* (*loc. cit.*) give m. p. 294·5—295°, $[\alpha]_D$ +33°. Dehydration of the monoacetate as described by Ames *et al.* yielded germanicyl acetate, plates (from chloroform–methanol), m. p. 277—279°, $[\alpha]_D$ +17° (*c*, 0·8). Simpson (*J.*, 1944, 283) gives m. p. 274°, $[\alpha]_D$ +18°. Alkaline hydrolysis yielded germanicol, needles (from methanol), m. p. 178—180°, $[\alpha]_D$ +5° (*c*, 0·6). Simpson (*loc. cit.*) gave m. p. 176—177°, $[\alpha]_D$ +6°.

We are glad to express our indebtedness to Mr. J. Adam for the preparation of intermediates and to Dr. A. C. Syme and Mr. Wm. McCorkindale for the micro-analyses and ultra-violet absorption spectra. Two of us (J. D. J. and L. C. McK.) thank the Department of Scientific and Industrial Research for Maintenance Awards.

THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, May 26th*, 1953.]