Triterpenoids. Part XLIII. The Constitution of Some Compounds obtained by the Dehydration of α-Amyrin and Related Alcohols.*

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The hydrocarbon, " *d*-α-amyradiene," obtained by the dehydration of α-amyrin (I) by using phosphorus pentachloride, is shown to be 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-diene (V), since it is obtained by Wolff–Kishner reduction of 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-dien-11-one (III) and when ozonised it gives acetone and the ketone (IV). The 3(4) : 12-diene (V) is isomerised by trichloroacetic acid to the 3(5) : 12-diene (V*a*), also obtained by Wolff–Kishner reduction of the αβ-unsaturated ketone (VI). The oxo-diene, " α-amyradienone-III," obtained by dehydration of 11-oxours-12-en-3β-ol (II) with hydriodic acid is 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X). Dehydration of ursa-9(11) : 12-dien-3β-ol (XIII) with phosphorus pentachloride gives a hydrocarbon, " *d*-α-amyratriene," identified as 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 9(11) : 12-triene (XIV). 5 : 8 : 14-Trimethylnovursa-1(10) : 9(11) : 12-triene (XV) is obtained from 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X) by treatment with lithium aluminium hydride. An isomeric triene, " *l*-α-amyratriene," previously obtained by dehydration of the alcohol (XIII) with phosphoric oxide, is also obtained from the triene (XV) by the action of mineral acid and is considered to be 5 : 8 : 14-trimethylnovursa-9(10) : 11 : 13(18)-triene (XVI).

THE experiments described in this and the following paper were designed to determine the constitution of a number of products obtained by the dehydration of α-amyrin (I) and related compounds. Dehydration of 3β-hydroxyurs-12-en-11-one (II) with phosphorus

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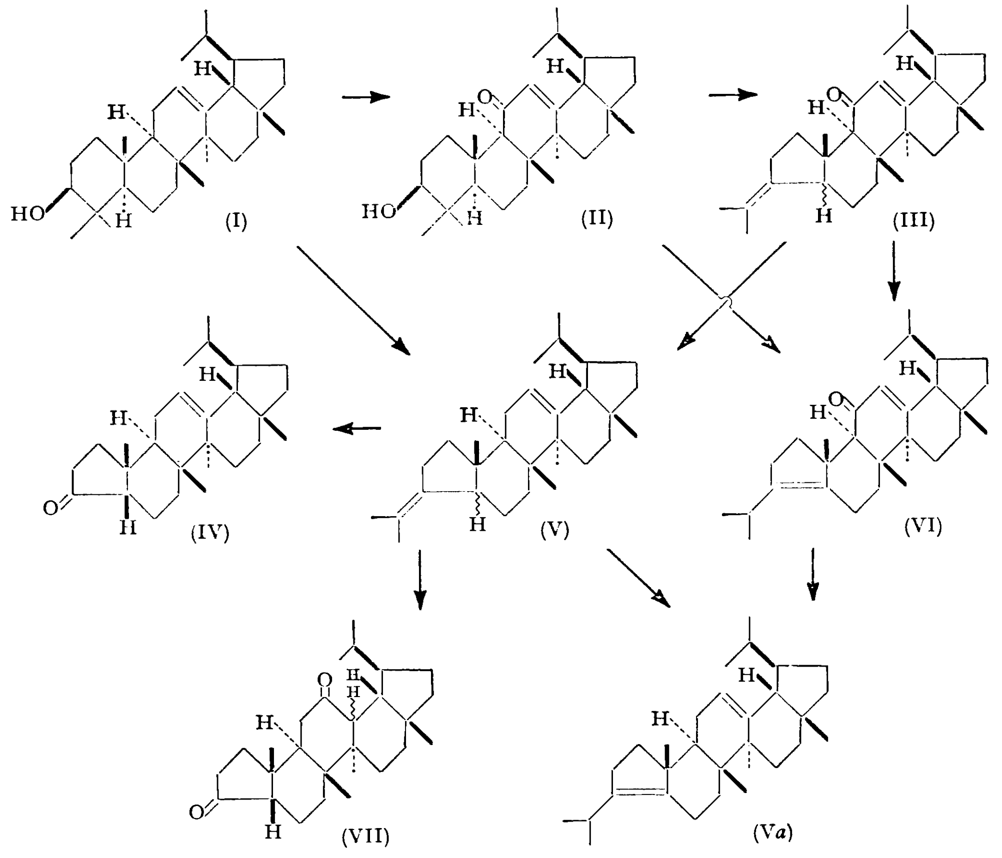
* Part XLII, *J.*, 1955, 3126.

pentachloride gives a mixture of two oxo-dienes (Spring and Vickerstaff, *J.*, 1937, 249), identified as 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-dien-11-one (" α-amyradienone-I ") (III) and 8 : 10 : 14-trimethylnovursa-3(5) : 12-dien-11-one (" α-amyradienone-II ") (VI) [*] (Ruzicka, Jeger, and Volli, *Helv. Chim. Acta*, 1945, **28**, 767, 1628). Ruzicka *et al.* (*loc. cit.*) showed that when the oxo-diene (III) is shaken with hydrogen and a palladium catalyst, it is converted into the isomer (VI); we find that the same isomerisation is brought about by treatment of (III) with hydrochloric–acetic acid. Many examples of similar ring A contractions accompanying ionic-type dehydrations of 3β-hydroxy-triterpenoids have since been described (for references, see Jeger, " Fortschritte der Chemie organischen Naturstoffe," Springer-Verlag, 1950, Vol. VII, p. 1).



Dehydration of α-amyrin (I) with phosphorus pentachloride yields " *d*-α-amyradiene " (Vesterberg and Westerlind, *Annalen*, 1922, **428**, 250), which does not show selective

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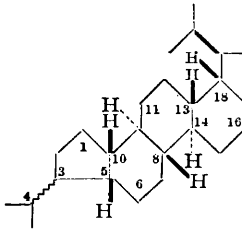
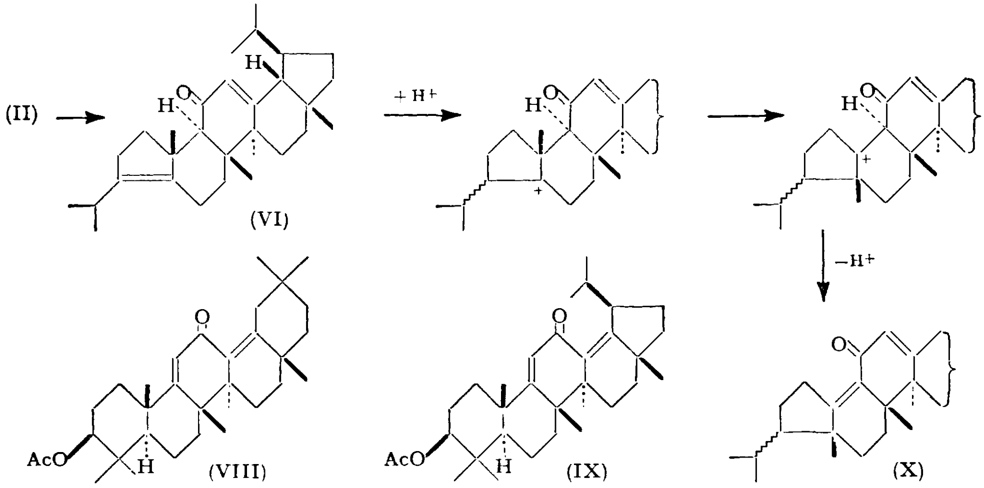
[*] As a basis for a more systematic nomenclature of the dehydration products described in this and the following paper, the hydrocarbon, $C_{27}H_{46}$, having the constitution and stereochemistry represented by (*A*) is called novursane.



(*A*)

absorption of high intensity above 2200 Å (Ewen, Gillam, and Spring, *J.*, 1944, 28). This hydrocarbon has now been identified as 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-diene (V). This identification is supported by the following facts. First, the diene (V) is obtained from 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-dien-11-one (III) by Wolff–Kishner reduction. Again, when treated with ozone it gives acetone, a compound, $C_{27}H_{42}O$, and a very small quantity of a compound $C_{27}H_{42}O_2$. The infrared absorption spectrum of the compound $C_{27}H_{42}O$ includes a strong band at 1740 cm.$^{-1}$ (in CCl_4) and consequently it contains a ketone group in a 5-membered ring. This ketone is therefore (IV) and in agreement with this formulation it gives a yellow colour with tetranitromethane and is recovered unchanged after treatment with alkali, thus proving that rings A and B are fused in the more stable form. The change in $[M_D]$ (+450°) accompanying the conversion of α-amyrin (I) into the ketone (IV) is in excellent agreement with the values observed for comparable reactions (Klyne, *J.*, 1952, 2916); this proves that rings A and B in (IV) are *cis*-β-fused. The second oxidation product, $C_{27}H_{42}O_2$, which does not give a colour with tetranitromethane, is considered to be the diketone (VII). Treatment of the diene (V) with trichloroacetic acid in chloroform gives the isomeric 8 : 10 : 14-trimethylnovursa-3(5) : 12-diene (V*a*), the structure of which follows from its formation by Wolff–Kishner reduction of 8 : 10 : 14-trimethylnovursa-3(5) : 12-dien-11-one (VI).

Dehydration of 3β-hydroxyurs-12-en-11-one (II) with hydriodic–acetic acid gives a third dienone, " α-amyradienone-III " (Ewen *et al.*, *loc cit.*) which, we find, can also be obtained by treatment of 8 : 10 : 14-trimethylnovursa-3(5) : 12-dien-11-one (IV) with hydriodic–acetic acid. The ultraviolet absorption spectrum of " α-amyradienone-III " shows maxima at 2040, 2580, and 2900 Å (ε 9900, 11,000, and 10,200) and in this respect closely resembles that of 12-oxo-oleana-9(11) : 13(18)-dien-3β-yl acetate (VIII) (Beaton, Johnston, McKean, and Spring, *J.*, 1953, 3660) and 12-oxoursa-9(11) : 13(18)-dien-3β-yl acetate (IX) (Beaton, Shaw, Spring, Stevenson, Strachan, and Stewart, *J.*, 1955, 2606), the characteristic absorption spectra of which have been related to the geometry of the ·C:C·CO·C:C chromophore. It follows that " α-amyradienone-III " contains a similarly constrained chromophore and that it is 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X); its formation from 8 : 10 : 14-trimethylnovursa-3(5)-12-dien-11-one (VI) is represented in the annexed formulæ :



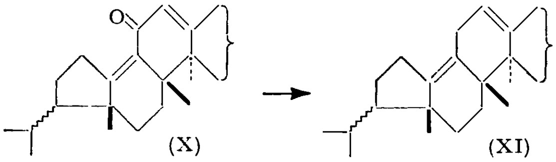
(VI)

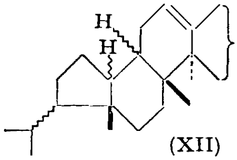
(VIII)

(IX)

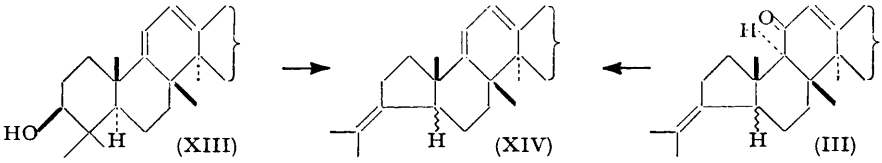
(X)

Reduction of 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X) either by the Wolff–Kishner method or by prolonged refluxing with lithium aluminium hydride in ether gives a non-conjugated diene, 5 : 8 : 14-trimethylnovursa-9(10) : 12-diene (XI) which shows strong ethylenic absorption in the region 2100—2200 Å and gives a strong positive reaction with tetranitromethane. This behaviour of the 11-oxo-9(10) : 12-diene (X) is similar to that of the oxo-diene (VIII). In one respect, however, the behaviour of 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X) differs from that of 12-oxo-oleana-9(11) : 13(18)-dien-3β-yl acetate and of 12-oxoursa-9(11) : 13(18)-dien-3β-yl acetate (IX). Catalytic hydrogenolysis of each of the last two compounds gives the corresponding non-conjugated diene, whereas similar treatment of the oxo-diene (X) results in the absorption of 3 mols. of hydrogen and the formation of a monoethylenic hydrocarbon, the optical properties of which suggest that it may be 5 : 8 : 14-trimethyl-9ξ : 10ξ-novurs-12-ene (XII).


(X) (XI)


(XII)

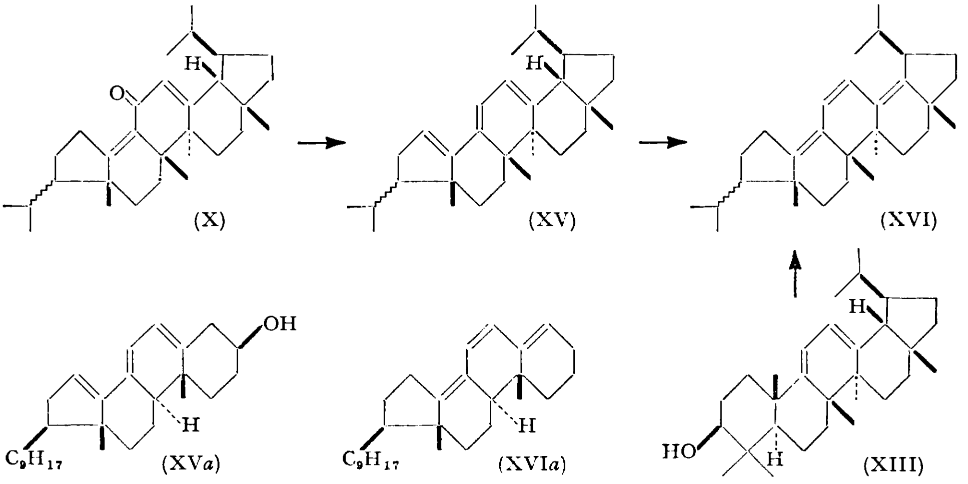
Treatment of 5 : 8 : 14-trimethylnovursa-9(10) : 12-diene (XI) with hydrochloric–acetic acid gives the conjugated " *l*-α-amyradiene " previously obtained by treatment of α-amyrin with phosphoric oxide (Vesterberg, *Ber.*, 1891, **24**, 3835; Ewen *et al.*, *loc. cit.*) and the constitution of this is discussed in the following paper. " *l*-α-Amyradiene " is also obtained from 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-diene (V) by treatment with boron trifluoride–acetic acid.


(XIII) (XIV) (III)

Dehydration of ursa-9(11) : 12-dien-3β-ol (XIII) with phosphorus pentachloride gives a dichloro-α-amyradiene, which with zinc yields " *d*-α-amyratriene "; the ultraviolet absorption spectrum of this shows that the double bond introduced by the dehydration is remote from the conjugated system in ring C (Ewen *et al.*, *loc. cit.*). In our hands, treatment of the dienol (XIII) with phosphorus pentachloride gives " *d*-α-amyratriene " directly, without the intervention of the dichloro-derivative. Although a reason for this different experience was not sought because it was not of direct significance to our study, minor changes in time of reaction and proportion of the pentachloride used are probably responsible. The constitution of " *d*-α-amyratriene" as 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 9(11) : 12-triene (XIV) has now been established since it is formed from 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-dien-11-one (III) by reduction with lithium aluminium hydride followed by treatment of the reaction product with phosphorus oxychloride in pyridine. The dichloro-compound obtained by Ewen *et al.* is consequently the 3 : 4-dichloride of (XIV).

Treatment of 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X) with lithium aluminium hydride in ether at 0° (and avoiding the use of mineral acid in the isolation procedure) gives a strongly lævorotatory triene ($[\alpha]_D$ −358°) which exhibits an absorption maximum at 3200 Å (ε 15,000). Its method of preparation and the position of its absorption maximum lead us to suggest that this hydrocarbon is 5 : 8 : 14-trimethylnovursa-1(10) : 9(11) : 12-triene (XV). The optical properties of the hydrocarbon are very similar to those of the similarly constituted ergosta-5 : 7 : 14 : 22-tetraen-3β-yl acetate (XV*a*) ($[\alpha]_D$ −322°, $\lambda_{max.}$ 3190 Å, ε 15,000) (Barton and Bruun, *J.*, 1951, 2728). When treated with hydrochloric–acetic acid, 5 : 8 : 14-trimethylnovursa-1(10) : 9(11) : 12-triene (XV) yields " *l*-α-amyratriene," previously obtained by dehydration of ursa-9(11) : 12-dien-3β-ol (XIII) by phosphoric oxide (Ewen *et al.*, *loc. cit.*). " *l*-α-Amyratriene " is strongly lævorotatory and exhibits a triple-maxima absorption spectrum, the principal band in which is at 2950 Å (ε 35,000). These properties are best explained if " *l*-α-amyratriene " is 5 : 8 : 14-trimethylnovursa-9(10) : 11 : 13(18)-triene (XVI) (cf. Beton and Halsall, *Chem.*

and Ind., 1954, 1560). Ergosta-4 : 6 : 8(14) : 22-tetraene (XVI*a*), which contains a chromophore comparable with that in (XVI), has similar absorption ($\lambda_{max.}$ 2830 Å, ε 33,000) (Fieser, Rosen, and Fieser, *J. Amer. Chem. Soc.*, 1952, **74**, 5397). The calculated value



(2940 Å) for the location of the absorption maximum of the triene (XVI), on the basis of Woodward's empirical rules, is in excellent agreement with the observed value.

EXPERIMENTAL

Rotations were measured in $CHCl_3$ and ultraviolet absorption spectra in EtOH solutions. Grade II alumina and light petroleum, b. p. 60—80°, were used for chromatography.

8 : 10 : 14-Trimethyl-5ξ-novursa-3(4) : 12-dien-11-one (" α-amyradienone-I ") was prepared by the action of phosphorus pentachloride on 3β-hydroxyurs-12-en-11-one (II). Crystallisation from chloroform–methanol gave the oxo-diene (yield, 60%) as needles, m. p. 197—199°, $[\alpha]_D$ +167° (*c*, 2·9). Spring and Vickerstaff (*loc. cit.*) give m. p. 197°, $[\alpha]_D$ +166°, and Ruzicka, Jeger, and Volli (*loc. cit.*) give m. p. 199—200° (high vacuum), $[\alpha]_D$ +167°.

8 : 10 : 14-*Trimethylnovursa*-3(5) : 12-*dien*-11-*one* (" α-*Amyradienone*-II ") (VI).—(*a*) The chloroform–methanol mother-liquors from the 11-oxo-3(4) : 12-diene were evaporated, and the residue dissolved in light petroleum and chomatographed on alumina. Elution with light petroleum–benzene (3 : 1) gave a fraction which crystallised from methanol to yield 8 : 10 : 14-trimethylnovursa-3(5) : 12-dien-11-one (10%) as needles, m. p. 155—156°, $[\alpha]_D$ +147° (*c*, 0·8). Spring and Vickerstaff (*loc. cit.*) give m. p. 156°, $[\alpha]_D$ +153°, and Ruzicka, Jeger, and Volli (*loc. cit.*) give m. p. 154—155°, $[\alpha]_D$ +149° for " α-amyradienone-II."

(*b*) A solution of 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-dien-11-one (III) (0·5 g.) in acetic acid (50 c.c.) containing concentrated hydrochloric acid (5 c.c.) was refluxed for 16 hr., with addition of concentrated hydrochloric acid (2 c.c.) every 4 hr. The product was isolated in the usual way and crystallised from methanol, to give the 11-oxo-3(5) : 12-diene (0·3 g.) as prismatic needles, m. p. 153—154° (no depression), $[\alpha]_D$ +149° (*c*, 1·7), $\lambda_{max.}$ 2520 Å (ε 13,000).

Wolff–Kishner Reduction of 8 : 10 : 14-*Trimethyl*-5ξ-*novursa*-3(4) : 12-*dien*-11-*one* (III).—A mixture of the oxo-diene (III) (800 mg.), sodium methoxide (from 1 g. of sodium) in methanol (15 c.c.) and 100% hydrazine hydrate (5 c.c.) was kept at 200° (autoclave) for 15 hr. The product was isolated in the usual way, dissolved in light petroleum (100 c.c.), and chromatographed on alumina. The fraction eluted by light petroleum (200 c.c.) crystallised from methanol, to yield 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-diene (V) (310 mg.) as prisms, m. p. 134—135°, $[\alpha]_D$ +109° (*c*, 1·3), undepressed in m. p. when mixed with a sample of " *d*-α-amyradiene," m. p. 133—135°, $[\alpha]_D$ +110°, prepared by the method of Vesterberg and Westerlind (*loc. cit.*).

Ozonolysis of 8 : 10 : 14-*Trimethyl*-5ξ-*novursa*-3(4) : 12-*diene* (V).—A solution of the diene (V) (1·0 g.) in chloroform (200 c.c.) was treated at −35° with ozone (2 mols.). After attaining room temperature the mixture was stirred with zinc dust (3 g.) and acetic acid (50 c.c.) for 1 hr.

The filtered solution was washed with water (5 × 250 c.c.; see below), the chloroform evaporated, and the residue triturated with methanol whereupon it crystallised. Two recrystallisations from methanol yielded a mixture (350 mg.), a solution of which in light petroleum was chromatographed on alumina. Light petroleum eluted a fraction (250 mg.; m. p. 146—147°, $[\alpha]_D$ +205°) which was thrice crystallised from methanol, to give the *ketone* (IV), as needles, m. p. 146—148°, $[\alpha]_D$ +210° (Found : C, 84·9; H, 11·1. $C_{27}H_{42}O$ requires C, 84·75; H, 11·1%). The ketone was recovered unchanged, m. p. 145—147° (no depression), $[\alpha]_D$ +201° (*c*, 0·5), after 2½ hours' refluxing with 5% ethanolic potassium hydroxide. The fraction eluted from the column with light petroleum–benzene (2 : 1) crystallised from methanol, to give the *diketone* (VII), as plates, m. p. 204—206°, $[\alpha]_D$ +184° (Found : C, 81·8; H, 10·6. $C_{27}H_{42}O_2$ requires C, 81·35; H, 10·6%).

The water washings (above) were adjusted to pH 7 and distilled. The first fraction (200 c.c.) was treated with 2 : 4-dinitrophenylhydrazine hydrochloride solution, to give acetone 2 : 4-dinitrophenylhydrazone (25 mg.), m. p. and mixed m. p. 121—124°.

8 : 10 : 14-*Trimethylnovursa*-3(5) : 12-*diene* (V*a*).—(*a*) A solution of 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-diene (V) (700 mg.) in chloroform (7 c.c.) containing trichloroacetic acid (700 mg.) was kept at room temperature for 1 hr. The chloroform was removed and the product crystallised from acetone, to yield 8 : 10 : 14-*trimethylnovursa*-3(5) : 12-*diene* as hexagonal prisms (200 mg.), m. p. 70—72°, $[\alpha]_D$ +123° (*c*, 1·4), ε at 2080 Å = 4500 (Found : C, 87·8; H, 11·9. $C_{30}H_{48}$ requires C, 88·2; H, 11·8%).

(*b*) A mixture of 8 : 10 : 14-trimethylnovursa-3(5) : 12-dien-11-one (VI) (1 g.), sodium methoxide (from 1 g. of sodium) in methanol (15 c.c.), and 100% hydrazine hydrate (5 c.c.) was kept at 200° (autoclave) for 15 hr. The product was isolated in the usual way, dissolved in light petroleum (50 c.c.), and chromatographed on alumina. The fraction eluted by petroleum (200 c.c.) was crystallised from acetone, to yield 8 : 10 : 14-trimethylnovursa-3(5) : 12-diene as prisms (200 mg.), m. p. 68—69° (no depression), $[\alpha]_D$ +120° (*c*, 2·1).

5 : 8 : 14-*Trimethylnovursa*-9(10) : 12-*dien*-11-*one* (α-*Amyradienone*-III) (X).—(*a*) Treatment of 3β-hydroxyurs-12-en-11-one (II) with hydriodic acid in acetic acid as described by Ewen *et al.* (*loc. cit.*) gave 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X) as large laminæ (from methanol), m. p. 170—171°, $[\alpha]_D$ +171° (*c*, 3·3), $\lambda_{max.}$ 2040, 2580, and 2900 Å (ε 9900, 11,000, and 10,200). It gives a yellow colour with tetranitromethane. Ewen *et al.* (*loc. cit.*) give m. p. 169°, $[\alpha]_D$ +170°. Similar treatment of 11-oxours-12-en-3β-yl acetate or benzoate gave the oxo-diene (X) in approximately the same yield.

(*b*) Hydriodic acid (*d*, 1·7; 5 c.c.) was added to a solution of 8 : 10 : 14-trimethylnovursa-3(5) : 12-dien-11-one (VI) (2 g.) in glacial acetic acid (10 c.c.) and the mixture refluxed for 8 hr. The product was isolated in the usual way and crystallised from methanol, to yield 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one as laminæ (1·2 g.), m. p. 170—172° (no depression), $[\alpha]_D$ +172° (*c*, 2·1).

5 : 8 : 14-*Trimethylnovursa*-9(10) : 12-*diene* (XI).—(*a*) A solution of 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X) (1·0 g.) in ether (500 c.c.) was refluxed with lithium aluminium hydride (1 g.) for 7 hr. After 16 hr. at room temperature, the mixture was worked up in the usual way and the product crystallised from acetone–methanol, to give 5 : 8 : 14-*trimethylnovursa*-9(10) : 12-*diene* (XI) (560 mg.) as plates m. p. 98—99°, $[\alpha]_D$ +120° (*c*, 2·8), ε at 2080 Å = 13,200 (Found : C, 87·95; H, 11·9. $C_{30}H_{48}$ requires C, 88·2; H, 11·8%). It gives an orange colour with tetranitromethane.

(*b*) A mixture of 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X) (1·0 g.), sodium methoxide (from 1 g. of sodium) in methanol (15 c.c.), and 100% hydrazine hydrate (5 c.c.) was kept at 200° (autoclave) for 15 hr. The product crystallised from methanol, to yield 5 : 8 : 14-trimethylnovursa-9(10) : 12-diene (XI) (250 mg.) as plates, m. p. 94—96° (no depression), $[\alpha]_D$ +118° (*c*, 0·9), ε at 2080 Å = 12,000.

Catalytic Hydrogenation of 5 : 8 : 14-*Trimethylnovursa*-9 : 12-*dien*-11-*one* (X).—A solution of the oxo-diene (X) (600 mg.) in glacial acetic acid (100 c.c.) was shaken with platinum (from 250 mg. of PtO_2) and hydrogen for 24 hr. The product was isolated in the usual manner and crystallised from acetone–methanol, to give 5 : 8 : 14-*trimethyl*-9ξ : 10ξ-*novurs*-12-*ene* (XII) (350 mg.) as plates, m. p. 95—96°, $[\alpha]_D$ +140° (*c*, 1·4), ε at 2060 Å = 2750 (Found : C, 87·7; H, 12·3. $C_{30}H_{50}$ requires C, 87·8; H, 12·2%). It gives a yellow colour with tetranitromethane; a mixture with (XI) had m. p. 65—73°.

Treatment of 5 : 8 : 14-*Trimethylnovursa*-9(10) : 12-*diene* (XI) *with Hydrochloric Acid.*—A solution of the 9(10) : 12-diene (150 mg.) in chloroform (5 c.c.) and acetic acid (50 c.c.) containing concentrated hydrochloric acid (10 c.c.) was refluxed for 16 hr. with the addition of concentrated hydrochloric acid (2 c.c.) every 2 hr. The product was isolated in the usual way and crystallised from chloroform–methanol, to give " *l*-α-amyradiene " (50 mg.) as plates, m. p. 193—194° (no depression), $[\alpha]_D$ −110° (*c*, 1·9), $\lambda_{max.}$ 2360, 2410, and 2500 Å (ϵ 13,200, 14,500, and 8550).

Treatment of 8 : 10 : 14-*Trimethyl*-5ξ-*novursa*-3(4) : 12-*diene* (V) *with Boron Trifluoride.*—A solution of the 3(4) : 12-diene (V) (250 mg.) in glacial acetic acid (100 c.c.) and boron trifluoride–acetic acid (3 c.c.) was refluxed for 80 hr. The product was isolated through ether and crystallised from chloroform–methanol, to give " *l*-α-amyradiene " as plates (130 mg.), m. p. 193—194° (no depression), $[\alpha]_D$ −104° (*c*, 1·5), $\lambda_{max.}$ 2360, 2410, and 2500 Å (ϵ 13,000, 14,500, and 8500).

8 : 10 : 14-*Trimethyl*-5ξ-*novursa*-3(4) : 9(11) : 12-*triene* (" d-α-*Amyratriene* ") (XIV).—(*a*) A solution of 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-dien-11-one (III) (500 mg.) in ether (200 c.c.) was refluxed with lithium aluminium hydride (500 mg.) for 3 hr. A solution of the product (isolated in the usual way) in pyridine (50 c.c.) was refluxed for 15 hr. with phosphorus oxychloride (20 c.c.). The product crystallised from methanol, from which 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 9(11) : 12-triene separated as needles (200 mg.), m. p. 132—133°, $[\alpha]_D$ +445° (*c*, 2·1). Ewen *et al.* (*loc. cit.*) give m. p. 131—133°, $[\alpha]_D$ +439°.

(*b*) A solution of ursa-9(11) : 12-dien-3β-ol (3·0 g.) in light petroleum (b. p. 60—80°; 80 c.c.) was shaken with phosphorus pentachloride (1·47 g.) for 1½ hr. After refluxing for 2 min., the mixture was treated with water and the product isolated in the usual way. Crystallisation from methanol–chloroform gave 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 9(11) : 12-triene as needles, m. p. 132—134° (no depression), $[\alpha]_D$ +439° (*c*, 0·9), $\lambda_{max.}$ 2780 Å (ϵ 9500) (Found : C, 88·4; H, 11·5. Calc. for $C_{30}H_{46}$: C, 88·6; H, 11·4%)

5 : 8 : 14-*Trimethylnovursa*-1(10) : 9(11) : 12-*triene* (XV).—A solution of 5 : 8 : 14-trimethylnovursa-9(10) : 12-dien-11-one (X) in dry ether (200 c.c.) was treated with lithium aluminium hydride at 0° and kept at this temperature for 72 hr. The product was isolated, the use of mineral acid being avoided, and crystallised from methanol, to yield 5 : 8 : 14-*trimethylnovursa*-1(10) : 9(11) : 12-*triene* (300 mg.) as needles, m. p. 145—146°, $[\alpha]_D$ −358° (*c*, 1·6), $\lambda_{max.}$ 3200 Å (ϵ 15,000) (Found : C, 88·8; H, 11·4%).

5 : 8 : 14-*Trimethylnovursa*-9(10) : 11 : 13(18)-*triene* (" l-α-*Amyratriene* ") (XVI).—A solution of the 1(10) : 9(11) : 12-triene (XV) (80 mg.) in acetic acid containing concentrated hydrochloric acid (2 c.c.) was heated at 100° for 2 hr. and then kept at room temperature for 48 hr. The mixture was again heated on the steam-bath for 3 hr. and the product isolated in the usual way. Crystallisation from methanol yielded 5 : 8 : 14-trimethylnovursa-9(10) : 11 : 13(18)-triene (50 mg.) as needles, m. p. 140—142°, $[\alpha]_D$ −450° (*c*, 0·5), $\lambda_{max.}$ 2860 (shoulder) 2950, and 3080 (shoulder) Å (ϵ 28,200, 33,800, and 24,500). A specimen perpared as described by Ewen *et al.* (*loc. cit.*) had m. p. and mixed m. p. 140—142°, $[\alpha]_D$ −455° (*c*, 3·1), $\lambda_{max.}$ 2860 (shoulder), 2950, and 3080 (shoulder) Å (ϵ 30,200, 35,500, and 25,500).

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