46. *The Triterpene Group. Part VI. The Oxidation of β-Amyrin Benzoate. A New Route to the Thio-compound,* $C_{30}H_{44}OS$.

By James C. E. Simpson.

The oxidation of β-amyrin benzoate is shown to be considerably more complex than would appear from the work of Beynon, Sharples, and Spring (J., 1938, 1233), and in consequence cannot be regarded as comparable with oxidations of certain derivatives of β-boswellic acid, which give rise to single products in high yield (Simpson and Williams, J., 1938, 1712). In view of this intrinsic dissimilarity, and also in consequence of the work of Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 758), the criticism of Spring (*Chem. and Ind.*, 1938, **57**, 1108) as to the validity of the evidence on which the present tentative structure of β-boswellic acid is based (Simpson and Williams, *loc. cit.*) is no longer justifiable.

Treatment of *dehydro-β-amyrenyl benzoate* with sulphur in boiling benzyl acetate yields the benzoate of the thio-compound $C_{30}H_{44}OS$, previously obtained by the partial dehydrogenation of β-amyrin; β-amyrenonyl benzoate and *β-amyranonyl benzoate* are unaffected under these conditions. It is shown, by a comparison of the

properties of β-*amyradienone* with those of certain ketones derived from the thio-compound, that the chromophoric group in the latter substance and its derivatives cannot consist of a system of two conjugated double bonds.

It has been stated by Beynon, Sharples, and Spring (J., 1938, 1233) that the oxidation of β-amyrin benzoate with chromic anhydride produces the αβ-unsaturated ketone ester, β-amyrenonyl benzoate, whereas a similar oxidation of β-amyrin acetate yields " β-amyrin acetate oxide ". [The latter compound is now considered on good evidence (Picard, Sharples, and Spring, J., 1939, 1045) to be a saturated ketonic acetate, and has in consequence been re-named β-amyranonyl acetate.] It would therefore appear that the nature of the acyl radical attached to C_2 controls the course of the oxidation at the double bond of β-amyrin, despite the fact that this is regarded as being in ring *C* and consequently in a position comparatively remote from C_2.

Using this argument, Spring (*Chem. and Ind.*, 1938, **57**, 1108) has questioned the validity of certain deductions made by Simpson and Williams (J., 1938, 1712) in connection with the structure of β-boswellic acid. These authors showed that the course of the ethylenic oxidation of certain derivatives of this acid is governed by the groups attached to C_1, and argued that this behaviour suggests a close association of C_1 with the double bond, thus indicating its location in ring *B*.

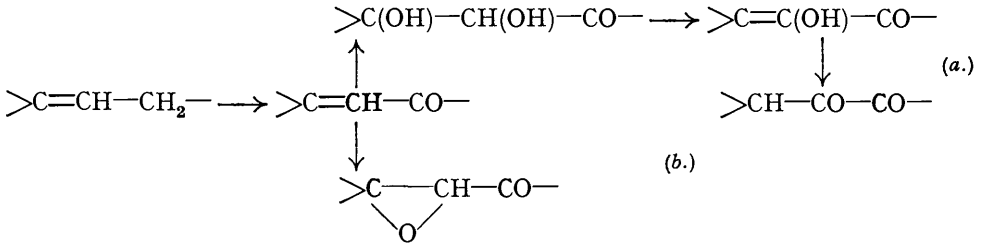
Inasmuch as additional (although admittedly not conclusive) evidence also supported the structure proposed for β-boswellic acid, the oxidation of the β-amyrin esters seemed to require further investigation. The study of this problem had been in progress for some time when it was anticipated in some degree by Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 758), who stated that, contrary to the observations of Beynon, Sharples, and Spring (*loc. cit.*), the oxidation of β-amyrin acetate is analogous to that of the benzoate, and yields β-amyrenonyl acetate and not β-amyranonyl acetate. There is, moreover, a considerable discrepancy between the physical constants of β-amyrenonol recorded by the Swiss authors and those given by Beynon, Sharples, and Spring (*loc. cit.*) (see Table I).

The results obtained in this laboratory from the oxidation of β-amyrin benzoate are described below. They show that the reaction is exceedingly complex, and that it can in no sense be regarded as comparable with the extremely smooth and simple oxidations of the β-boswellic acid derivatives, referred to above, which give rise to high yields of pure products. In view of the author's results and of the work of Ruzicka, Müller, and Schellenberg (*loc. cit.*), the criticism of Spring (*loc. cit.*) can no longer be regarded as justified.

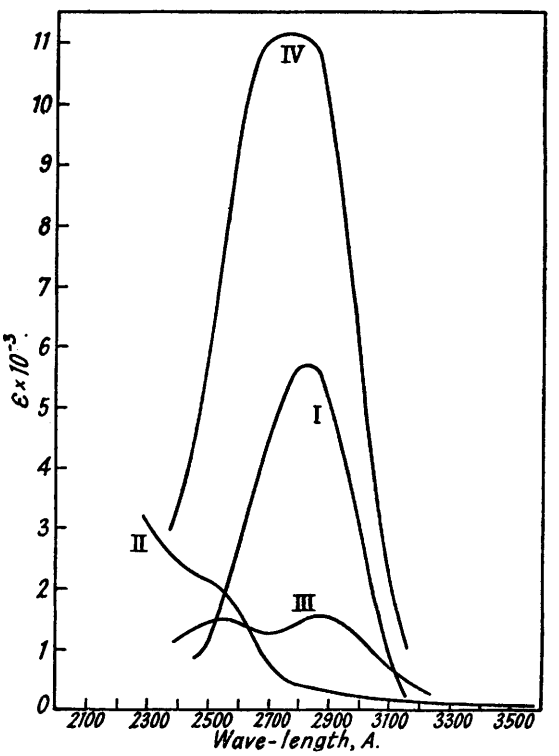
The experimental conditions which permit of the isolation of pure β-amyrenonyl benzoate (by direct crystallisation from acetic acid) appear to be highly critical, for whereas oxidations carried out under the exact conditions described by Beynon, Sharples, and Spring (*loc. cit.*) yielded a keto-benzoate of constant m. p. 263—264°, yet comparatively slight variations, made in the hope of improving the rather unsatisfactory yield of pure material, yielded a mixture which could not be purified by further crystallisation from acetic acid. This mixture was shown to consist principally of β-amyrenonyl benzoate by its hydrolysis and subsequent acetylation, whereby pure β-amyrenonyl acetate, having the constants shown in Table I, was readily isolated. On hydrolysis of either the pure keto-acetate or the pure keto-benzoate, β-amyrenonol was obtained with constants (Table I) in good agreement with those of Ruzicka, Müller, and Schellenberg (*loc. cit.*). In no case was a preparation obtained having the physical properties ascribed to it by Beynon, Sharples, and Spring (*loc. cit.*).

The mother-liquors from the impure β-amyrenonyl benzoate contained appreciable quantities of acidic material. This was removed, and the neutral residue hydrolysed and acetylated, leading to the isolation in small yield (approximately 2%) of a sparingly soluble, lævorotatory *acetate*, m. p. 324°. Ultimate analysis indicated the formula $C_{32}H_{48}O_4$, which is difficult to reconcile with any feasible structure. The alternative formula $C_{32}H_{50}O_4$, however, is not excluded, and this is supported by the analysis of the related *alcohol*, which gave figures in good agreement with the formula $C_{30}H_{48}O_3$. In view of the failure of this alcohol to give a positive tetranitromethane test, and of the absence, as

revealed by spectrographic evidence, of the αβ-unsaturated ketonic group, the only structures consistent with its molecular formula are those of an α-diketone and a ketonic oxide, formed by mechanisms (*a*) and (*b*) respectively:



Of these alternatives, (*b*) is to be preferred, since the compound fails to react with alcoholic ferric chloride and with *o*-phenylenediamine, and shows little selective absorption in the ultra-violet (inflexion at 2500 A., log ε = 3·32; curve II in the figure).



I. *Dehydro-β-amyrenyl acetate* (*m. p.* 221·5—223°).
II. *Alcohol*, $C_{30}H_{48}O_3$ (*m. p.* 262—264°).
III. *β-Amyradienone* (*m. p.* 176·5—178°).
IV. *Keto-acetate*, $C_{32}H_{46}O_4$. (*All in alcohol.*)

Methylation and rebenzoylation of the acid fraction (roughly 20% of the total oxidation products) gave rise to two further crystalline substances. One of these proved to be a methoxyl-free, neutral *benzoate*, m. p. 293—294°, which gave analytical data suggestive of the formula $C_{37}H_{50}O_4$. (This substance was present in extremely small amount; a possible reason for its occurrence in the acid fraction is given in the experimental part.) The filtrate from this compound contained a crystalline *methyl* ester, m. p. 230°, which failed to react with hydroxylamine acetate in boiling alcohol. Four highly concordant analyses gave a mean value (C, 74·5; H, 7·85%) which cannot be reconciled with any

molecular formula corresponding to a simple oxidation product. The only formula in good agreement with these figures is $C_{45}H_{56}O_8$, corresponding to the dibenzoate of an (enolised) hydroxy-keto-methyl ester $C_{31}H_{48}O_6$, with two uncharacterised oxygen atoms. These oxidation products are being further investigated as material accumulates.

The present work was planned with the additional objective of making a comparative study of the partial dehydrogenation of simple oxidation products of β-amyrin by means of sulphur. It was hoped in this way to throw light on the mode of formation from β-amyrin of the thio-compound $C_{30}H_{44}OS$, to the importance of which, in connection with the structure of the β-amyrin group of triterpenes, attention has recently been drawn (Simpson, J., 1938, 1313; 1939, 755). For this purpose *β-amyranonyl benzoate*, m. p. 261°, and *dehydro-β-amyrenyl benzoate*, m. p. 239°, have been prepared. The latter compound was obtained from the hitherto unknown *dehydro-β-amyrenol*, the product of hydrolysis of dehydro-β-amyrenyl acetate, which has been shown by Beynon, Sharples, and Spring (*loc. cit.*) to result from β-amyrenonol on reduction, followed by simultaneous dehydration and acetylation. The physical constants of the dehydro–acetate prepared in this laboratory are not in good agreement with those recorded by Beynon, Sharples, and Spring; they appear to vary with small changes in experimental conditions (compare Ruzicka, Müller, and Schellenberg, *Helv. Chim. Acta*, 1939, **22**, 767; Ewen, Spring, and Vickerstaff, J., 1939, 1303), and are summarised in Table I. The author's dehydro-acetate, m. p. 221·5—223°, showed an absorption maximum at 2820 A., log $\varepsilon = 3{\cdot}76$ (curve I in the figure).

The action of sulphur on the two new benzoates, and also on β-amyrenonyl benzoate, was studied under the improved conditions recently described (J., 1939, 755). Both ketonic esters were recovered unchanged * in good yield; dehydro-β-amyrenyl benzoate, on the other hand, was smoothly converted into the benzoate of the thio-compound, the identity of which with the product from β-amyrin was established beyond question.

It is not proposed at this stage to discuss in detail the significance of these results; attention is however directed to the fact that the available evidence precludes the possibility that the dehydrogenation of β-amyrin to the thio-compound involves preliminary formation of dehydro-β-amyrenol and subsequent entry of a sulphur atom at some other part of the molecule. Such a mechanism, which would be in harmony with the similarity, both in position and in intensity, of the maxima of the absorption spectra exhibited by the dehydro-β-amyrenyl acetate of Beynon, Sharples, and Spring and (curve IV) the keto-acetate $C_{32}H_{46}O_4$ (the primary product of oxidation of the acetate of the thio-compound), appears at first glance to be strongly supported by the conversion of the author's dehydro-β-amyrenyl acetate into the thio-compound. This hypothesis would however imply the presence of two conjugated double bonds in the keto-acetate $C_{32}H_{46}O_4$, and this is excluded by previous observations (Simpson, *loc. cit.*), which indicate that the thio-compound and its oxidation products are saturated substances.

In a detailed study (to be communicated later) of the behaviour of the oxidation products of the thio-compound towards unsaturation tests, it has been found that, although all the products so far prepared give completely negative tetranitromethane reactions (except the unsaturated dihydroxy-acid $C_{30}H_{50}O_4$), weakly positive responses to the Liebermann–Burchard test are given by substances in which there is a hydroxy- or an acetoxy-group on C_2. These weak reactions are ascribable to dehydration (preceded by hydrolysis if necessary) in the strongly acid medium employed, with consequent production of unsaturation, and are entirely inhibited by conversion of the C_2-group into carbonyl; for example, the C_2-ketones $C_{30}H_{42}O_3$ and $C_{30}H_{40}O_4$ [compounds (V) and (VIII); J., 1939, 755] give completely negative Liebermann–Burchard reactions. In order to compare the colour reactions of the " thio-compound series " with those of a β-amyrin derivative in which no participation in the Liebermann–Burchard test by the C_2-group should be possible, dehydro-β-amyrenol (m. p. 221·5—223°) has been converted into a ketone, *β-amyradienone*

* Boiling quinoline, likewise, is without effect on β-amyrenonyl benzoate (observation of Miss T. Sen-Gupta in this laboratory), thus indicating that the conversion of keto-acetyl oleanolic acid under these conditions into the keto-acetate, $C_{31}H_{46}O_3$, m. p. 208—210° (Ruzicka, Cohen, Furter, and Sluys-Veer, *Helv. Chim. Acta*, 1938, **21**, 1735), involves the loss of carbon dioxide and hydrogen without migration or elimination of alkyl groups.

(yield, 25—30%), which shows selective absorption at 2540 and 2860 A., log $\varepsilon = 3{\cdot}18$ (curve III).

β-Amyradienone gives strongly positive tests for unsaturation, and the complete contrast between this behaviour and that of the C_2-ketones, $C_{30}H_{42}O_3$ and $C_{30}H_{40}O_4$, derived from the thio-compound leads to the seemingly inescapable conclusion that the chromophoric group in the thio-compound and its derivatives cannot consist of a conjugated system of two double bonds. A point of interest in this connexion is that the compound $C_{33}H_{46}O_6$ (from methyl *O*-acetyloleanolate and selenium dioxide; Ruzicka, Grob, and Sluys-Veer, *Helv. Chim. Acta*, 1939, **22**, 788) is strongly unsaturated towards tetranitromethane, and yet virtually indistinguishable, spectrographically, from the keto-acetate $C_{32}H_{46}O_4$ derived from the thio-compound.

The author is indebted to Dr. R. A. Morton for the spectrographic determinations recorded in the figure.

TABLE I.

β-Amyrenonol.		β-Amyrenonyl acetate.		β-Amyrenonyl benzoate.		Dehydro-β-amyrenyl acetate.		
M. p.	$[\alpha]_D$.	M. p.	$[\alpha]_D$.	M. p.	$[\alpha]_D$.	M. p.	$[\alpha]_D$.	
175°	+113°	260—261°	+158°	265°	+127°	208—209°	+331°	(1)
230—231	102	264—265	—	262—263	155	—	—	(2)
233—234	104	261—262	97	263—264	—	(a) 216—217	319	
						(b) 221·5—223	221	(3)

(1) Beynon, Sharples, and Spring, *loc. cit.* (2) Ruzicka, Müller, and Schellenberg, *loc. cit.*; m. p.'s corrected. (3) This paper.

EXPERIMENTAL.

(Melting points are uncorrected; specific rotations were measured in chloroform solution.)

Oxidation of β-Amyrin Benzoate.—A suspension of the benzoate (10 g.) in glacial acetic acid (450 c.c.) was treated under reflux with a solution of chromic anhydride (7 g.) in water (30 c.c.) and acetic acid (30 c.c.), added drop by drop during 35—45 minutes; a clear solution resulted after approximately one-quarter of the reagent had been added. When the addition was complete, the solution was refluxed for a further ½ hour and then completely precipitated with water. Recrystallisation of the crude material from a boiling saturated solution in aqueous acetic acid gave a product (A) which crystallised in plates, m. p. 255—260° (yield, 50%), and gave no depression in m. p. when mixed with authentic β-amyrenonyl benzoate (prismatic needles, m. p. 263—264°, prepared by the method of Beynon, Sharples, and Spring; yield, 30—35%); an appreciable depression was however observed when it was mixed with β-amyranonyl benzoate. The melting point could neither be sharpened nor raised appreciably by further crystallisation from glacial acetic acid.

Product (A) was hydrolysed under reflux for 3—3½ hours with 9% benzene-alcoholic potassium hydroxide solution (20 vols.), and the product isolated by concentration, precipitation with water, and extraction with ether. Evaporation of the washed and dried extract gave a crystalline residue, which separated from aqueous alcohol in soft needles, m. p. 206—208°, unchanged by further crystallisation. The crude acetate, obtained by refluxing this material for ¾ hour with 8—10 times its weight of acetic anhydride, had m. p. 215—235°, and was highly soluble in alcohol. By digestion with methanol a main fraction, sparingly soluble in alcohol, was obtained; this was fairly pure β-amyrenonyl acetate {needles, m. p. 255—257°, $[\alpha]_D^{18°} + 95°$ ($l = 1$, $c = 3{\cdot}57$)}. Two or three crystallisations from ethyl acetate yielded the pure acetate in stout, blunt needles, m. p. 261·5—262·5°, $[\alpha]_D^{22°} + 96°$ ($l = 1$, $c = 2{\cdot}12$). The acetate was also readily isolated by acetylation of the material contained in the mother-liquor of the alcohol mixture of m. p. 206—208°.

Acetate, $C_{32}H_{50}O_4$.—The filtrate from product (A) was precipitated with water and extracted with ether. An acid fraction (B) was removed from the ethereal extract by means of 3% sodium hydroxide solution; the neutral solution was then washed with water and evaporated. The residue was refluxed for 6 hours with a large excess of benzene–alcoholic potash (10%); water was then added, and the suspension extracted with ether.* The extract was washed with dilute hydrochloric acid and water, dried, and evaporated, and the residual red resin (30—35% of the total oxidation products) was refluxed for ½ hour with acetic anhydride (3

* In some experiments the preliminary washing with 3% sodium hydroxide solution was omitted, the removal of the acid fraction and hydrolysis of the neutral benzoates being effected in one stage with hot alkali.

parts by weight). On cooling, a crystalline product rapidly separated, part of which was sparingly soluble in ethyl acetate. Continued recrystallisation of this fraction from benzene–ethyl acetate furnished the new *acetate* in small rods, m. p. 322—324° after preliminary sintering, $[\alpha]_D^{18°}$ − 110° (l = 1, c = 3·34). The compound gave a very faint coloration with tetranitromethane in chloroform (Found: C, 77·2; H, 9·6. $C_{32}H_{50}O_4$ requires C, 77·0; H, 10·1. $C_{32}H_{48}O_4$ requires C, 77·3; H, 9·75%).

Alcohol, $C_{30}H_{48}O_3$.—A solution of the foregoing acetate (150 mg.) in hot benzene (3 c.c.) was refluxed for 6 hours with 0·1N-alcoholic potassium hydroxide (15 c.c.). The *alcohol*, isolated by precipitation with water and extraction with ether, separated after six crystallisations from methanol in well-formed needles, m. p. 284—285°, which gave negative reactions with tetranitromethane in chloroform and with ferric chloride (Found: C, 78·7; H, 10·5. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%). The mother-liquors contained considerable amounts of lower-melting material, and in a different experiment the alcohol (from another hydrolysis) melted constantly at 262—264°. This preparation also crystallised in needles; a mixture of it with the product of higher m. p. melted intermediately.

The lower-melting modification was heated for an hour at 155—160° with *o*-phenylenediamine; the recovered material had m. p. 273—275° (needles from methanol) and gave no depression in m. p. when mixed with either the higher- or the lower-melting form.

Isolation of Compound, $C_{37}H_{50}O_4$, *and Methyl Ester, m. p.* 230°.—The acid fractions (B), which were obtained by the action of both cold and hot sodium hydroxide, were combined and acidified with hydrochloric acid, and the precipitated resinous acids (8·8 g.; 20—25% of total oxidation products) collected with ether. After treatment with diazomethane in ethereal solution and standing for 2 days, a crystalline product (0·6 g.), very sparingly soluble in ether, had separated. This was removed and treated with benzoyl chloride (1 c.c.) in pyridine (6 c.c.) on the steam-bath. The product, isolated in the usual manner, was a mixture, which was resolved by means of benzene–alcohol into (*a*) a small amount of a sparingly soluble * *compound* which formed small dull needles, m. p. 293—294°, and gave no coloration with tetranitromethane in chloroform (Found: C, 79·9; H, 9·25; OMe, nil. $C_{37}H_{50}O_4$ requires C, 79·5; H, 9·0%), and (*b*) a soluble *methyl* ester (main fraction), which separated from methyl alcohol containing a little acetone in heavy brittle cubes or prisms, m. p. 228—229°, $[\alpha]_D^{24°}$ + 16·7° (l = 1, c = 3·62) (Found: C, 74·4, 74·7; H, 7·8, 7·9; OMe, 5·0. $C_{45}H_{56}O_8$ requires C, 74·5; H, 7·8; OMe, 4·3%. $C_{38}H_{48}O_7$ requires C, 74·0; H, 7·85; OMe, 5·0%). The tetranitromethane reaction was negative.

The ethereal mother-liquor containing the non-crystalline esters was evaporated, and the residue benzoylated in pyridine solution. A solution of the product, isolated in the usual manner, in methyl alcohol first deposited some resinous matter, which was removed, and then slowly crystallised. The product (0·4 g.) was crystallised from methyl alcohol–ether and then from methyl alcohol and a little acetone, yielding glassy tablets of the above methyl ester, m. p. 229—230° (Found: C, 74·5, 74·4; H, 7·85, 7·85%).

β-*Amyranonyl Benzoate*.—β-Amyranonol [1·5 g., prepared by Spring's method (J., 1933, 1345)] was heated for 1 hour at 100° in pyridine (3 c.c.) and benzoyl chloride (2·5 c.c.). After standing over-night, the product was treated with methyl alcohol, and the precipitated *benzoate* recrystallised from acetone; it separated in brittle glassy rectangles, m. p. 260·5—261·5°, $[\alpha]_D^{22°}$ + 7·3° (l = 1, c = 2·21) (Found: C, 81·5; H, 10·0. $C_{37}H_{54}O_3$ requires C, 81·3; H, 10·0%).

β-*Amyrenonol*.—This compound was prepared by hydrolysis under reflux (*a*) of authentic β-amyrenonyl benzoate (5 hours with 10% benzene–alcoholic potash), and (*b*) of β-amyrenonyl acetate (7 hours with 5% benzene–alcoholic potash), which was obtained from product (A) as already described. All preparations crystallised from aqueous methanol or ethanol in hair-like needles, m. p. 233—234°, $[\alpha]_D^{18°}$ + 104° (l = 1, c = 4·14). On continued recrystallisation from aqueous methanol the m. p. fell to 212—214° after preliminary sintering, and was unchanged by further crystallisation; this low-melting modification formed soft needles. Treatment of β-amyrenonol (*ex* benzoate) with boiling acetic anhydride gave the acetate, m. p. 259—260°, $[\alpha]_D^{18°}$ + 101° (l = 1, c = 1·68).

Dehydro-β-amyrenol.—(a) The reduction of β-amyrenonol (1·25 g.) was carried out by the method of Beynon, Sharples, and Spring (*loc. cit.*). The crude reduction product was crystallised once from alcohol; it then had m. p. 195—205° (small prismatic needles), and gave a lemon-yellow coloration with tetranitromethane in chloroform. Without further purification, this material was refluxed with approximately its own weight of fused sodium acetate in acetic

* This is possibly a lactone which had previously been saponified by the treatment with hot alkali.

anhydride (9 parts) for 2½ hours. The crystalline product (m. p. 180—190°) which separated on cooling could not be purified by crystallisation from slightly aqueous acetic acid, but readily yielded dehydro-β-amyrenyl acetate, m. p. 216—217°, $[\alpha]_D^{18°}$ + 319° (l = 1, c = 1·88), on repeated crystallisation from benzene–alcohol (clusters of needles). The compound gave an intense brown coloration with tetranitromethane in chloroform (Found: C, 82·4; H, 10·8. Calc. for $C_{32}H_{50}O_2$: C, 82·3; H, 10·8%). Hydrolysis of the acetate with excess of boiling 0·1N-alcoholic potassium hydroxide for 3 hours gave *dehydro-β-amyrenol*, which separated from acetone in well-formed needles, m. p. 209—211° after sintering at 203° (Found: C, 84·9; H, 11·3. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%).

(b) In the course of the reduction of a larger quantity (6 g.) of β-amyrenonol, the sodium was added during 1¾ hours. The crude reduction product, after treatment with acetic anhydride–sodium acetate, furnished the dehydro-acetate (from benzene–alcohol) in inch-long, flattened needles, m. p. 221·5—223°, $[\alpha]_D^{24°}$ + 223°, + 222°, + 218° (l = 1, c = 1·68, 1·38, 1·13) (Found: C, 82·5; H, 11·0%). Hydrolysis of this preparation (4½ hours under reflux) with 0·5N-alcoholic potassium hydroxide gave a product which formed needles from acetone, m. p. 188—190°, clearing at 200°, and raised to 195—197° (clear at 208°) by recrystallisation. The melting point of this preparation was not appreciably changed after 5 hours' heating at 130°/0·1 mm. Reacetylation of the (not recrystallised) material gave a quantitative yield of the acetate, m. p. and mixed m. p. 222—223°.

Dehydro-β-amyrenyl Benzoate.—Dehydro-β-amyrenol [0·5 g., prepared by method (b) above] was heated for 1½ hours at 100° with pyridine (3 c.c.) and benzoyl chloride (0·5 c.c.). After standing over-night, the solvent was removed under reduced pressure, and the residue, after digestion with methyl alcohol, was crystallised from benzene–alcohol, *dehydro-β-amyrenyl benzoate* being obtained in large, heavy, shining laminæ, m. p. 238—239°, $[\alpha]_D^{22°}$ + 219° (l = 1, c = 2·21) (Found: C, 84·1; H, 10·3. $C_{37}H_{52}O_2$ requires C, 84·05; H, 9·9%).

β-Amyradienone.—Dehydro-β-amyrenol [method (b); 400 mg.] was dissolved in hot acetic acid (50 c.c.) and water (5 c.c.). The solution was cooled to 40—45° (a small amount of the solute crystallised), and treated during 50 minutes at this temperature with a solution of chromic anhydride (0·15 g.) in water (0·5 c.c.) and acetic acid (5·5 c.c.) with mechanical stirring. The suspension had cleared when roughly one-third of the reagent had been added, and was still susceptible to further rapid oxidation under the same conditions even when the addition was complete. After 20 minutes, methyl alcohol was added, the solvent removed under reduced pressure, and the residue treated with water and extracted with ether. Evaporation of the washed and dried extract (which contained no acidic material) gave a resin, which crystallised (m. p. 140—145°) from slightly diluted methanol. After several crystallisations, *β-amyradienone* separated in small prismatic needles, m. p. (constant) 170—171°, $[\alpha]_D^{22°}$ + 108° (l = 1, c = 1·20) (Found: C, 84·7; H, 11·3. $C_{30}H_{46}O$ requires C, 85·2; H, 11·0%). The compound gave an intense, deep yellow colour with tetranitromethane in chloroform, and the Liebermann–Burchard reagent produced an immediate, intense, purplish-crimson coloration. In another experiment, performed under strictly analogous conditions, the ketone (from 300 mg. of the alcohol) separated in needles, m. p. (constant) 176·5—178° (Found: C, 84·8; H, 11·3%).

The *oxime* of the ketone (m. p. 171°), prepared in the usual manner, separated from alcohol containing a little benzene in shining platelets or prismatic needles, m. p. 268·5—270° (efferv.) (Found: C, 81·8; H, 11·2; N, 3·2. $C_{30}H_{47}ON$ requires C, 82·3; H, 10·8; N, 3·2%).

Thio-compound, $C_{30}H_{44}OS$, *from Dehydro-β-amyrenol.*—300 Mg. of dehydro-β-amyrenyl benzoate were refluxed under nitrogen for 3½ hours with sulphur (150 mg.) in benzyl acetate (1 c.c.). The product was precipitated with methyl alcohol, and, without purification, hydrolysed under reflux in benzene (5 c.c.) with 10% alcoholic potassium hydroxide (10 c.c.) for 2 hours; the product was then isolated by ether extraction and crystallised once from methyl alcohol. Its identity with the thio-compound derived from β-amyrin was established by its conversion into the acetate, which formed needles, m. p. 196—197° (197—198° when mixed with an authentic specimen); by the hydrolysis of the acetate into the free alcohol, m. p. 198—199° alone and on admixture with authentic material; and finally by the preparation of the benzoate, m. p. and mixed m. p. 226—227°.

Attempted Dehydrogenation of β-Amyrenonyl and β-Amyranonyl Benzoates.—(a) β-Amyrenonyl benzoate (500 mg.) and sulphur (250 mg.) were refluxed in benzyl acetate (1·5 c.c.) for 4 hours under nitrogen. The product, isolated by the addition of methyl alcohol, was freed from sulphur and coloured impurities by hydrolysis with benzene–alcoholic potassium hydroxide (10%). The β-amyrenonol so formed was isolated by extraction with ether, and identified by the preparation of the acetate, m. p. 258—259° (260·5—261·5° when mixed with authentic β-amyr-

enonyl acetate), and of the benzoate, which crystallised in laminæ, m. p. 258·5—259·5°, from benzene–alcohol; this is presumably a polymorphic modification, for it gave no depression when mixed with authentic β-amyrenonyl benzoate (prismatic needles) of m. p. 263—264°.

(b) The procedure with β-amyranonyl benzoate (500 mg.), and the identification of the product, were carried out exactly as in (a). The benzoate had m. p. 260—261° alone and mixed with authentic β-amyranonyl benzoate, and the acetate melted at 300—302°. β-Amyranonyl acetate, prepared by Spring's method (*loc. cit.*), melted (after recrystallisation from benzene–alcohol) at 297—299° (sintering at 290°), and a mixture of the two samples at 299—301°. The oxidation product thus appears to contain a small amount of impurity which is removed by the treatment with sulphur.

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