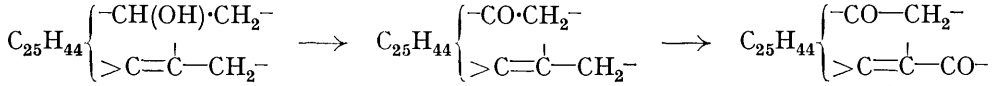
45. *The Resinols. Part IV. The Structure of α-Amyrenol.**

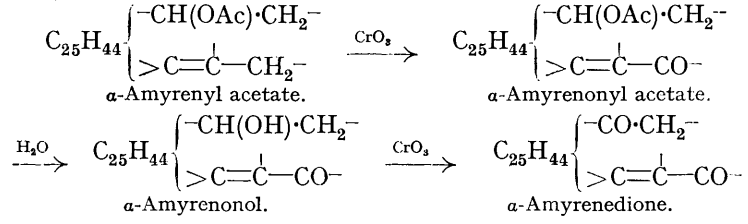
By F. S. Spring and T. Vickerstaff.

Oxidation of α-amyrenol or of α-amyrenone with chromic anhydride has been shown to give α-amyrenone oxide I, m. p. 193°, to which the formula $C_{30}H_{48}O_2$ has been ascribed. It is established that one of the oxygen atoms of α-amyrenone oxide I is present as a carbonyl group which originates in the secondary hydroxyl group of α-amyrenol (Spring and Vickerstaff, J., 1934, 650, 1859).

An analytical study of α-amyrenone oxide I and its allies has now established that its molecular formula is $C_{30}H_{46}O_2$ and not $C_{30}H_{48}O_2$: hence the formation of α-amyrenone oxide from α-amyrenone is consequent upon the oxidation of a methylene group in the α-position to the ethylenic linkage, to a carbonyl group; α-amyrenone oxide is therefore an α-amyrenedione and the oxidation of α-amyrenol proceeds according to the scheme:

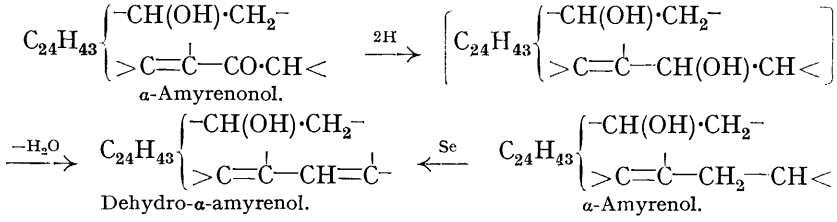


Similarly, α-amyrenol oxide (Spring and Vickerstaff, *loc., cit.*; Vesterberg, *Ber.*, 1891, **24**, 3836) has the molecular formula $C_{30}H_{48}O_2$ and not $C_{30}H_{50}O_2$. In addition to the secondary hydroxyl group of α-amyrenol, α-amyrenol oxide contains a carbonyl group introduced thus,



and is therefore to be designated α-amyrenonol. Dehydration of α-amyrenonol with phosphorus pentachloride gives a mixture of two unsaturated ketones, *α-amyradienones* I and II, a reaction which is paralleled by the dehydration of α-amyrenol to dextro-α-amyradiene and α-amyradiene (Vesterberg, *Ber.*, 1887, **20**, 1242; 1891, **24**, 3834).

The carbonyl group of α-amyrenonol is completely inactive towards the usual ketonic reagents; the presence of the group has been confirmed indirectly by reduction with sodium and amyl alcohol, whereby dehydro-α-amyrenol was obtained, identical with that prepared by Jacobs and Fleck (*J. Biol. Chem.*, 1930, **88**, 137) by the partial dehydrogenation of α-amyrenol with selenium; the formation of dehydro-α-amyrenol is represented by the scheme:

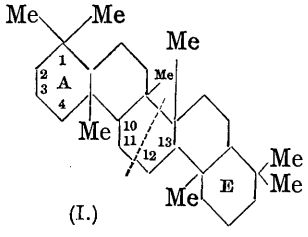


* In order to rationalise the nomenclature of the series, all derivatives of the amyrins will be referred to the unknown saturated hydrocarbons α- and β-amyranes; the naturally occurring monoethenoid alcohols will therefore be designated α- and β-amyrenols.

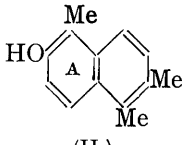
Final confirmation of the correctness of the molecular structure suggested for α-amyrenonol was obtained in the observation that it exhibits the typical ultra-violet absorption spectrum of an αβ-unsaturated ketone. The fact that both α-amyrenedione and α-amyrenonol fail to give colorations with tetranitromethane in chloroform (Spring and Vickerstaff, *loc. cit.*) is in harmony with previous experience of this reagent with αβ-unsaturated ketones (Werner, *Ber.*, 1909, **42**, 4324; Ostromisslensky, *J. pr. Chem.*, 1911, **84**, 489; Ruzicka, Huyser, Pfeiffer, and Seidel, *Annalen*, 1929, **471**, 21).

Hitherto there has been no satisfactory proof of the presence of an ethylenic linkage in α-amyrenol, the alcohol and its esters being completely resistant to catalytic hydrogenation. Again, whilst α-amyrenyl acetate is recovered unchanged after treatment with perbenzoic acid, we find that dehydro-α-amyrenyl acetate gives a monoxide, thus affording a proof that it contains one ethylenic linkage more than α-amyrenol. The recognition of α-amyrenonol as an αβ-unsaturated ketone affords a very necessary confirmation of the unsaturated nature of α-amyrenol, whilst the reduction of the ketone to dehydro-α-amyrenol defines this unsaturated centre as $>C=\overset{|}{C}-CH_2-CH<$.

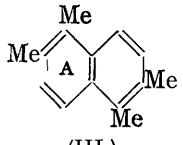
Dehydrogenation of α-amyrenol with selenium gives a mixture, from which 1 : 2 : 7-trimethylnaphthalene (sapotalin), 1 : 2 : 5 : 6-tetramethylnaphthalene, 1 : 5 : 6-trimethyl-β-naphthol (II), and the hydrocarbon $C_{25}H_{20}$ (?), m. p. 306°, have been isolated; each of these products has previously been obtained by the dehydrogenation of the mixed α- and β-amyrenols (Ruzicka and Huyser, *Annalen*, 1929, **471**, 35; Ruzicka, Silbermann, and Pieth, *Helv. Chim. Acta*, 1932, **15**, 1285). The hydrocarbon $C_{25}H_{20}$ (?) is a picene homologue (Ruzicka, Hosli, and Ehmann, *Helv. Chim. Acta*, 1934, **17**, 442; Ruzicka and Mörgeli, *ibid.*, 1936, **19**, 377; Bernal and Crowfoot, J., 1935, 93), the formation of which proves that α-amyrenol has the hydropicene structure of oleanolic acid and hederagenin. A satisfactory representation of the carbon skeleton of the pentacyclic triterpenes that give the hydrocarbon $C_{25}H_{20}$ (?) on dehydrogenation is (I) (Spring, *J. Soc. Chem. Ind.*, 1936, **55**, 1050).



(I.)



(II.)



(III.)

The structure of α-amyrenol is to be derived from (I) by the introduction of a secondary hydroxyl group and one ethenoid linkage. The isolation of the naphthol (II) from the dehydrogenation products of α-amyrenol locates the secondary hydroxyl group of the latter at C_2; preliminary retropinacolinic rearrangement of the hydroxylated ring A satisfactorily interprets the formation of 1 : 2 : 5 : 6-tetramethylnaphthalene (III) (Ruzicka, Hofmann, and Schellenberg, *Helv. Chim. Acta*, 1936, **19**, 1391). Since the ethenoid linkage of α-amyrenol is present in the system $>C=\overset{|}{C}-CH_2-\overset{|}{C}H-$, it must be located at either $C_{10} - C_{11}$ or $C_{12} - C_{13}$. This decision is dependent upon the assumption that dehydro-α-amyrenol contains the same carbon skeleton as α-amyrenol.

Experimental.

α-Amyrenonol.—A more efficient method for the preparation of α-amyrenonol is oxidation of α-amyrenyl benzoate, and hydrolysis of the resulting *α-amyrenonyl benzoate*. A suspension of α-amyrenyl benzoate (4 g.) in boiling acetic acid (50 c.c.) was treated with a solution of chromic anhydride (2 g.) in 85% acetic acid (10 c.c.), added during 1 hour. After boiling for 1 hour, the solution was cooled and the solid separating was repeatedly crystallised from benzene–alcohol, from which *α-amyrenonyl benzoate* separated in colourless laminæ, m. p. 266° (Table I, 3). The benzoate (13 g.) in benzene (35 c.c.) was added to 12% alcoholic potassium hydroxide (150 c.c.), and the mixture heated under reflux for 20 hours. After dilution with water the mixture was

extracted with benzene. The dry benzene extract was concentrated, and crystallisation effected by the addition of ligroin (b. p. 40—60°). Recrystallisation of this solid gave α-amyrenonol in stout needles, m. p. 208°, showing no depression on admixture with the material prepared by the method of Vesterberg (*loc. cit.*) (Table I, 1). *Light absorption in alcohol* :* maxima, (*a*) 2500 A., log ε = 4·08; (*b*) 3150 A., log ε = 1·7.

TABLE I.

	% C.*			% H.*		
	Found.	A.	B.	Found.	A.	B.
1. α-Amyrenonol	82·0	81·75	81·4	11·1	11·0	11·4
,,	82·2			11·1		
2. α-Amyrenonyl acetate	79·4	79·6	79·3	10·6	10·5	10·8
3. α-Amyrenonyl benzoate	81·5	81·6	81·3	9·4	9·6	10·0
4. α-Amyrenedione	82·5	82·1	81·75	10·4	10·6	11·0
5. α-Amyradienone I	85·2	85·2	84·8	11·15	11·0	11·4
6. α-Amyradienone II	85·3	85·2	84·8	11·1	11·0	11·4

* The theoretical values under A and B are calculated from the formulæ $C_{30}H_{48}O_2$ and $C_{30}H_{50}O_2$ respectively for α-amyrenonol.

α-Amyradienones I and II.—Finely powdered α-amyrenonol (10 g.) was added during 1 hour to a suspension of phosphorus pentachloride (6·4 g.) in ligroin (b. p. 40—60°; 60 c.c.), and after 3 hours the mixture was boiled under reflux for 30 minutes. The solution was washed with water and dried and the residue obtained after removal of the solvent was crystallised from alcohol, from which *α-amyradienone I* separated in needles, m. p. 197°, $[\alpha]_D^{20°}$ + 166° (l = 1, c = 0·042 in chloroform) (Table I, 5). The alcoholic mother-liquor from the dienone I on long standing deposited prisms containing a trace of chlorine which could not be removed by crystallisation. Removal of halogen was effected by warming with alcoholic sodium ethoxide and repeated crystallisation then gave *α-amyradienone II* in prisms, m. p. 156°, $[\alpha]_D^{20°}$ + 153° (l = 1, c = 0·088 in chloroform) (Table I, 6). If the amyrenonol is added in one portion to the phosphorus pentachloride suspension in ligroin, and the mixture kept overnight, α-amyradienone II is obtained as sole product.

Dehydro-α-amyrenol.—A solution of α-amyrenonol (5 g.) in boiling amyl alcohol (150 c.c.) was treated with sodium (10 g.), added as quickly as the reaction would permit. The mixture was boiled for 1 hour, cooled, and the amyl alcohol removed by distillation in steam. The separated solid was isolated by means of ether and repeatedly crystallised from benzene, from which dehydro-α-amyrenol separated in feathery needles, m. p. 160°. It was characterised by the preparation of its benzoate, m. p. 174° (Found: C, 83·9; H, 9·6. Calc. for $C_{37}H_{52}O_2$: C, 84·0; H, 9·9%), by oxidation to dehydro-α-amyrenone, m. p. 135—137° (Found: C, 85·1; H, 11·15. Calc. for $C_{30}H_{46}O$: C, 85·2; H, 11·0%), and by the preparation of the oxime of the latter, m. p. 236°. Jacobs and Fleck (*loc. cit.*) give m. p. 171—172° for dehydro-α-amyrenyl benzoate, m. p. 133—134° for dehydro-α-amyrenone, and m. p. 235° for the oxime of the ketone. The *acetate* was prepared by refluxing dehydro-α-amyrenol with acetic anhydride (50 c.c.) and potassium acetate (1 g.) for 1 hour. The solid separating from the cooled solution was recrystallised from acetic acid, from which the acetate separated in long needles, m. p. 170° (Found: C, 82·2; H, 10·9. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8%).

Dehydro-α-amyrenyl Acetate Oxide.—Dehydro-α-amyrenyl acetate (0·8 g.) was treated with a chloroform solution of perbenzoic acid (0·6 *N*; 25 c.c.) and set aside for 14 days. The chloroform solution was washed with aqueous sodium carbonate, dried (sodium sulphate), and the solvent removed; repeated crystallisation of the residue from methyl alcohol gave the *oxide* in needles, m. p. 192° (Found: C, 80·0; H, 10·6. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·5%).

Dehydrogenation of α-Amyrenol.—An intimate mixture of α-amyrenol (90 g.) and selenium (130 g.) was heated under an air-condenser by means of a bath of sodium nitrate–sodium nitrite. The first vigorous reaction having abated, the bath temperature was raised to and maintained at 350° for 40 hours. After cooling, the reaction mixture was extracted with ether (Soxhlet), the extract filtered, and the solvent removed. Distillation of the residual oil gave the following fractions: (*a*) 80—120°/7 mm., mobile yellow oil (1 g.); (*b*) 120—150°/5 mm., yellow oil (5 g.); (*c*) 150—210°/4 mm., brown viscous oil (4 g.); (*d*) 200—270°/1 mm., red resin (5 g.); (*e*) 300°/0·1 mm., red resin (7 g.). Fraction (*b*) was treated with an equal weight of picric acid in alcohol. The separated picrate mixture was washed with alcohol, and the hydrocarbon regenerated by solution in ether, followed by washing with dilute aqueous ammonia. Removal of the solvent

* The authors' thanks are due to Mr M. S. El. Ridi for these measurements.

from the dried ethereal solution gave the hydrocarbon mixture as a viscous yellow oil, which, on standing at 0° for 14 days, partly solidified. The crystalline hydrocarbon, m. p. 110°, was freed from oil by washing with light petroleum and treated with an equal weight of picric acid in alcohol. The picrate separated in red needles, which attained the constant m. p. 156° after repeated crystallisation (Ruzicka, Ehmann, and Mörgeli, *Helv. Chim. Acta*, 1933, **16**, 314, give m. p. 154—154·5° for the picrate of synthetic 1 : 2 : 5 : 6-tetramethylnaphthalene). One half of the oily hydrocarbon obtained by removal of the solvent from the light petroleum washings of tetramethylnaphthalene was treated with a solution of picric acid in alcohol. Recrystallisation of the picrate from alcohol gave 1 : 2 : 7-trimethylnaphthalene picrate in orange-red needles, m. p. 129·5—130° (Ruzicka and Ehmann, *Helv. Chim. Acta*, 1932, **15**, 140, give m. p. 129° for the picrate of synthetic 1 : 2 : 7-trimethylnaphthalene) (Found : C, 57·3; H, 4·5. Calc. for $C_{19}H_{17}O_7N_3$: C, 57·1; H, 4·3%). The remaining portion of the hydrocarbon was converted into its styphnate, which had the constant m. p. 156°(Ruzicka and Ehmann, *loc. cit.*, give m. p. 156° for the styphnate of synthetic 1 : 2 : 7-trimethylnaphthalene).

Fraction (*c*) was redistilled at 75°/10^{-3} mm., a yellow oil collecting in the receiver which partly solidified on cooling. After trituration with light petroleum, the solid was repeatedly crystallised from the same solvent, from which 1 : 5 : 6-trimethyl-β-naphthol separated in colourless needles, m. p. 155°, completely soluble in dilute potassium hydroxide solution to a blue fluorescing solution. For analysis the naphthol was sublimed, without, however, raising the m. p. (Found : C, 83·75; H, 7·8. Calc. for $C_{13}H_{14}O$: C, 83·8; H, 7·6%).

A solution of fraction (*e*) in boiling butyl alcohol was allowed to cool slowly, the amorphous yellow solid separating being collected and washed with the same solvent. Sublimation of this solid at 200—240°/10^{-3} mm., followed by repeated crystallisation of the sublimate from pyridine–butyl alcohol, gave trimethylpicene(?) in needles, m. p. 306° (Found : C, 93·7; H, 6·3. Calc. for $C_{25}H_{20}$: C, 93·7; H, 6·3%).

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