90. *Triterpenoids. Part XLVII.* The Constitution of Some Compounds Obtained by the Dehydration of β-Amyrin and Related Alcohols: Further Observations on the Stereochemistry of α-Amyrin.*

By G. G. Allan, M. B. E. Fayez, F. S. Spring, and Robert Stevenson.

Experiments are described which establish the steric identity of all the ring junctions in the ursane and the oleanane group of pentacyclic triterpenoids.

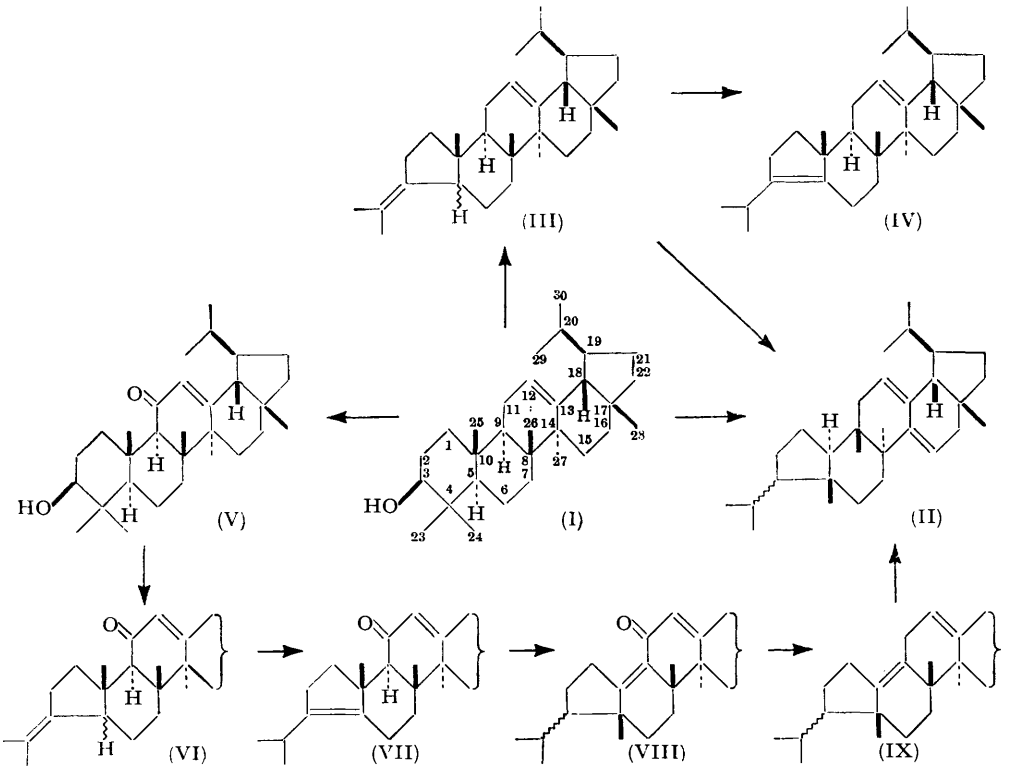
The hydrocarbon "*l*-α-amyradiene," which is obtained in high yield by treatment of α-amyrin (I) in benzene with phosphoric oxide at room temperature, has been identified as 5 : 8α : 9β-trimethyl-10α-novursa-12 : 14-diene (II). This reaction involves contraction of ring A and migration of three axial methyl groups and one axial hydrogen atom, and is considered to be fully synchronous (Fayez, Grigor, Spring, and Stevenson, *J.*, 1955, 3378). In contrast, the same treatment of β-amyrin gives an oil, the ultraviolet absorption of which has an ill-defined single maximum (2420—2500 Å) of low intensity, whereas the crystalline "*l*-diene" (II) derived from α-amyrin has a spectrum with three intense, well-defined maxima, the principal band of which is at 2400 Å. The "*l*-diene" (II) is also obtained by treatment of α-amyrin (or its acetate) with hydriodic–acetic acid, but similar treatment of β-amyrin gives an oil, the ultraviolet absorption of which shows that it does not contain an appreciable amount of a conjugated diene.

During the investigation which led to the elucidation of the structure of the "*l*-diene" (II), it was shown that 8 : 10 : 14-trimethyl-11-oxonovursa-3(5) : 12-diene (VII) [obtained from 11-oxours-12-en-3β-ol (V) *via* the isomeric 11-oxo-3(4) : 12-diene (VI)] is isomerised to 5 : 8 : 14-trimethyl-11-oxonovursa-9(10) : 12-diene (VIII) by hydriodic–acetic acid. The oxo-diene (VIII) is reduced by lithium aluminium hydride to the non-conjugated 5 : 8 : 14-trimethylnovursa-9(10) : 12-diene (IX) which with hydrochloric–acetic acid gives the conjugated diene (II). The last reaction, described by Allan, Spring, Stevenson, and Strachan (*J.*, 1955, 3371), is the most remarkable stage in the series of reactions included in the conversion of α-amyrin into the "*l*-diene" (II), remarkable in that conjugation does not occur by the most direct route, but only as a consequence of the movement of two axial methyl groups. It emerges from the discussion below that this is the critical stage in the conversion of α-amyrin into a conjugated 12 : 14-diene.

Allan *et al.* (*loc. cit.*) showed that dehydration of α-amyrin by phosphorus pentachloride gives 8 : 10 : 14-trimethyl-5ξ-novursa-3(4) : 12-diene (III) which is isomerised to the 3(5) : 12-diene (IV) by treatment with trichloroacetic acid. It was also found that treatment of the diene (III) with boron trifluoride–acetic acid yields the conjugated diene (II).

* Part XLVI, following note.

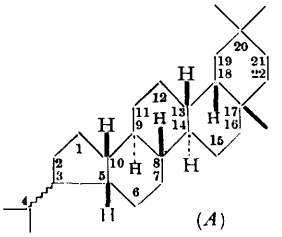
Short treatment of β-amyrin (X) with phosphorus pentachloride gives "β-amyrilene-I" (Vesterberg, *Ber.*, 1887, **20**, 1242; 1890, **23**, 2189; Ruzicka, Silbermann, and Furter, *Helv. Chim. Acta*, 1932, **15**, 482; Winterstein and Stein, *Annalen*, 1933, **502**, 223) which, as we expected, is 8 : 10 : 14-trimethyl-5ξ-novoleana-3(4) : 12-diene (XI),* since on ozonolysis



it yields acetone and a ketone, $C_{27}H_{42}O$ (XII). As in the case of its novursane analogue, a consideration of molecular-rotation relations shows that rings A and B in the ketone (XII) are *cis*-β-fused. Treatment of the 3(4) : 12-diene (XI) with trichloroacetic acid (or prolonged treatment of β-amyrin with phosphorus pentachloride) yields an isomer "β-amyrilene-III" (Dieterle, Brass, and Schaal, *Arch. Pharm.*, 1937, **275**, 557). A comparison of the specific rotations (Table 1) supports the view that this isomer is 8 : 10 : 14-trimethylnovoleana-3(5) : 12-diene (XIII). This comparison also shows that the 12 : 13-double bond does not move during the conversion of β-amyrin into the two dienes (XI) and (XIII).

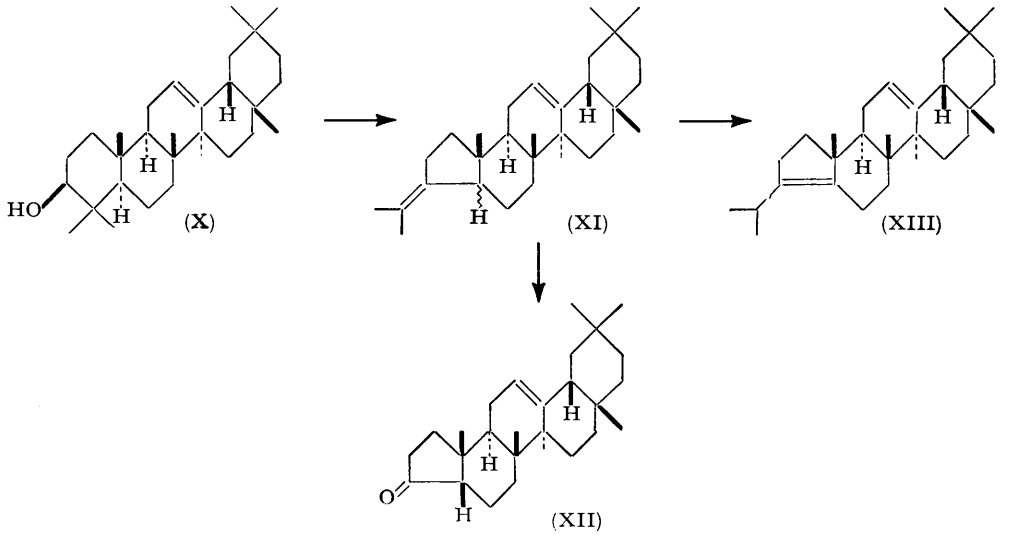
An important difference in behaviour of the 3(4) : 12-dienes derived from α- and β-amyrin is to be noted. Whereas the novursadiene (III) gives the conjugated diene (II) when

* Following the system adopted for naming ring-A contracted derivatives of ursane (Allan *et al.*, *loc. cit.*), the hydrocarbon $C_{27}H_{46}$ having the constitution and stereochemistry represented by (*A*) is called novoleanane.

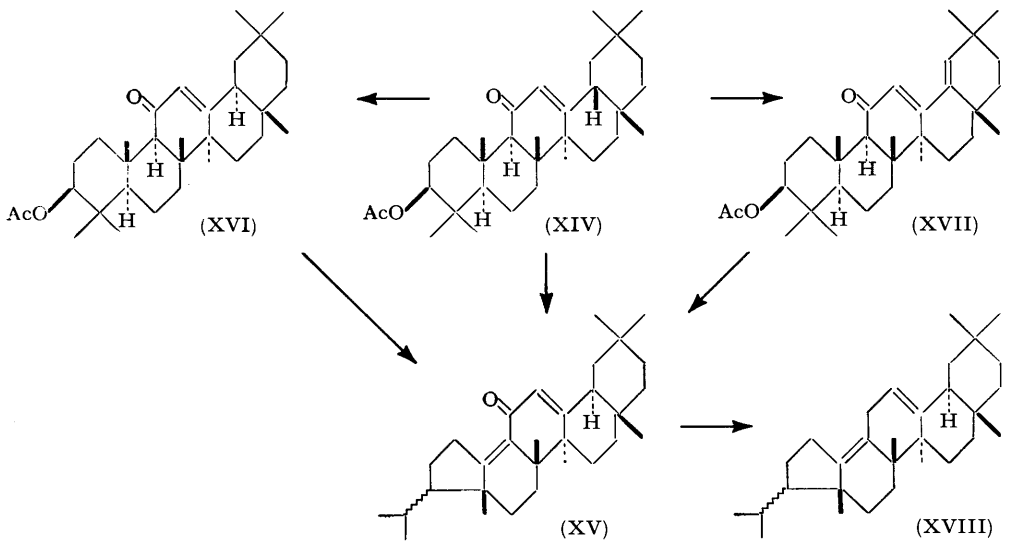


treated with boron trifluoride, similar treatment of the novoleanadiene (XI) gives an oil, the ultraviolet absorption of which indicates the presence of only a small proportion of a conjugated diene.

When 11-oxo-olean-12-en-3β-yl acetate (XIV) is refluxed with hydriodic–acetic acid, it gives an oxo-diene which shows maximal absorption at 2060, 2560, and 2870 Å, and is



consequently identified as 5 : 8 : 14-trimethyl-11-oxo-18α-novoleana-9(10) : 12-diene (XV), the analogue of the novursane oxo-diene (VIII). The 18-hydrogen atom in the oxo-diene has the stable α-configuration, *i.e.*, inversion at $C_{(18)}$ has occurred during the reaction,



because this compound is also obtained by treatment of 11-oxo-18α-olean-12-en-3β-yl acetate (XVI) (Budziarek, Manson, and Spring, *J.*, 1951, 3336) with hydriodic acid. The same treatment of 11-oxo-oleana-12 : 18-dien-3β-yl acetate (XVII) (Picard and Spring, *J.*, 1941, 35) also gives the conjugated oxo-diene (XV); in this reaction reduction of the

terminal ethylene bond has occurred, the 18-hydrogen atom adopting the α-configuration, in addition to ring contraction and movement of the methyl group from $C_{(10)}$ to $C_{(5)}$.

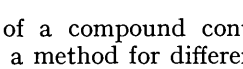
The ultraviolet absorption of a compound containing a  (conjugated enonene) chromophore provides a method for differentiating between a di-transoid and a cisoid-transoid geometry in this chromophore. The ultraviolet absorption spectra of many di-transoid conjugated enonenes have been measured and, apart from minor differences in the position of the maximum attributable to the degree of substitution, they show a single absorption peak at approximately 2400 Å. The ultraviolet absorption spectra of the cisoid-transoid conjugated enonenes described in this Series are shown in Table 2. Without exception, they have spectra with the characteristic three maxima.

TABLE 1.

	$[\alpha]_D$ (in chloroform)	
	Novursane derivative [1]	Novoleanane derivative [2]
8 : 10 : 14-Trimethyl-5ξ-, 3(4) : 12-diene	+109°	+110°
8 : 10 : 14-Trimethyl-, 3(5) : 12-diene	+123	+120
Ketone, $C_{37}H_{42}O$	+210	+215
5 : 8 : 14-Trimethyl-11-oxo-, 9(10) : 12-diene	+171	+122 (18α)
5 : 8 : 14-Trimethyl-, 1(10) : 9(11) : 12-triene	−358	−450 (18α)
5 : 8 : 14-Trimethyl-, 9(10) : 11 : 13(18)-triene	−450	−400
5 : 8 : 14-Trimethyl-, 9(10) : 12-diene	+120	+103 (18α)
8 : 10 : 14-Trimethyl-5ξ-, 3(4 or 5) : 9(11) : 12-triene	+445	+356
5 : 8α : 9β-Trimethyl-12-oxo-10α-, 13-ene	− 41	− 32 (18ξ)
5 : 8α : 9β-Trimethyl-10α-, 12 : 14-diene	−110	− 83 (18ξ)
5 : 8α : 9β-Trimethyl-12 : 15-dioxo-10α-, 13-ene	+ 86	− 7 (18ξ)

[1] Allan, Spring, Stevenson, and Strachan, *J.*, 1955, 3371; Fayez, Grigor, Spring, and Stevenson, *J.*, 1955, 3378. [2] This paper.

TABLE 2.

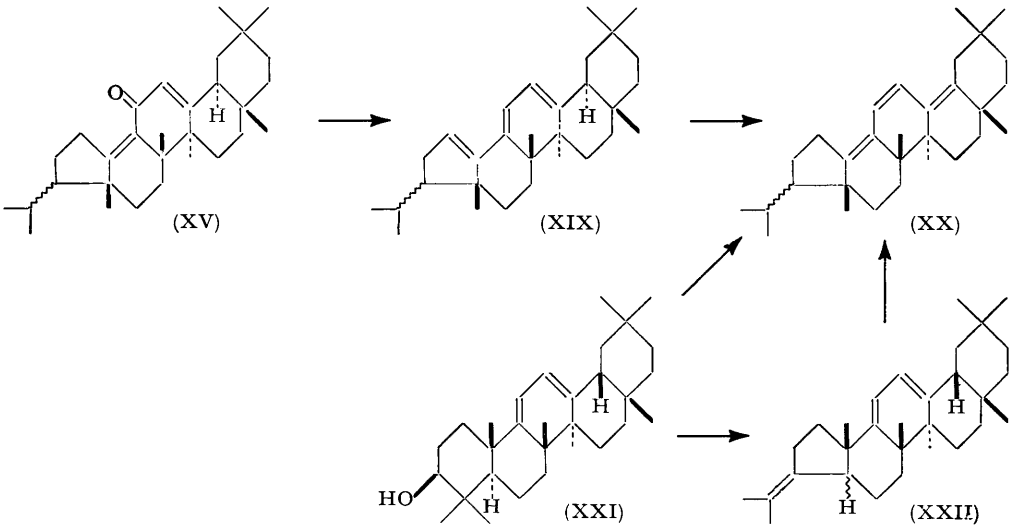
	Maxima (Å) (ε in parentheses)
12-Oxo-oleana-9(11) : 13(18)-dien-3β-yl acetate [1]	2080 (9000), 2600 (9250), 2950 (8450)
12-Oxo-oleana-9(11) : 13(18)-dien-3β-ol [1]	2100 (7600), 2600 (8600), 2950 (8100)
12-Oxoursa-9(11) : 13(18)-dien-3β-yl acetate [2]	2070 (9000), 2610 (9700), 2940 (8100)
12-Oxoursa-9(11) : 13(18)-dien-3β-ol [2]	2080 (8050), 2630 (9600), 2950 (7400)
5 : 8 : 14-Trimethyl-11-oxonovursa-9(10) : 12-diene [3]	2040 (9900), 2580 (11,000), 2900 (10,200)
5 : 8 : 14-Trimethyl-11-oxo-18α-novoleana-9(10) : 12-diene [4]	2060 (6900), 2560 (10,700), 2870 (9300)

[1] Beaton, Johnston, McKean, and Spring, *J.*, 1953, 3600. [2] Beaton, Shaw, Spring, Stevenson, Strachan and Stewart, *J.*, 1955, 2606. [3] Allan, Spring, Stevenson, and Strachan, *J.*, 1955, 3371, [4] This paper.

Thus, when treated with hydriodic acid, 11-oxo-olean-12-en-3β-yl acetate behaves in the same way as 11-oxours-12-en-3β-yl acetate, apart from inversion at $C_{(18)}$ in the former case. In each case, contraction of ring A occurs and conjugation is subsequently achieved by the transfer of a methyl group from $C_{(10)}$ to $C_{(5)}$. Moreover, with one important exception, there is a general similarity between the reactions of the conjugated enonenes (VIII) and (XV). Treatment of 5 : 8 : 14-trimethyl-11-oxo-18α-novoleana-9(10) : 12-diene (XV) with lithium aluminium hydride at 0° gives 5 : 8 : 14-trimethyl-18α-novoleana-1(10) : 9(11) : 12-triene (XIX). This conjugated triene is strongly lævorotatory ($[\alpha]_D$ −450°) and it shows intense maximal absorption at 3150 Å. It is similar in these respects to the analogously constituted novursatriene (Allan *et al.*, *loc. cit.*) and ergosta-5 : 7 : 14 : 22-tetraenyl acetate ($[\alpha]_D$ −322°, $\lambda_{max.}$ 3190 Å, ε 15,000) (Barton and Bruun, *J.*, 1951, 2728). The novoleanatriene (XIX) is isomerised by mineral acid to 5 : 8 : 14-trimethylnovoleana-9(10) : 11 : 13(18)-triene (XX) which shows three maxima in the absorption spectrum, the principal band in which is at 2950 Å (ε 35,000). The triene (XX) is also obtained by treatment of oleana-9(11) : 12-dien-3β-ol (XXI) (Picard and Spring, *J.*, 1940, 1198) with phosphoric oxide. Dehydration of the dienol (XXI) by phosphorus pentachloride gives a triene which shows the characteristic ultraviolet spectrum of a homoannular diene and which we formulate as either 8 : 10 : 14-trimethyl-5ξ-novoleana-3(4) : 9(11) : 12-triene (XXII) or the 3(5) : 9(11) : 12-triene isomer. This hydrocarbon is isomerised by trichloroacetic acid to the conjugated

triene (XX). The various methods described above for the conversion of β-amyrin into the conjugated triene (XX) duplicate those used for the conversion of α-amyrin into 5 : 8 : 14-trimethylnovursa-9(10) : 11 : 13(18)-triene (Allan *et al.*, *loc. cit.*) and we observe that this series of reactions does not involve the movement of the methyl groups attached to $C_{(8)}$ and $C_{(14)}$.

The exception to the rule of general similarity between the reactions of the isomeric conjugated enonenes (VIII) and (XV) and their derivatives, to which reference was made above, is to be found in the following reactions. Reduction of the conjugated enonene (XV) with a refluxing solution of lithium aluminium hydride in ether gives 5 : 8 : 14-trimethyl-18α-novoleana-9(10) : 12-diene (XVIII), the structure of which follows from its method of formation and from the fact that it does not show selective absorption in the ultraviolet region above 2200 Å. Treatment of the non-conjugated diene (XVIII) with hydrochloric–acetic acid, in conditions which convert the analogous non-conjugated ʟovursadiene (IX) into the conjugated " *l*-diene " (II) in high yield, failed to give a conjugated diene. This difference can be defined as the inability of the 18α-oleanane derivative (XVIII) to undergo a reaction involving migration of the methyl groups attached to $C_{(8)}$ and $C_{(14)}$ to $C_{(9)}$ and $C_{(8)}$ respectively.

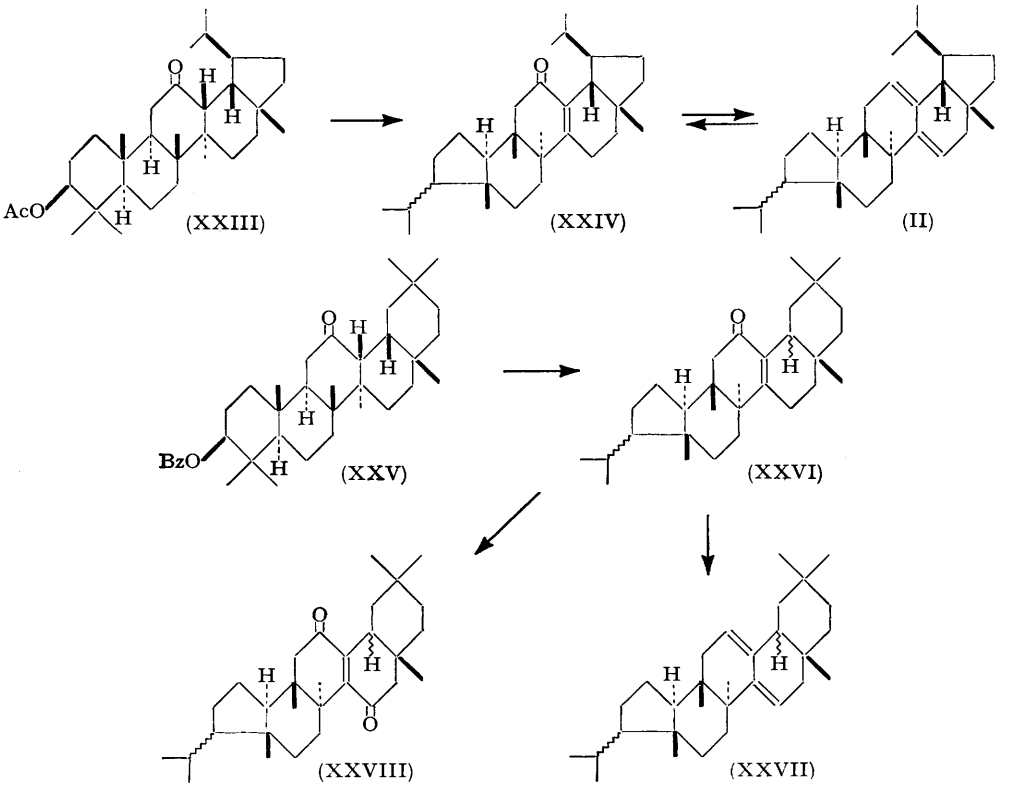


At this stage of the investigation, it appeared probable that the driving force responsible for the final stages of the conversion of α-amyrin into 5 : 8α : 9β-trimethyl-10α-novursa-12 : 14-diene (II) was a conformational constraint imposed by the (stable) *cis*-locking of rings D/E (cf. Beton and Halsall, *Chem. and Ind.*, 1954, 1560) and that the failure of β-amyrin to give a similarly constituted diene is due to the fact that the *cis*-locking of rings D/E in β-amyrin is not stable in an acid medium. We argued that, if this view is correct, it should be possible to achieve an " *l*-diene " type of reaction starting from a β-amyrin derivative in which the *cis*(β)-junction of rings D/E is locked. Experiments were designed to test this hypothesis.

Fayez *et al.* (*loc. cit.*) found that treatment of 12-oxoursanyl acetate (XXIII) with hydriodic–acetic acid gives 5 : 8α : 9β-trimethyl-12-oxo-10α-novurs-13-ene (XXIV), a reaction analogous to the conversion of α-amyrin into the conjugated diene (II), since it includes contraction of ring A and synchronous movement of axial methyl groups from $C_{(10)}$, $C_{(8)}$, and $C_{(14)}$ to $C_{(5)}$, $C_{(9)}$, and $C_{(8)}$ respectively. The relation of the αβ-unsaturated ketone (XXIV) and the conjugated diene (II) was confirmed by their interconversion. We find that treatment of 12-oxo-oleananyl benzoate (XXV) with hydriodic–acetic acid gives 5 : 8α : 9β-trimethyl-12-oxo-10α : 18ξ-novolean-13-ene (XXVI), the structure of which

followed from its properties and the reactions described below. It shows maximal absorption at 2600 Å (ε 10,000) thus confirming the view that the chromophore is an ααββ-tetrasubstituted αβ-unsaturated ketone group. Reaction of the αβ-unsaturated ketone (XXVI) with lithium aluminium hydride and treatment of the product with hydrochloric acid gave 5 : 8α : 9β-trimethyl-10α : 18ξ-novoleana-12 : 14-diene (XXVII). This diene has three maxima in its absorption spectrum [$\lambda_{max.}$ 2340 (ε 15,000), 2410 (ε 16,000), and 2490 Å (ε 10,700)]. It is lævorotatory ([α]$_D$ −83°) and in these respects and in its origin it is the exact analogue of the " *l*-diene " (II). The relations implied by the formulations proposed for the αβ-unsaturated ketone (XXVI) and the conjugated diene (XXVII) were confirmed by oxidation of the former to a transoid enedione, 5 : 8α : 9β-trimethyl-12 : 15-dioxo-10α : 18ξ-novolean-13-ene (XXVIII) which shows an absorption maximum at 2780 Å (ε 8000).*

Further support for the view that the driving force supporting reactions (XXIII) ⟶ (XXIV) and (XXV) ⟶ (XXVI) is the constraint imposed by a *cis*(β)-locking of rings D and E was obtained by a study of 12-oxo-18α-oleanan-3β-yl acetate (XXIX) (Budziarek *et al.*,

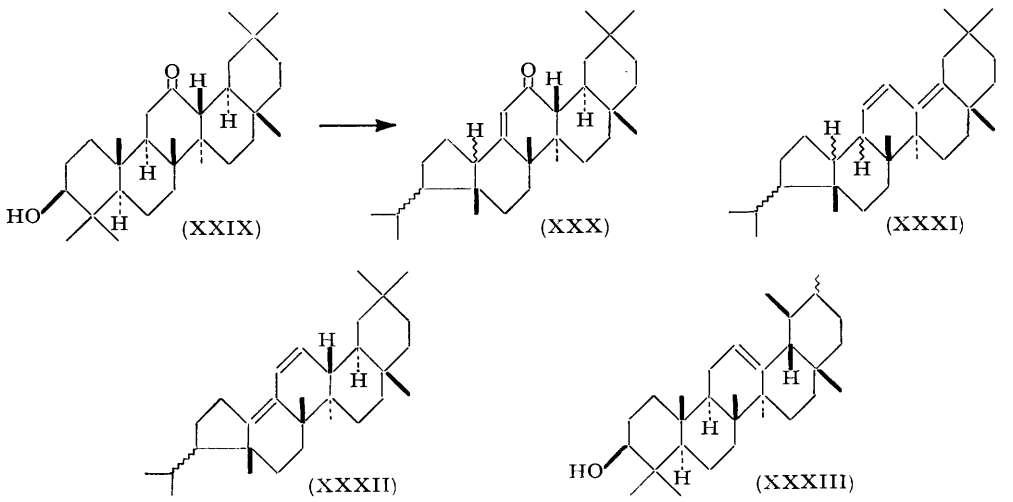


loc. cit.). With hydriodic–acetic acid this gives an αβ-unsaturated ketone, which we formulate as 5 : 8 : 14-trimethyl-12-oxo-10ξ : 18α-novolean-9(11)-ene (XXX) since it shows an absorption maximum at 2440 Å (ε 11,200) and in this respect differs markedly from the two αβ-unsaturated ketones (XXIV) and (XXVI). Unlike the last two compounds, moreover, the 9(11)-en-12-one (XXX) is dextrorotatory. The structure of (XXX) was confirmed

* It is possible that an ultimate consequence of the conversion of the saturated keto-benzoate (XXV) into the αβ-unsaturated ketone (XXVI) is inversion at $C_{(18)}$; the configuration at this centre in the related compounds (XXVI), (XXVII), and (XXVIII) is undecided for the time being. It may be of significance that there is a general correspondence in the specific rotations of analogous novoleanane and novursane derivatives (Table 1) with the exception of the enedione (XXVIII) and its novursane analogue.

by reduction with lithium aluminium hydride followed by treatment of the product with acetic anhydride and sodium acetate, which yielded a hydrocarbon which, we believe, is either the 11 : 13(18)-diene (XXXI) or the 9 : 11-diene (XXXII), since, like oleana-11 : 13(18)-dienyl acetate, it shows three maxima [λ 2450, 2520, and 2600 Å (ε 24,600, 27,000, and 26,000)].

We now summarise the more important implications of the comparison of the behaviour of analogous oleanane and ursane derivatives made above. The *cis*-locking of rings D and E in β-amyrin is unstable in that, if a carbonyl group or a double bond is immediately adjacent to $C_{(18)}$, inversion to a *trans*-fused 18α-oleanane isomer can occur. In our opinion, a reaction strictly analogous to the conversion of α-amyrin into the "*l*-diene" is not observed with β-amyrin, because the 12 : 13-double bond in this compound is not stable to strong acid. On the other hand, the locking of rings D and E in α-amyrin is stable (Beaton, Spring, Stevenson, and Strachan, *J.*, 1955, 2610); urs-12-en-3-one, unlike olean-12-en-3-one, is recovered unchanged after vigorous treatment with mineral acid (Davy, Halsall, and Jones, *J.*, 1951, 458). The conversion of 12-oxo-oleananyl acetate, but not its 18α-epimer, into a 12-oxo-13 : 14-ene in our opinion shows that the *cis*-locking of rings D and E is the driving force supporting the "*l*-diene" type of reaction. It is established that the $C_{(17)}$-methyl group in α-amyrin is β-orientated (Beaton *et al.*, *loc. cit.*). The similar behaviour of 12-oxoursanyl acetate and 12-oxo-oleananyl acetate when treated with hydriodic–acetic acid leads inevitably to the conclusion that rings D and E in α-amyrin are *cis*-β-fused (cf. Corey and Ursprung, *Chem. and Ind.*, 1954, 1387; Allan and Spring, *J.*, 1955, 2125). It follows that α- and β-amyrin have identical configurations at all the ring junctions. We conclude that the constitution and stereochemistry of α-amyrin must be represented by either (I) or (XXXIII). The former, in which ring E is 5-membered, was proposed by Beaton *et al.* (*loc. cit.*) and is used to illustrate the reactions described in this paper. In the latter, the 20α-form of which was proposed by Corey and Ursprung (*loc. cit.*), ring E is 6-membered. Experiments designed to determine the size of ring E in α-amyrin are in progress.



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-*novoleana*-3(4) : 12-*diene* ("β-*Amyrilene*-I") (XI).—β-Amyrin (5·0 g.) was added to a suspension of phosphorus pentachloride (3·2 g.) in light petroleum (b. p. 60—80°; 40 c.c.), and the mixture shaken for 30 min. and filtered. The filtrate was washed with warm water, dried (Na_2SO_4), and evaporated, and the residue crystallised from acetone to give 8 : 10 : 14-trimethyl-5ξ-novoleana-3(4) : 12-diene (XI) as needles, m. p. 167—172°, $[\alpha]_D$ +110°

(*c* 1·8), ε 9200 at 2080 Å (Found : C, 88·5; H, 12·0. Calc. for $C_{30}H_{48}$: C, 88·2; H, 11·8%). It gives a yellow colour with tetranitromethane.

Treatment of β-amyrin in benzene with phosphoric oxide, as described for the preparation of the " *l*-diene " from α-amyrin (Vesterberg, *Ber.*, 1891, **24**, 3835), gave a gum, $\lambda_{max.}$ 2070 and 2420 Å (ε 4500 and 4400).

8 : 10 : 14-Trimethylnovoleana-3(5) : 12-diene (" β-amyrilene-III ") (XIII) was obtained as described by Dieterle, Brass, and Schaal (*loc. cit.*), by treatment either of β-amyrin with phosphorus pentachloride in light petroleum (b. p. 60—80°) or of the isomer (XI) with trichloroacetic acid; it crystallised from chloroform–methanol as plates, m. p. 102—104°, $[\alpha]_D$ +120° (*c* 1·8) and gives a yellow colour with tetranitromethane.

Ozonolysis of 8 : 10 : 14-*Trimethyl*-5ξ-*novoleana*-3(4) : 12-*diene* (XI).—A solution of the diene (XI) (1·0 g.) in dry chloroform (200 c.c.) was treated at −40° with ozone (1·2 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 (3 × 500 c.c., see below), the chloroform removed under reduced pressure, and the residue dissolved in light petroleum and chromatographed. Light petroleum (100 c.c.) eluted unchanged diene (XI) (263 mg.). The fraction (427 mg.) eluted with benzene–light petroleum (1 : 4; 300 c.c.) was recrystallised five times from chloroform–methanol, to give the *ketone* (XII) as plates, m. p. 192—194°, $[\alpha]_D$ +215° (*c* 2·7), ε 5700 at 2060 Å (Found : C, 85·05; H, 10·8. $C_{27}H_{42}O$ requires C, 84·75; H, 11·1%). It gives a yellow colour with tetranitromethane.

The water washings (above) were adjusted to pH 7 by addition of sodium hydrogen carbonate, and the solution distilled. The first fraction (250 c.c.) was treated with 2 : 4-dinitrophenylhydrazine hydrochloride solution to give acetone 2 : 4-dinitrophenylhydrazone (117 mg.) as orange blades, m. p. 123—125° (no depression).

5 : 8 : 14-*Trimethyl*-11-*oxo*-18α-*novoleana*-9(10) : 12-*diene* (XV).—(*a*) Hydriodic acid (15 c.c.; *d* 1·7; distilled from hypophosphorous acid) was added to a solution of 11-oxo-olean-12-en-3β-yl acetate (5·0 g.) in acetic acid (50 c.c.), and the mixture refluxed for 16 hr., diluted with water, and extracted with ether. The product crystallised from methanol to give 5 : 8 : 14-*trimethyl*-11-*oxo*-18α-*novoleana*-9(10) : 12-*diene* as needles (1·3 g.), m. p. 191—192°, $[\alpha]_D$ +122° (*c* 2·3), $\lambda_{max.}$ 2060, 2560, and 2870 Å (ε 6900, 10,700, and 9300) (Found : C, 85·3; H, 11·3. $C_{30}H_{46}O$ requires C, 85·2; H, 11·0%). It does not give a colour with tetranitromethane.

(*b*) Similar treatment of (i) 11-oxo-18α-olean-12-en-3β-yl acetate (XVI) or (ii) 11-oxo-oleana-12 : 18-dien-3β-yl acetate (XVII) with hydriodic acid gave the oxo-diene (XV), m. p. and mixed m. p. 191—192°, $[\alpha]_D$ (i) +125° (*c* 3·1), (ii) +124° (*c* 1·7), in the same yield.

5 : 8 : 14-*Trimethyl*-18α-*novoleana*-1(10) : 9(11) : 12-*triene* (XIX).—Lithium aluminium hydride (0·5 g.) was added to a solution of 5 : 8 : 14-trimethyl-11-oxo-18α-novoleana-9(10) : 12-diene (XV) (400 mg.) in dry ether (200 c.c.) at 0° and the mixture kept at this temperature for 72 hr. The product, isolated without the use of mineral acid, was crystallised from methanol to give 5 : 8 : 14-*trimethyl*-18α-*novoleana*-1(10) : 9(11) : 12-*triene* (XIX) as plates (250 mg.), m. p. 140—142°, $[\alpha]_D$ −450° (*c* 0·9), $\lambda_{max.}$ 3150 Å (ε 14,000) (Found : C, 88·6; H, 11·5. $C_{30}H_{46}$ requires C, 88·6; H, 11·4%). It gives a strong yellow colour with tetranitromethane.

5 : 8 : 14-*Trimethyl*-18α-*novoleana*-9(10) : 12-*diene* (XVIII).—Lithium aluminium hydride (1·0 g.) was added to a solution of the oxo-diene (XV) (800 mg.) in dry ether (500 c.c.), and the mixture refluxed for 7 hr. The product, isolated without the use of mineral acid, was crystallised from chloroform–methanol, to give 5 : 8 : 14-*trimethyl*-18α-*novoleana*-9(10) : 12-*diene* (XVIII) as matted needles (400 mg.), m. p. 160—162°, $[\alpha]_D$ +103° (*c* 0·7), ε 10,500 at 2080 Å (Found : C, 88·0; H, 12·0. $C_{30}H_{48}$ requires C, 88·2; H, 11·8%). It gives a yellow colour with tetranitromethane.

Treatment of the diene (XVIII) with hydrochloric–acetic acid, under conditions used to convert the analogous novursadiene into the " *l*-diene " (II), yielded a brown gum, the ultraviolet spectrum of which had no high intensity-absorption above 2200 Å.

5 : 8 : 14-*Trimethylnovoleana*-9(10) : 11 : 13(18)-*triene* (XX).—(*a*) A solution of oleana-9(11) : 12-dien-3β-ol (XXI) (2·0 g.) in dry benzene (60 c.c.) was shaken with phosphoric oxide (3·0 g.) for 20 hr. The product, isolated in the usual way and crystallised from methanol, yielded 5 : 8 : 14-*trimethylnovoleana*-9(10) : 11 : 13(18)-*triene* (XX) as needles (600 mg.), m. p. 135—136° $[\alpha]_D$ −400° (*c* 1·8), $\lambda_{max.}$ 2860, 2950, and 3080 Å (ε 31,000, 36,000 and 25,400) (Found : C, 88·9; H, 11·7. $C_{30}H_{46}$ requires C, 88·6; H, 11·4%). It gives a red-brown colour with tetranitromethane.

(*b*) Concentrated hydrochloric acid (2 c.c.) was added to 5 : 8 : 14-trimethyl-18α-novoleana-1(10) : 9(11) : 12-triene (XIX) (50 mg.) in acetic acid (50 c.c.), and the mixture left at room

temperature for 72 hr. The product, isolated by means of ether, was crystallised from methanol to give the triene (XX) (20 mg.), m. p. 132—135° (no depression), $[\alpha]_D$ −407° (*c* 0·4).

(*c*) A solution of 5 : 8 : 14-trimethyl-11-oxo-18α-novoleana-9(10) : 12-diene (XV) (0·7 g.) (in dry ether (200 c.c.) was added dropwise to a suspension of lithium aluminium hydride (0·7 g.) in dry ether (200 c.c.), and the mixture refluxed for 2 hr. The product was worked up as usual and the residue, obtained on evaporation of the ether, dissolved in light petroleum and chromatographed. Elution with light petroleum (300 c.c.) gave a solid (147 mg.) which was crystallised from chloroform–methanol to give 5 : 8 : 14-trimethyl-18α-novoleana-9(10) : 12-diene (XVIII) as matted needles, m. p. and mixed m. p. 161—162°, $[\alpha]_D$ +101° (*c* 0·85). Further elution with the same solvent (100 c.c.) yielded a solid (33 mg.) which was not examined. Benzene–light petroleum (1 : 9; 650 c.c.) gave a fraction (464 mg.), which after repeated crystallisation from chloroform–methanol gave 5 : 8 : 14-trimethylnovoleana-9(10) : 11 : 13(18)-triene (XX) as needles, m. p. and mixed m. p. 135—136°, $[\alpha]_D$ −400° (*c* 1·8).

(*d*) A solution of 8 : 10 : 14-trimethyl-5ξ-novoleana-3(4) : 9(11) : 12-triene (XXII) (40 mg.; see below) and trichloroacetic acid (40 mg.) in chloroform (1 c.c.) was kept at room temperature for 1 hr., and the solvent removed under reduced pressure. The product, isolated by means of ether, crystallised from chloroform–methanol to yield the triene (XX) as needles, m. p. 133—134° (no depression), $[\alpha]_D$ −388° (*c* 0·60).

8 : 10 : 14-*Trimethyl*-5ξ-*novoleana*-3(4 or 5) : 9(11) : 12-*triene*.—Oleana-9(11) : 12-dien-3β-ol (0·8 g.) was shaken with phosphorus pentachloride (0·42 g.) in light petroleum (b. p. 60—80°; 25 c.c.) for 1 hr. and then refluxed for 2 min. The product, isolated in the usual way, was recrystallised five times from acetone, to give 8 : 10 : 14-*trimethyl*-5ξ-*novoleana*-3(4 or 5) : 9(11) : 12-*triene* as needles, m. p. 150—152°, $[\alpha]_D$ +356° (*c* 2·7), $\lambda_{max.}$ 2060 and 2800 Å (ε 8300 and 8000) (Found : C, 88·2; H, 11·8. $C_{30}H_{46}$ requires C, 88·6; H, 11·4%). It gives a deep red-brown colour with tetranitromethane.

5 : 8α : 9β-*Trimethyl*-12-*oxo*-10α : 18ξ-*novolean*-13-*ene* (XXVI).—Hydriodic acid (4 c.c.; *d* 1·7; distilled from hypophosphorous acid) was added to a solution of 12-oxo-oleanan-3β-yl benzoate (XIV) (1·0 g.) in acetic acid (30 c.c.), the mixture refluxed for 16 hr., diluted with water, and extracted with ether. The product was worked up in the usual way, and the crude product (0·36 g.; m. p. 155—159°) crystallised three times from aqueous methanol to give 5 : 8α : 9β-*trimethyl*-12-*oxo*-10α : 18ξ-*novolean*-13-*ene* as long plates, m. p. 171—172°, $[\alpha]_D$ −32° (*c*, 2·5), $\lambda_{max.}$ 2600 Å (ε 9700) (Found : C, 84·5; H, 11·6. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%). It does not give a colour with tetranitromethane.

5 : 8α : 9β-*Trimethyl*-10α : 18ξ-*novoleana*-12 : 14-*diene* (XXVII).—A solution of 5 : 8α : 9β-trimethyl-12-oxo-10α : 18ξ-novolean-13-ene (XXVI) (1·0 g.) in dry ether (200 c.c.) was added dropwise to a suspension of lithium aluminium hydride (1 g.) in dry ether (200 c.c.), and the mixture refluxed for 2 hr. The product (880 mg.), isolated in the usual way, gave a yellow colour with tetranitromethane and exhibited ultraviolet light absorption at 2130 Å. Concentrated hydrochloric acid (2 c.c.) was added to a solution of this solid (100 mg.) in chloroform (3 c.c.) and acetic acid (25 c.c.), and the mixture heated on the steam-bath for 30 min. On cooling, the crystalline product was collected and recrystallised from chloroform–methanol to give 5 : 8α : 9β-*trimethyl*-10α : 18ξ-*novoleana*-12 : 14-*diene* (75 mg.) as needles, m. p. 155—156°, $[\alpha]_D$ −83° (*c* 2·5), $\lambda_{max.}$ 2340 (shoulder), 2410, and 2490 (shoulder) Å (ε 15,000, 16,000, and 10,700) (Found : C, 88·1; H, 11·7. $C_{30}H_{48}$ requires C, 88·2; H, 11·8%). It gives an orange-brown colour with tetranitromethane.

5 : 8α : 9β-*Trimethyl*-12 : 15-*dioxo*-10α : 18ξ-*novolean*-13-*ene* (XXVIII).—(*a*) Chromium trioxide (0·6 g.) in 90% acetic acid (7 c.c.) was added to 5 : 8α : 9β-trimethyl-12-oxo-10α : 18ξ-novolean-13-ene (XXVI) (1·0 g.) in acetic acid (72 c.c.), and the mixture stirred on the steam-bath for 1 hr. After the addition of methanol, the product was isolated in the usual way, and its solution in benzene–light petroleum (3 : 7) was chromatographed on alumina. Elution with the same solvent (200 c.c.) yielded a solid (600 mg.), which, after four recrystallisations from aqueous methanol gave 5 : 8α : 9β-*trimethyl*-12 : 15-*dioxo*-10α : 18ξ-*novolean*-13-*ene* as yellow needles, m. p. 145—146°, $[\alpha]_D$ −8°, −7° (*c* 2·2, 1·9), $\lambda_{max.}$ 2220 and 2780 Å (ε 3100 and 8000) (Found : C, 82·3; H, 10·7. $C_{30}H_{46}O_2$ requires C, 82·1; H, 10·6%). It does not give a colour with tetranitromethane.

(*b*) A solution of the αβ-unsaturated ketone (XXVI) (120 mg.) in 10% ethanolic potassium hydroxide (100 c.c.) was refluxed for 2 hr. The product was isolated by using ether, and crystallised four times from aqueous methanol, to give the enedione (XXVIII) as yellow needles, m. p. 144—145° (no depression), $[\alpha]_D$ −7° (*c* 2·4), $\lambda_{max.}$ 2220 and 2770 Å (ε 3200 and 7700).

Action of Hydriodic Acid on 12-*Oxo*-18α-*oleanan*-3β-*yl Acetate* (XXIX).—Hydriodic acid

(4 c.c.; *d* 1·7; distilled from hypophosphorous acid) was added to a solution of the saturated keto-acetate (XXIX) (1·0 g.) in acetic acid (20 c.c.), and the mixture refluxed for 16 hr. and worked up in the usual way. The product was dissolved in light petroleum and chromatographed on alumina. Benzene–light petroleum (1 : 9; 100 c.c.) eluted a fraction (165 mg.) which was crystallised from chloroform–methanol to give 8 : 10 : 14-*trimethyl*-12-*oxo*-18α-*novolean*-3(4 or 5)-*ene* as long plates, m. p. 181—182°, $[\alpha]_D$ +50° (*c* 2·5), ε 6200 at 2100 Å (Found : C, 85·0; H, 11·6. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%). It gives a yellow colour with tetranitromethane. Elution with the same solvent (400 c.c.) and benzene–light petroleum (3 : 7; 50 c.c.) gave a mixture (267 mg.). Further elution with benzene–light petroleum (3 : 7; 200 c.c.) yielded a solid (106 mg.), which was crystallised from chloroform–methanol to give 5 : 8 : 14-*trimethyl*-12-*oxo*-10ξ : 18α-*novolean*-9(11)-*ene* (XXX) as needles, m. p. 247—248°, $[\alpha]_D$ +99° (*c* 0·9), $\lambda_{max.}$ 2440 Å (ε 11,200) (Found : C, 85·1; H, 11·6. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%). It does not give a colour with tetranitromethane.

Preparation of the Heteroannular Diene (XXXI) *or* (XXXII) *from* 5 : 8 : 14-*Trimethyl*-12-*oxo*-10ξ : 18α-*novolean*-9(11)-*ene* (XXX).—A solution of the αβ-unsaturated ketone (XXX) (55 mg.) in dry ether (50 c.c.) was added to lithium aluminium hydride (100 mg.) in ether (50 c.c.), and the mixture refluxed for 2 hr. and worked up in the usual way. A solution of the product in acetic anhydride (20 c.c.) containing freshly fused sodium acetate (100 mg.) was refluxed for 2 hr. Isolation through ether, and crystallisation from chloroform–methanol, gave the *diene* (XXXI) or (XXXII) as plates, m. p. 178—179°, $[\alpha]_D$ +30° (*c* 0·5), $\lambda_{max.}$ 2450 (shoulder), 2520, and 2600 (shoulder) Å (ε 24,600, 27,000, and 20,000) (Found : C, 88·1; H, 12·2. $C_{30}H_{48}$ requires C, 88·2; H, 11·8%). It gives a dark brown colour with tetranitromethane.

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