67. *The Triterpene Resinols and Related Acids. Part XVI. A Preliminary Examination of a Major Oxidation Product of the* β-*Amyrin Group.*

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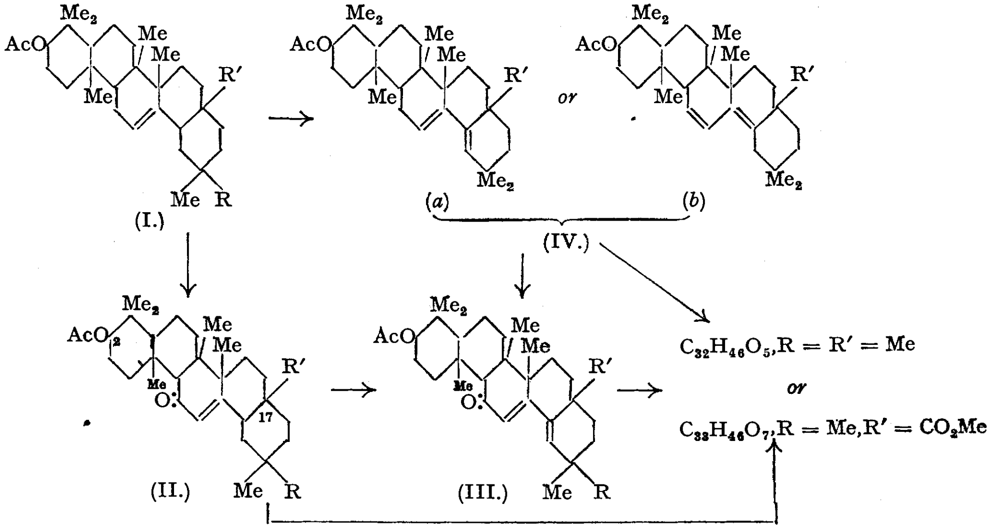
Oxidation of either β-amyrenonyl acetate, $C_{32}H_{50}O_3$ (II, R = R′ = Me), or β-amyradienonyl acetate, $C_{32}H_{48}O_3$ (III, R = R′ = Me), with selenium dioxide gives an acetate, $C_{32}H_{46}O_5$ ("O_5-acetate"), in high yield. Similar oxidation of β-amyrenonyl and β-amyradienonyl benzoates gives the corresponding *benzoate*, $C_{37}H_{48}O_5$. The "O_5-acetate" is also obtained, together with β-amyradienonyl acetate, by a chromic acid oxidation of β-amyradienyl-II acetate (IV*a* or IV*b*, R′ = Me). Treatment of the "O_5-acetate" with potassium hydroxide gives, in high yield, a yellow amorphous product, acetylation of which does not regenerate the parent "O_5-acetate" but yields a crystalline *diacetate*, $C_{33}H_{46}O_5$ (or a near homologue). The "O_5-acetate" is hydrolysed by mineral acid to yield the corresponding alcohol, $C_{30}H_{44}O_4$, reacetylation of which yields the parent "O_5-acetate." The "O_5-acetate" does not contain a hydroxyl group or a reactive carbonyl group and is resistant to catalytic hydrogenation.

This new type of oxidation product is found to be characteristic of the β-amyrin group; treatment either of methyl ketoacetyloleanolate (II; R = Me, R′ = CO_2Me) with selenium dioxide or of methyl acetyldehydro-oleanolate (IV*a* or *b*; R′ = CO_2Me) with chromic acid gives an acetate, $C_{33}H_{46}O_7$, which is an exact analogue of the "O_5-acetate."

THE αβ-unsaturated ketone, β-amyrenonyl benzoate, is obtained by the oxidation of β-amyrin benzoate with chromic acid (Beynon, Sharples, and Spring, J., 1938, 1233; Picard and Spring, J., 1940, 1198). The corresponding acetate, β-amyrenonyl acetate (II, R = R′ = Me), was found to be resistant to oxidation by selenium dioxide (Picard and Spring, J., 1941, 35), using conditions more drastic than those which readily result in the oxidation of β-amyrin acetate (I, R = R′ = Me) to the conjugated β-amyradienyl-II acetate (IV*a* or IV*b*, R′ = Me) (Ruzicka, Müller, and Schellenberg, *Helv. Chim. Acta*, 1939, 22, 767; Picard and Spring, J., 1941, 35). [The structure (IV*b*) appears to be less satisfactory than (IV*a*) in view of the dehydration of methyl 2-acetylsiaresinolate to methyl acetyldehydro-oleanolate (IV; R = CO_2Me) (Bilham, Kon, and Ross, J., 1942, 540); this reaction, however, could involve bond migration. In other respects—behaviour on oxidation (this paper) and catalytic reduction (Ruzicka and Jeger, *Helv. Chim. Acta*, 1941, **24**, 1236)—either formula gives a satisfactory interpretation of the reactions of β-amyradienyl-II acetate.] The introduction of a second ethylenic linkage into β-amyrenonyl acetate and the corresponding benzoate was readily achieved by Picard and Spring (J., 1941, 35) by a very facile reaction consisting in the treatment of a hot acetic acid solution of the unsaturated ketone with 1 mole of bromine in the presence of a trace of hydrogen bromide. This general reaction has proved to be of great diagnostic value in the triterpene series. When applied to saturated ketones such as β-amyranonyl acetate, methyl ketoacetyldihydro-oleanolate (Picard, Sharples, and Spring, J., 1939, 1045), and α-amyranonyl benzoate (Seymour, Sharples, and Spring, J., 1939, 1075), it gives *iso*-αβ-unsaturated ketones. In the case of "normal" αβ-unsaturated ketones of the series such as β-amyrenonyl acetate (II, R = R′ = Me) (or the corresponding benzoate) (Picard and Spring, *loc. cit.*), methyl acetylglycyrrhetate (II; R′ = Me, R = CO_2Me) (Ruzicka and Jeger, *Helv. Chim. Acta*, 1942, **25**, 775; Kon and Ross, J., 1942, 741), and ketoacetyloleanolic acid (II; R′ = CO_2H, R = Me) (Ruzicka, Jeger, and Winter, *Helv. Chim. Acta*, 1943, **26**, 265), the reaction leads to the formation of the corresponding dienones (III), which exhibit a characteristic absorption spectrum with a maximum at approximately 2800 A. (log $\varepsilon \simeq 4{\cdot}1$). In view of the relative ease with which bromine partially dehydrogenates β-amyrenonyl acetate, we have reinvestigated the action of various oxidising agents upon this αβ-unsaturated ketone; this paper reports upon the oxidation of β-amyrenonyl acetate and various related compounds with selenium dioxide.



β-Amyrenonyl acetate and β-amyradienonyl acetate are unchanged after prolonged treatment with selenium dioxide in aqueous acetic acid solution. The oxidation of β-amyrenonyl acetate, however, proceeds smoothly if a solution in acetic acid is boiled with selenium dioxide, water being excluded from the reaction mixture. There is thus formed in high yield (*ca.* 70%) an acetate, $C_{32}H_{46}O_5$, m. p. 252—253°. Under these anhydrous conditions, β-amyradienonyl acetate is likewise oxidised in high yield to give the same "O_5-acetate," and β-amyrenonyl benzoate and β-amyradienonyl benzoate give the corresponding *benzoate*, $C_{37}H_{48}O_5$, m. p. 263°.

Ruzicka and Jeger (*Helv. Chim. Acta*, 1941, **24**, 1236) oxidised β-amyradienyl-II acetate (IV*a* or *b*) with chromic acid and obtained an acetate, $C_{32}H_{46}O_5$ (m. p. 256°, corr.), which we find is identical with the selenium dioxide oxidation product from both β-amyrenonyl acetate and β-amyradienonyl acetate. By slight modification of the reaction conditions we also find that chromic acid oxidation of the dienyl-II acetate gives a mixed crystal, m. p. 219—221°, which has been resolved by the chromatographic method into β-amyradienonyl acetate (III, R = R′ = Me) and the "O_5-acetate," m. p. 252—253°. The conversion of the dienyl-II acetate into β-amyradienonyl acetate has previously been effected by oxidation with lead tetra-acetate (Ruzicka, Jeger, and Norymberski, *Helv. Chim. Acta*, 1942, **25**, 457).

The "O_5-acetate" is unaffected by prolonged boiling with acetic anhydride and it does not contain any active hydrogen as estimated by the Zerewitinoff method; it cannot contain a free hydroxyl group. It does not contain a reactive carbonyl group, since it is recovered unchanged after heating with alcoholic hydroxylamine acetate at 150° for 3 hours, and it is likewise recovered unchanged after an attempted reduction by the Clemmensen method. In solution in either alcohol or dioxan it does not give a coloration with aqueous ferric chloride and presumably cannot contain a 1 : 2- or 1 : 3-diketone system; furthermore, the "O_5-acetate" does not give the positive Legal reaction characteristic of αβ-unsaturated lactones. In an attempt to determine whether the "O_5-acetate" contains an oxido-group, we found that it is recovered unchanged (*a*) after heating with 2% hydrochloric acid in acetic acid for 3 hours, (*b*) after treatment with 25% hydrogen bromide in acetic acid for 20 hours at 17°, and (*c*) after heating under reflux for 3 hours with 10% hydrogen bromide in acetic acid.

The " O_5-acetate " and the corresponding " O_5-benzoate " are unstable to alcoholic potassium hydroxide, giving a yellow, amorphous, neutral product in high yield, reacetylation of which does not regenerate the original " O_5-acetate " but gives a crystalline *compound*, $C_{33}H_{46}O_5$ (or a near homologue), m. p. 249—251°, in which the presence of two acetyl groups has been demonstrated.

Simple hydrolysis of the " O_5-acetate " is readily accomplished by means of alcoholic hydrogen chloride, which yields the *alcohol*, $C_{30}H_{44}O_4$, m. p. 280·5—281·5°, in almost quantitative yield. The alcohol is readily reacetylated to yield the parent O_5-acetate.

The " O_5-acetate " does not absorb hydrogen, a platinum catalyst being used with ethyl acetate as solvent. However, it gives a faint but definite yellow coloration with the tetranitromethane reagent, which we consider to be of constitutional significance (*i.e.*, indicative of unsaturation), since specimens of the " O_5-acetate " from four different sources all show the same behaviour. The absorption spectrum of the " O_5-acetate " exhibits a band at approximately 2300 A., ε = 3000, together with a low-intensity inflexion at 3000 A. This spectrum we again consider to be of constitutional significance and not due to the presence of an intensely absorbing impurity, since it is exhibited by specimens of the " O_5-acetate " prepared by four different routes and also by the parent alcohol, $C_{30}H_{44}O_4$.

The remote possibility that the angular methyl group attached to C_{17} in β-amyrenonyl acetate (II, R = R′ = Me) may be involved in the formation of the " O_5-acetate " led us to examine the oxidation of methyl ketoacetyloleanolate (II; R = Me, R′ = CO_2Me) in which this angular methyl group is replaced by a carbomethoxy group. When oxidised with selenium dioxide, under anhydrous conditions, methyl ketoacetyloleanolate gives an *acetate*, $C_{33}H_{46}O_7$, m. p. 253—254°, $[\alpha]_D^{15°}$ +15·9°. Like the " O_5-acetate," this compound gives a faint yellow coloration with the tetranitromethane reagent and exhibits an absorption maximum at 2280 A., ε = 3,700. Again like the " O_5-acetate," it is unstable to alkali, but simple hydrolysis of the C_2-acetyl group is accomplished by means of alcoholic hydrogen chloride to give the corresponding *alcohol*, $C_{31}H_{44}O_6$, m. p. 255—256°.

The general nature of the oxidation reactions described in this paper was further demonstrated by treatment of methyl acetyldehydro-oleanolate (IV*a* or IV*b*, R′ = CO_2Me) with chromic acid, the acetate $C_{33}H_{46}O_7$ being obtained. The complete correspondence in behaviour between comparable derivatives of β-amyrin and oleanolic acid shows that the C_{17}-angular methyl group of β-amyrin acetate cannot be involved in the formation of the " O_5-acetate."

From the evidence available it is not possible to formulate a structure for the " O_5-acetate " (and for the corresponding derivative from methyl ketoacetyloleanolate) in terms of the hypothetical structure of β-amyrenonyl acetate (II, R = R′ = Me). In general terms, however, it is to be noted that the oxidation of β-amyradienonyl acetate to the " O_5-acetate " has involved the elimination of two hydrogens and the introduction of two oxygen atoms, this change resulting in a very considerable modification of the original dienone chromophore. This modification does not result in the formation of either an αβ-unsaturated ketone or a 1 : 2-diketone. Of particular significance is the formation of the diacetate, m. p. 249—251°, by hydrolysis of the " O_5-acetate " [which, according to Ruzicka and Jeger (*loc. cit.*), contains one acetyl group *], followed by reacetylation.

In view of its ease of formation in high yield, the elucidation of the structure of the " O_5-acetate " appears to be of importance as a means of testing the hypothetical formula (I) for the β-amyrin group.

EXPERIMENTAL.

Benzoate, $C_{37}H_{48}O_5$.—(*a*) A solution of β-amyrenonyl benzoate (Picard and Spring, J., 1940, 1200) (1·0 g.) in glacial acetic acid (25 c.c.) was heated under reflux with selenium dioxide (1·0 g.). The hot solution was filtered from black selenium, and the latter washed with hot acetic acid; the solvent was removed under reduced pressure, and the solid residue collected and dried. A solution of this solid in benzene–light petroleum (1 : 1, 20 c.c.) was filtered through a column of activated alumina (Brockmann), and the column washed with benzene (20 c.c.). The solvent was removed from the combined filtrates, and the solid crystallised twice from alcohol to give the *benzoate* in colourless needles (0·65 g.), m. p. 262—263°, $[\alpha]_D^{21°}$ +42° (l = 0·5, c = 2·0). A mixture of equal parts of the new benzoate and β-amyrenonyl benzoate (m. p. 265°) had m. p. 225—229°. The benzoate gives a very pale yellow coloration with tetranitromethane in chloroform (Found : C, 77·8; H, 8·6. $C_{37}H_{48}O_5$ requires C, 77·6; H, 8·45%).

(*b*) Oxidation of β-amyradienonyl benzoate (Picard and Spring, *loc. cit.*) (m. p. 251—252°) was effected as described under (*a*), except that the reaction mixture was heated under reflux for 6 hours. After three crystallisations from alcohol, the product formed fine needles, m. p. 263°, undepressed by the benzoate described under (*a*); $[\alpha]_D^{19°}$ +40° (l = 0·5, c = 2·1); it gave a faint yellow coloration with the tetranitromethane reagent (Found : C, 77·5, 77·3; H, 8·4, 8·3%).

Acetate, $C_{32}H_{46}O_5$.—(*a*) A solution of β-amyrenonyl acetate (Picard and Spring, *loc. cit.*) (1·0 g.) in glacial acetic acid (30 c.c.) was refluxed with selenium dioxide (1·0 g.) for 20 hours. The solution was filtered hot, fine needles separating from the solution on cooling. After three crystallisations from methyl alcohol the acetate was obtained in needles, m. p. 252—253°, unchanged by further crystallisation; $[\alpha]_D^{23°}$ +35° (l = 0·5, c = 2·1). By combination and concentration of the mother-liquors a further crop of " O_5-acetate " separated, which on purification attained the constant m. p. 252—253° (total yield, 68%) (Found : C, 75·4; H, 9·3. Calc. for $C_{32}H_{46}O_5$: C, 75·25; H, 9·1%). *Light absorption in alcohol :* Maximum at 2300 A., ε = 3600 with an inflexion at 3000 A., ε = 340.

* (*Note added in proof.*) In order to confirm that the " O_5-acetate " is a monoacetate, it was submitted for a micro-acetyl determination. Surprisingly, the result indicated a diacetate (Found: Ac, 16·7. $C_{32}H_{46}O_5$ requires 1Ac, 8·4; 2Ac, 16·8%.) Employing a macro-method for the estimation of acetyl (using 0·4—0·5 g. of material) we find that the " O_5-acetate " is a mono-acetate (Found : Ac, 8·6, 8·7, 8·6%), and that the micro-estimation of acetyl is untrustworthy in this case. This result raises doubts concerning the " diacetate," m. p. 249—251°, in which the acetyl was estimated by a micro-method; we have not as yet had an opportunity of re-determining the acetyl by a macro-method, but in the meantime it is to be observed that, apart from the acetyl value, the analytical data for this compound are compatible with a *mono*-acetate, $C_{32}H_{46}O_5$, *i.e.*, an isomer of the " O_5-acetate."

(*b*) The oxidation of β-amyradienonyl acetate (Picard and Spring, *loc. cit.*) (100 mg.) with selenium dioxide (80 mg.) was effected as described under (*a*) except that the reaction mixture was refluxed for 8 hours only. After two crystallisations the acetate was obtained in fine needles from methyl alcohol, m. p. 252°, $[\alpha]_{D}^{23^\circ}$ +35° (l = 0·5, c = 1·24) (yield, 65%). It was undepressed in m. p. when mixed with the specimen prepared by method (*a*).

(*c*) A solution of chromic anhydride (4·6 g.) in hot stabilised glacial acetic acid (150 c.c.) was added during 30 minutes to a boiling solution of β-amyradienyl-II acetate (Ruzicka, Müller, and Schellenberg, *Helv. Chim. Acta*, 1939, **22**, 767) (5 g.) in glacial acetic acid (360 c.c.), the mixture being stirred and heated under reflux for 1 hour after the addition was complete. The solvent was removed under reduced pressure, and the residue shaken with ether and dilute sulphuric acid. The ethereal solution was washed with sodium hydroxide solution (5%) and with water. Only a trace of acidic matter was obtained by acidification of the alkaline washings. Removal of the solvent from the dried (sodium sulphate) ethereal solution gave a crude neutral fraction (4·0 g.), which crystallised from methanol in needles, m. p. 211—217° (2·2 g.). When recrystallised from the same solvent, the product formed well-defined homogeneous needles, m. p. 219—221°, which remained constant after two further crystallisations (Found : C, 77·0, 77·1 ; H, 9·2, 9·0. $C_{32}H_{48}O_3$ requires C, 80·0 ; H, 10·1%. $C_{32}H_{46}O_5$ requires C, 75·25 ; H, 9·1%). *Light absorption in alcohol :* Maxima at 2290 (ε = 3000) and 2810 A. (ε = 4500). A solution of the neutral fraction (2·0 g.), m. p. 211—217°, in light petroleum (b. p. 60—80°) was filtered through a column of activated alumina (Brockmann ; 30 g.), and the column washed with light petroleum and then with ether, the following fractions being collected :

Fraction.	Solvent, c.c.	Wt. of product, g.	M. p.
1	Light petroleum, 250	0·7	197—204°
2	,, ,, ,,	0·2	216—220
3	,, ,, ,,	0·05	222—244
4	Ether ,,	0·8	247—250
5	,, ,,	nil	—

Crystallisation of fraction 1 from methyl alcohol (from which it separated in needles) was not a satisfactory method of purification, leading to considerable wastage of material and a slow continual increase of the m. p. The top crop and its various mother-liquors were combined, the solvents removed, and the dried residue dissolved in light petroleum (b. p. 40—60° ; 70 c.c.) and filtered through a column of activated alumina (Brockmann ; 30 g.). The column was washed with light petroleum (b. p. 60—80°) and then with light petroleum–benzene (1 : 1 ; 750 c.c.), and the following fractions collected :

Fraction.	Solvent, c.c.	Wt. of product, g.	M. p.
1a	Light petroleum, 250	nil	—
1b	,, ,, 200	0·1	177—181°
1c	,, ,, ,,	0·3	219—226
1d	,, ,, ,,	0·1	225—229
1e	,, ,, ,,	0·05	224—229
1f	Light petroleum–benzene, 250	0·05	220—225
1g	,, ,, ,, ,,	0·05	240—247
1h	,, ,, ,, ,,	nil	—

Fractions 1c, 1d, 1e and 1f were combined (0·5 g.) and crystallised from methanol–acetone to yield fine needles, m. p. 241—250°, which after two recrystallisations from the same solvent gave β-amyradienonyl acetate, m. p. 248—249°, undepressed by an authentic specimen, m. p. 250—251° ; $[\alpha]_{D}^{15^\circ}$ +338° (l = 0·5, c = 1·0 in pyridine). *Light absorption in alcohol :* Maximum at 2850 A., ε = 13,000.

Fraction 4 from the original chromatogram was crystallised twice from methanol, from which the acetate, $C_{32}H_{46}O_5$, separated as fine needles, m. p. 252—253°, undepressed by a specimen prepared by method (*a*). It gave a very faint yellow coloration with the tetranitromethane reagent (Found : C, 75·65 ; H, 8·9. Calc. for $C_{32}H_{46}O_5$: C, 75·25 ; H, 9·1%). *Light absorption in alcohol :* Maximum at 2285 A., ε = 3300.

(*d*) A solution of chromic anhydride (0·5 g.) in water (0·5 c.c.) was diluted with glacial acetic acid (15 c.c.) and this mixture was added to a boiling solution of β-amyradienyl-II acetate (0·5 g.) in glacial acetic acid (40 c.c.) during 30 minutes. The mixture was refluxed for a further hour and worked up as described under (*c*). The neutral fraction (0·35 g.) was crystallised four times from methyl alcohol to give the " O_5-acetate " in fine needles, m. p. 251—252°, $[\alpha]_{D}^{22^\circ}$ +32·5° (l = 0·5 ; c = 1·97). *Light absorption in alcohol :* Maximum at 2300 A., ε = 3800, with a low-intensity inflexion at 3000 A.

" Acid " Hydrolysis of the Acetate, $C_{32}H_{46}O_5$.—The acetate (m. p. 252—253°) (200 mg.) was heated under reflux with methyl-alcoholic hydrogen chloride (5% ; 25 c.c.) for 2 hours ; after the addition of more methyl-alcoholic hydrogen chloride (25 c.c.) the solution was boiled for a further 2½ hours and then concentrated until crystals began to separate and set aside. The crystalline solid was collected (m. p. 274—276°) and recrystallised from methyl alcohol, from which the *alcohol*, $C_{30}H_{44}O_4$, separated in fine needles, m. p. 280·5—281·5°. It was dimorphous, separating as large flat prisms from dilute solutions or as needles when the crystallisation was rapid. Both forms had the same m. p. either alone or when mixed. The alcohol gave a faint yellow colour with the tetranitromethane reagent but no coloration with aqueous ferric chloride (Found : C, 76·9 ; H, 9·2. $C_{30}H_{44}O_4$ requires C, 76·9 ; H, 9·5%). *Light absorption in alcohol :* Maximum at 2280 A., ε = 3000. The alcohol (90 mg.) was set aside at room temperature with acetic anhydride (1 c.c.) and pyridine (2 c.c.) for 14 hours, and then heated on the steam-bath for 15 minutes. The product separated from methyl alcohol as fine needles, m. p. 253°, undepressed by the acetate $C_{32}H_{46}O_5$.

Alkaline Hydrolysis of the Acetate, $C_{32}H_{46}O_5$.—A solution of the acetate (800 mg.) in methyl-alcoholic potassium hydroxide (2 g. of hydroxide, 2 c.c. of water, 18 c.c. of methyl alcohol) was heated in an autoclave at 200° for 15 hours. The yellow solution was diluted with water and extracted with ether, and the ethereal solution washed with water and dried (sodium sulphate). The neutral fraction (550 mg.) obtained after removal of the ether was a yellow oil which could not be obtained crystalline from acetone, methyl alcohol, or alcohol. The dry neutral fraction was treated with acetic anhydride (1 c.c.) and pyridine (1 c.c.) and set aside at 16° for 16 hours. The solution was then heated on the steam bath for 15 minutes, and the product, which was isolated in the usual manner, crystallised from methyl alcohol–acetone, from which the *diacetate* separated in long fine needles, m. p. 249—251°, not altered by recrystallisation from 95% alcohol, from which the acetate also separated in needles. A mixture of equal parts of the new acetate and the acetate $C_{32}H_{46}O_5$ (m. p. 253°) was completely molten at 223°. The diacetate did not give a coloration with tetranitromethane (in contrast to the acetate $C_{32}H_{46}O_5$) or with aqueous ferric chloride and it did not exhibit selective absorption of any appreciable intensity above 2200 A.; $[\alpha]_{D}^{22^\circ}$ +149° (l = 0·5, c = 0·7) (Found : C, 75·7, 75·7 ; H, 9·0, 9·2 ; Ac, 17·4. $C_{33}H_{46}O_5$ requires C, 75·8 ; H, 8·9 ; 2Ac, 16·4%). The original alkaline solution was acidified with dilute hydrochloric acid, which produced a white opalescence. The mixture was extracted with ether, the ethereal solution washed and dried (sodium sulphate), and the solvent removed. The residue crystallised from acetone in small prisms. The crystalline solid was collected, washed with ether, and recrystallised from acetone to yield an acid as prisms, m. p. 292—293° (decomp.) after sintering at 290°. The acid did not give a coloration with the tetranitromethane reagent and a solution of the acid in alcohol did not give a coloration with aqueous ferric chloride. An examination of the light absorption properties of an alcoholic solution shows the absence of any selective absorption of appreciable intensity above 2200 A., but this does not preclude the presence of isolated carbonyl groups. The acid was obtained in extremely low yield and its further examination must await attempts to improve this yield.

The neutral diacetate was also obtained in high yield (65%) by hydrolysis of either the " O_5-acetate " or the benzoate, $C_{37}H_{48}O_5$, by heating under reflux with 2% alcoholic potassium hydroxide for 3 hours. In the latter case the neutral fraction was obtained as a yellow amorphous powder which could not be crystallised from aqueous alcohol or acetone. A solution of the neutral fraction (0·6 g.) in benzene–light petroleum (b. p. 60—80°) (1 : 1; 40 c.c.) was filtered through a column of activated alumina (8 × 1 cm.). A yellow zone on the chromatogram gradually moved down the column when it was washed with benzene–light petroleum (1 : 1) (250 c.c.). The colourless filtrate did not contain any material; the column was next washed with benzene (150 c.c.), which eluted the yellow band. Removal of the benzene gave an amorphous yellow solid (0·5 g.) which separated from hot aqueous alcohol as a yellow powder. Acetylation of the powder by heating with acetic anhydride and pyridine for 2 hours on the steam-bath gave the diacetate, in long fine needles from 95% alcohol, m. p. 249—251° (Found : C, 75·7; H, 9·2%). The diacetate, when mixed with the specimen prepared by acetylation of the neutral hydrolysis product of the acetate $C_{32}H_{46}O_5$, showed no depression in m. p.

Methyl Ketoacetyloleanolate.—Ketoacetyloleanolic acid, prepared by the oxidation of acetyloleanolic acid with chromic acid, was obtained from methanol–acetone in fine needles, m. p. 268—270° (yield, 10%). Ruzicka and Cohen (*Helv. Chim. Acta*, 1937, **20**, 804) give m. p. 282—284° (corr.) for this acid, but later Ruzicka, Cohen, Furter, and Sluys-Veer (*ibid.*, 1938, **21**, 1735) recorded m. p. 272—273° (corr.), and Bilham, Kon, and Ross (J., 1942, 539) find m. p. 288° (uncorr.). Methylation of this keto-acid with diazomethane gave methyl ketoacetyloleanolate, which formed prismatic needles from methyl alcohol, m. p. 238—239° (yield, 90%).

The direct oxidation of methyl acetyloleanolate to methyl ketoacetyloleanolate has been described by Kitasato and Sone (*Acta Phytochim.*, 1932, **6**, 213). The oxidation was carried out at 15°, and the product described as prisms, m. p. 224°, later corrected to 237° [*idem, ibid.*, 1933, **7**, 25 (footnote)]. We find that the following modification of the Kitasato and Sone experiment is the best method for the preparation of methyl ketoacetyloleanolate. A boiling solution of methyl acetyloleanolate (5 g.) in glacial acetic acid (45 c.c.) was treated with a solution of chromic anhydride (5 g.) in acetic acid (90%; 50 c.c.), added during 30 minutes with stirring; the solution was then refluxed for 90 minutes. Water (35 c.c.) was added, and the solution set aside overnight. The crystalline (plates) solid was collected and recrystallised from methanol, from which it separated in prisms (1·16 g.), m. p. 238—239°. A solution of this solid in light petroleum (b. p. 60—80°; 50 c.c.) and benzene (40 c.c.) was filtered through a column of activated alumina (Brockmann) (17 cm. × 3 cm.), and the column washed successively with light petroleum–benzene (5 : 4), benzene, and ether, the following fractions being collected :

Fraction.	Solvent, c.c.	Wt. of fraction, g.	M. p.
1	Light petroleum–benzene, 400	nil	—
2	,, ,, ,, 350	0·17	239—240°
3	Benzene, 300	0·45	240·5—241
4	,, ,,	0·17	240·5—241
5	Ether, 250	0·3	237—238
6	,, ,,	nil	—

Fractions 2, 3 and 4 were combined and crystallised from methyl alcohol–acetone to yield methyl ketoacetyloleanolate (0·62 g.) in prismatic needles, m. p. 240·5—241°, $[\alpha]_D^{17^\circ}$ +66° ($l = 1$, $c = 1{\cdot}5$ in pyridine). Kitasato and Sone (*loc. cit.*) give m. p. 237° for the ester prepared by the direct oxidation of methyl acetyloleanolate and m. p. 236—238° for a specimen prepared by methylation of ketoacetyloleanolic acid. Ruzicka, Cohen, Furter, and Sluys-Veer, however, record m. p. 252—253° (corr.) for the ester prepared by the latter method. A mixture of the ester, m. p. 240·5—241°, with the ester, m. p. 238—239°, prepared by method (*a*) had m. p. 239—240° (Found for material of m. p. 240·5—241° : C, 75·0; H, 9·8. Calc. for $C_{33}H_{50}O_5$: C, 75·2; H, 9·6%).

Acetate, $C_{33}H_{46}O_7$.—(*a*) Methyl ketoacetyloleanolate (2·3 g.) in glacial acetic acid (30 c.c.) was heated under reflux with selenium dioxide (2·3 g.) for 30 hours. The hot solution was filtered, and the solvent removed from the filtrate, under reduced pressure. The dark red oil crystallised from methanol (charcoal) in needles, m. p. 251—252·5°, which after two recrystallisations from the same solvent gave the *acetate*, $C_{33}H_{46}O_7$, m. p. 253—254°, $[\alpha]_D^{15^\circ}$ +15·9° ($l = 0{\cdot}5$; $c = 4{\cdot}6$ in pyridine). The O_7-acetate did not give a coloration with aqueous-alcoholic ferric chloride (Found : C, 71·1, 71·3; H, 8·3, 8·6. $C_{33}H_{46}O_7$ requires C, 71·5; H, 8·5%). *Light absorption in alcohol :* Maximum at 2280 A., $\varepsilon = 3{,}700$.

(*b*) A boiling solution of methyl acetyldehydro-oleanolate (Ruzicka, Grob, and Sluys-Veer, *Helv. Chim. Acta*, 1939, **22**, 791) (m. p. 224°) (0·9 g.) in glacial acetic acid (35 c.c.) was treated dropwise during 20 minutes with a solution of chromic anhydride (0·9 g.) in acetic acid (90%; 16 c.c.). The solution was refluxed for a further 90 minutes and then evaporated to dryness under reduced pressure. The neutral fraction obtained by extraction with ether was crystallised from methanol to give needles (0·5 g.), m. p. 244—247°. A solution of this solid (0·35 g.) in light petroleum (b. p. 40—60°; 50 c.c.) and benzene (20 c.c.) was filtered through a column of activated alumina (30 g.), and the following fractions collected :

Fraction.	Solvent, c.c.	Weight, g.
1	Light petroleum–benzene (5 : 2), 240	0·015
2	,, ,, ,, ,, 200	0·010
3	Ether, 200	0·300
4	,, ,,	nil

Fraction 3 was crystallised thrice from methanol to give the acetate, $C_{33}H_{46}O_7$, in fine needles, m. p. 251—252° either alone or when mixed with the specimen described under (*a*). *Light absorption in alcohol :* Maximum at 2280 A., $\varepsilon = 3{,}600$.

Alcohol, $C_{31}H_{44}O_6$.—The acetate $C_{33}H_{46}O_7$ (160 mg.) was heated under reflux for 4 hours with methanolic hydrogen chloride (5%; 15 c.c.), and the solution concentrated until crystallisation set in. After cooling, the solid was collected and recrystallised from methanol, from which the *alcohol* $C_{31}H_{44}O_6$ separated in small prisms, m. p. 255—256°. The alcohol gave a faint yellow coloration with tetranitromethane in chloroform but no colour with aqueous alcoholic ferric chloride solution; $[\alpha]_D^{16^\circ}$ −3·55° ($l = 0{\cdot}5$, $c = 2{\cdot}8$ in pyridine) (Found : C, 72·6; H, 9·0. $C_{31}H_{44}O_6$ requires C, 72·6; H, 8·7%).

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