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THESIS

submitted to

THE UNIVERSITY OF GLASGOW

in fulfilment of the
requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

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October, 1955.
The author wishes to record his sincere appreciation for the guidance and encouragement given by Professor F.S. Spring, F.R.S., during the course of these investigations. He also wishes to express his gratitude to Dr. R. Stevenson for much invaluable advice and helpful discussion.
DEHYDRATION

OF

SOME TRITERPENOID ALCOHOLS
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HISTORICAL
The pentacyclic triterpenoids are a class of naturally occurring compounds, containing thirty carbon atoms, arranged in six isopentane units. The majority of the triterpenoids occur in the plant kingdom, often in association with phyto-sterols (1), where they occur in resins and saps either in the free state as esters, or glycosidically linked with sugars as saponins. A few triterpenoids are found in the animal kingdom. Comprehensive reviews of the occurrence, structures, reactions, and interrelationships of the triterpenoids are available (2 to 9).

Apart from the pentacyclic and tetracyclic triterpenoids which constitute the majority of triterpenoids, there are a few which contain a lesser number of alicyclic rings. For example, the aliphatic squalene (I), the tricyclic ambrein (II) and the tetracyclic onocerin (III) (10) comprise the Squalene Group. Lanosterol, agnosterol, and euphol are classed as tetracyclic triterpenoids.
The recently characterised cyclopropanoid pentacyclic compounds; cycloartenol and cyclolaudenol can also be included among the tetracyclic triterpenoids (11, 12, 13). Mono- and dicyclic triterpenoids are unknown.

The pentacyclic triterpenoids are classified into three main groups:

I  The Oleanane Group
II  The Ursane Group
III  The Lupane Group

The parent member of the oleanane group is the unsaturated alcohol, β-amyrin (olean-12-en-3β-ol) (IV). Other members of this group, which have almost been fully characterised, and for the inter-conversions of which reviews are available (7,8,9)
are oleanolic acid, erythrodiol, maniladiol, genin A, say sapogenin A, B and C, a-boswellic acid, hederagenin, sumaresinolic acid, echinocystic acid, siaresinolic acid, gypsogenin, quilliac acid, glycyrrhetic acid, \( \delta \) -amyrin, germanicol and morolic acid.

Recently, triterpenoids have been isolated from cacti sources. Four of these have been related to various members of the oleanane group - gummisogenin, longispinogenin, machaeric acid and cochalic acid (14, 15, 16). Other members of the oleanane group which have recently been discovered and the structures of which have been established are rehmannic acid and icterogenin (17) and lantadene-B (18). Terminolic acid (19) of yet unidentified structure might again be a member of this group. Taraxerol (V) (formerly
known as skimmiol) has recently been converted into \(\beta\)-amyrin and partially synthesised from a \(\beta\)-amyrin derivative. Friedelin and cerin have also been related to known oleanane triterpenoids. Various workers have recently presented substantial evidence in favour of structure (VI) for friedelin.

The parent member of the ursane group is the unsaturated alcohol, \(\alpha\)-amyrin, which has been represented by structure (VII), proposed by Meisels, Jeger and Ruzicka and found general acceptance. The stereochemistry of this compound will be discussed in the introductory part to the Theoretical section of this Thesis.
The other members of the ursane group are ursolic acid, asiatic acid, quinovic acid, β-boswellic acid, brein and uvaol. The cyclopropanoid hexacyclic phyllanthol is also a member of this group since it was converted into α-amyrin (109) and has been synthesised from quinovic acid (30) and from α-amyrin (31).

The lupane group comprises the parent member, lupeol (VIII) and two others, betulin and betulic acid. Associated with this group is the heterobetulin group, consisting of heterobetulin, farodiol, and arnidiol.
Many of the compounds within each of these groups have been interrelated and some compounds of different groups have been interconverted or converted into common intermediates (2-9). \( \alpha \)-Amyrin, which has for long been an exception to the rule, has only recently been related to the oleanane series (32).

One of the important classical methods used as a degradative procedure in the elucidation of the structures of the triterpenoids is the action of dehydrating agents, notably phosphorus pentachloride. This has been used to determine the presence of a gem dimethyl group at the \( C(4) \)-position adjacent to the almost ubiquitous hydroxyl group attached to \( C(6) \). This leads to the contraction of ring A into a five-membered ring, giving an isopropylidene side chain. The presence of the isopropylidene side chain is established by oxidation with osmium tetroxide to give a glycol which, on subsequent cleavage, affords acetone and a saturated ketone, viz.
This procedure has been applied inter alia to α-amyrin (as α-amyradienone-I) (33, 34), lupeol (35, 36), 18α-oleanolic acid lactone (37), quinovic acid dimethyl ester (38), sumaresinolic acid (using the 6-oxo-lactone and a slightly modified procedure) (39) and dihydrolanosterol (40).

This Thesis is concerned with the stereochemistry of α-amyrin, as revealed by a study of the products obtained by dehydration methods, and a comparison of these with analogous products obtained from β-amyrin. It includes observations on the stability of the double bond and C(10)-hydrogen atom in the oleanane group.
INTRODUCTION

The stereochemistry of the Pentacyclic Criteranoids

The elucidation of the stereochemistry of β-amyri
(clean-12-en-3β-ol) was chiefly due to the elegant
researches of D.H.R. Barton and co-workers (5, 6) to 47
Considerable information was derived by application of
conformational theory (49), and of J.S. Johnson's
interpretations (49) of the researches of Hineau and
co-workers (48) on para-hydroxyacetophenones. Of the two
alternative stereochemical structures for β-amyri
proposed by Barton and Holness (48), a decision in
favour of (I) has been made on a basis of molecular
rotational differences (50). This decision has
recently been supported by Cardile and El-Rahni (51)
by an X-ray examination of methyl oleandrate iodo-
acetate. An excellent summary of the work leading
to the adoption of formulation (I) for β-amyri is
available in the Tilden Lecture, 1933, delivered by
Barton (5).

The structure and stereochemistry of report
and the family of compounds related to β-amyri...
INTRODUCTION

The Stereochemistry of the Pentacyclic Triterpenoids.

The elucidation of the stereochemistry of \( \beta \)-amyrin (olean-12-en-3\( \beta \)-ol) was chiefly due to the elegant researches of D.H.R. Barton and co-workers (6, 41 to 47). Considerable information was derived by application of conformational theory (45), and of W.S. Johnson's interpretation (48) of the researches of Linstead and co-workers (49) on perhydrophenanthrenes. Of the two alternative stereochemical structures for \( \beta \)-amyrin proposed by Barton and Holness (45), a decision in favour of (I) has been made on a basis of molecular rotational differences (50). This decision has recently been supported by Carlisle and El-Rahim (51) by an X-ray examination of methyl oleanolate iodoacetate. An excellent summary of the work leading to the adoption of formulation (I) for \( \beta \)-amyrin is available in the Tilden Lecture, 1953, delivered by Barton (6).

The structure and stereochemistry of "lupeol and the family of compounds related to it follow
from its conversion into known β-amyrin derivatives (52, 53) and are thus established beyond doubt.

Lupeol has the structure and stereochemistry represented by formula (II)

From the work of Hoshina et al. (20) the fact emerges that the configurations at C(4), C(8), C(10) and C(20) in a-amyrin and its relatives are identical with those of the corresponding centers in β-amyrin. This conclusion follows from degradation reactions carried out on lupeol-glucoside-3β-ol (IV) which afforded (IV), which on acidolysis, afforded (IV), and (IV), and (IV), was arrived at.

α-Amyrin (urs-12-en-3β-ol) and the family of compounds related to it, however, stand alone as the only one of the three major groups of pentacyclic triterpenoids which lacks satisfactory and complete formulation, particularly with respect to
stereochemistry. When this work was commenced, on the basis of evidence available, the accepted constitution of α-amyrin was represented by formula (III) proposed by Meisels, Jeger and Ruzicka (28).

From the work of Ruzicka et al. (28) the fact emerges that the configurations at C(3), C(5), C(8) and C(10) in α-amyrin and its relatives are identical with those at the corresponding centres in β-amyrin. This decision follows from degradation reactions carried out on 12-oxo-isourea-9(11):14-dienol (IV) which led to a diketone (V) from which two enol ethers, formulated as (VI) and (VII), were derived. These were also obtained from β-amyrin via 12-oxo-isooleana-9(11):14-dienol (VIII), by a series of parallel reactions (28, 54, 55).
The same workers also suggested that the configurations at \( C(9) \) and \( C(14) \) may be identical in both series of triterpenoids.

Easton (110) showed that the \( C(9) \)-hydrogen in \( \alpha \)-amyrin has the more stable arrangement, since 11-oxours-12-en-3\( \beta \)-yl acetate (IX) was recovered unchanged after vigorous treatment with alkali and acetylation. The same decision was made by Barton (45) who showed that methyl-11-oxours-12-en-3\( \beta \)-olate...
acetate (X) is stable to strong alkali. More recently, Spring (32) proved that this centre is not amperisable by showing that 11-oxo-12-en-3β-yl acetate (IX) gives an enol acetate (XI) from which the αβ-unsaturated keto-acetate (IX) was regenerated upon hydrolysis using either acid or alkali.

The fact that, in both α- and β-amyrin series, the α-brominated 12-ketones (XII) lose hydrogen with extreme ease to give 12-oxo-9(11)-enes (XIII) (57), taken together with the fact that bromine is axial (β) in both compounds, as determined by infra-red examination (58), has led Corey and Ursprung to conclude that the hydrogen at C(9) is axial with respect to ring C.
These observations led to the conclusion that either configuration at $C(18)$ is the more stable in the amyrin group, since oxidation of $\alpha$-amyrin acetate with selenium in 1950, spring (52) proved that a hydrogen atom exists at $C(18)$, hence orientation of $\alpha$-amyrin acetate with selenium with a hydrogen atom exists at $C(18)$. In 1950, spring (52) proved that a hydrogen atom exists at $C(18)$, since oxidation of $\alpha$-amyrin acetate with selenium with a hydrogen atom exists at $C(18)$.

This is a strong evidence, therefore, that the hydrogen at $C(18)$ is $\alpha$-orientated, and that both $\alpha$- and $\beta$-amyrins possess the trans-anti-trans-arrangement of rings A, B and C.

The fact that 11-oxo-12-enyl acetate (XIV) is stable to vigorous treatment with acid or alkali (110) serves, also, to indicate that the substituent at $C(18)$ has the stable configuration. This observation is to be contrasted with the behaviour of 11-oxo-18a-olean-12-en-3$\beta$-yl acetate (XV) which readily isomerises, upon treatment with alkali, to give 11-oxo-18a-olean-12-en-3$\beta$-ol (XVI) (59).
These observations led to the conclusion that either the configuration at \( C(18) \) is the more stable in the \( \alpha \)-amyrin group, or there is no hydrogen attached to \( C(18) \) (45). In 1955, Spring (32) proved that a hydrogen atom exists at \( C(18) \), since oxidation of \( \alpha \)-amyrin acetate with selenium dioxide gave ursa-11:13(18)-dien-3\( \beta \)-yl acetate (XVII) (56), the dihydro derivative of which (XVIII) could be isomerised by mineral acid to \( \alpha \)-amyrin acetate. Again this proves that \( \alpha \)-amyrin has the more stable configuration at \( C(18) \).

While the work described in this Thesis was in progress, a number of important researches were
published advancing views concerning the stereochemistry at the centres C(14), C(17) and C(18) in α-amyrin. Spring (60) reported that there is a marked similarity in behaviour between 12-oxo-urs-9(11)-en-3β-yl acetate (XIX) and its oleanane analogue, 12-oxo-olean-9(11)-en-3β-yl acetate (XX) towards the action of selenium dioxide in acetic acid. Each compound gives the corresponding 12-oxo-9(11):14-dienyl acetate (IV) and (VIII) (60, 61, 62), reactions which involve the migration of the C(14)-methyl group to C(15).
In contrast, however, 12-oxo-16α-cleane-9(11)-en-3β-yl acetate (XXI) is not affected under the same experimental conditions (60). The further observation that isocleane-9(11):14-dien-3β-yl acetate (XXII) and isocleane-9(11):14-dien-3β-yl acetate (XXIII) behave similarly with mineral acid (as depicted above) (63, 64) has led Spring (60) to suggest that the configurations at C(13), C(14), C(17) and C(18) in both αβ-unsaturated keto-acetates (XIX) and (XX) and, consequently, in the parent amyrins are identical.

In 1955, the important interconversion of an α-amyrin derivative into a β-amyrin derivative was announced. This was achieved when Spring and co-workers (32) converted the three ursadien-3β-yl acetates (XXIV), (XXV) and (XXVI) by treatment with mineral acid, into cleane-11:13(18)-dien-3β-yl acetate (XXVII).
Such conversions led Spring (32) to conclude that α- and β-amyrin have identical configurations at C(9), C(14) and C(17), i.e. that the fusions of rings A/B, B/C and C/D were identical in both series. In the same paper, the cipher (XXVIII) is proposed for the constitution and stereochemistry of α-amyrin.

In this formulation, ring E is considered to be five-membered with an isopropyl group attached to C(18); this formulation will be used throughout.
In this discussion. The choice of the conformation (XXVIII) for α-amyrin, in which the isopropyl group is given β-configuration, is particularly attractive since, among other reasons, the chosen configuration permits the side chain to exert a protective effect upon the double bond in α-amyrin and the carbonyl group in 12-oxoursan-3β-yl acetate, thus affording a satisfying explanation for the inert character of these two functional groups.

The situation concerning the stereochemistry of the D/E-ring junction was still, however, subject to much controversy. This is well illustrated by the fact that there are four theoretically possible arrangements for the locking of rings D and E, and each of these has been included in recent representations of the stereochemistry of α-amyrin. In 1954, Corey and Ursprung (58) suggested that rings D and
E in α-amyrin are cis-β-fused and that the C(18)-methyl group is α-orientated, a conclusion also reached by Spring (32, 60) as outlined above. The argument is based upon the observation that the reactivities of ursolic acid and its β-lactone bear a greater resemblance to those of oleanolic acid (D/E-cis-β) and its β-lactone than to 18α-oleanolic acid (D/E-trans-) and its β-lactone. These observations were supported by a study of the optical rotational differences of the β-lactones and the free acids and their methyl esters. These workers proposed the structure (XXIX) for α-amyrin in which the methyl groups at C(19) and C(20) (β- and α- respectively) have equatorial conformations; the stability of the cis-D/E ring fusion is considered to be due to the fact that inversion at C(18) to a trans-D/E fusion necessitates the rearrangement of the methyl groups at C(18) and C(20) from the thermodynamically more stable equatorial to the less stable axial arrangement.
In 1951, Jeger (65) presented evidence that the configurations at C(17) in α- and β-amyryns are enantiomorphous. Degradation of α- and β-amyryns, as shown below, yielded the monocyclic pyrolysis fragments (XXX) and (XXXI) respectively, which were further degraded to give two esters of equal and opposite rotation and containing the original C(17) of the amyryns as the only asymmetric centre. This observation led Jeger (65) to propose either of partial formulae (XXXII) and (XXXIII) to represent the junction of rings D and E in α-amyrin.

In 1955, Rusinek (66) postulated, without experimental support, a transannular ring D and E for α-amyrin as represented by (XXXIII). Küchler, Jeger and Rusinek, however, in 1964 (90) favoured a cis-cis-arrangement for the D/E-ring junction (XXXV).
In 1953, Huzicka (66) postulated, without experimental support, a trans-fusion for rings D and E, for α-amyrin, as represented by (XXXIV). Zürcher, Jeger and Huzicka, however, in 1954 (30) favoured a cis-a-arrangement for the D/E-ring junction (XXXV).
Finally, in 1954, Beton and Halsall (67) suggested that α-amyrin has a different D/E ring junction from β-amyrin. This suggestion is based upon their observation that α-amyrin can give rise to a hydrocarbon "1-α-amyradiene", by dehydration with phosphorus pentoxide, a reaction not undergone by β-amyrin. They proposed the 17α:18β-fusion (XXXVI) for rings D and E in α-amyrin and formulation (XXXVII) for "1-α-amyradiene".

This Thesis is concerned with a study of the action of dehydrating agents on α- and β-amyrins and derived alcohols, undertaken in the hope that the elucidation of the structures of the products would provide information, concerning the nature of the locking of rings D/E in α-amyrin.

For the sake of clarity of exposition, the Theoretical section is subdivided into the following parts:

A. The Constitution of the Products obtained by Dehydration of α-Amyrin.

B. The Constitution of the Products obtained by Dehydration of β-Amyrin and Related Alcohol
C. The Stereochemistry of the D/E-Ring Junction in \( \alpha \)-Amyrin.

D. The behaviour of Olean-12-ene, 18\( \alpha \)-Olean-12-ene, Olean-13(18)-ene and Olean-18-ene with Mineral Acid.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>( \beta )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-Amyradiene-I ( (\delta )-Amyradiene)</td>
<td>133-135°</td>
<td>+110°</td>
</tr>
<tr>
<td>( \alpha )-Amyradiene-II</td>
<td>110-120°</td>
<td>+127°</td>
</tr>
<tr>
<td>( \alpha )-Amyradiene-III ( (\Lambda )-Amyradiene)</td>
<td>134-136°</td>
<td>-126°</td>
</tr>
<tr>
<td>( \alpha )-Amyradiene-IV</td>
<td>129-131°</td>
<td>+140°</td>
</tr>
</tbody>
</table>

Of these four hydrocarbons, the structure of only \( \alpha \)-Amyradiene-II had been established [73]. This rests consequently only with the elucidation of the structure of \( \Delta ^{2}-\)Amyradienes and \( \alpha \)-Amyradiene-IV.
A. The Constitution of the Products obtained by Dehydration of α-Amyrin.

Reference has already been made in the Historical section to the action of dehydrating agents on triterpenoid compounds. Depending on the reaction conditions employed, four different dienes have been obtained by dehydration of α-amyrin (urs-12-en-3β-ol). The physical constants of these are listed in Table I.

Table I.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>m.p.</th>
<th>[α]D</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Amyradiene-I (d-α-amyradiene)</td>
<td>133-135°</td>
<td>+110°</td>
</tr>
<tr>
<td>α-Amyradiene-II</td>
<td>119-120°</td>
<td>+137°</td>
</tr>
<tr>
<td>α-Amyradiene-III (l-α-amyradiene)</td>
<td>194-195°</td>
<td>-112°</td>
</tr>
<tr>
<td>α-Amyradiene-IV</td>
<td>129-131°</td>
<td>+148°</td>
</tr>
</tbody>
</table>

Of these four hydrocarbons, the structure of only α-amyradiene-II had been established (73). This section consequently deals with the elucidation of the structure of l-α-amyradiene and α-amyradiene-IV.
As a system of nomenclature for the dehydration products of \( \alpha \)-amyren, Allan, Spring, Stevenson, and Strachan (73) proposed that the hydrocarbon, \( C_{27}H_{48} \), having the constitution and stereochemistry represented by (I) be called novursane; this system is used in this Thesis. The configurations of the substituents at \( C(1\alpha), C(1\beta) \) and \( C(1\varphi) \) as well as the nature of ring \( E \) are those recently proposed by Beaton, Spring, Stevenson and Strachan (32) for \( \alpha \)-amyren (II) and are used throughout this discussion.

The Constitution of \( \alpha \)-Amyradiene-I.

This compound was first prepared in 1897 by Vesterberg (68) by dehydration of \( \alpha \)-amyren in light petroleum with phosphorus pentachloride at room temperature. The hydrocarbon, \( C_{27}H_{48} \), isolated has
also been referred to as d-α-amyradiene and α-
amyrilene-I (69, 70, 71, 72). Among other considerations, the observation that α-amyradiene-I gave, on ozonolysis a mixture of acetone and a ketone, C_{11}H_{20}O, led Allan et al. (73) to conclude that it is 8:10:14-trimethyl-5\textsuperscript{\#}-novursa-3(4):12-diene (III), and that the ketone has the structure (IV). The same authors showed that α-amyradiene-I (III) was readily isomerised by trichloroacetic acid to 8:10:14-trimethylnovursa-3(5):12-diene (V).

In 1931, Fosterberg (75) reported the preparation of this hydrocarbon, C_{13}H_{22}, by treatment of α-amyrin with phosphorus pentoxide in benzene at room temperature. Subsequently, Wark obtained a benzene, oil-like hydrocarbon (76), by treatment of α-amyrin or its acetate with hydrochloric acid mixture, and by Killer and Barat (77) by thermal decomposition of α-amyrin methanesulphonic ester.

1-α-Amyradiene is not reduced by sodium and

The Constitution of α-Amyradiene-II.

This hydrocarbon was prepared by Winterstein and Stein (72) by the action of heat on α-amyrin benzoate. Its formation has been considered to occur by cis-elimination of benzoic acid (72, 74).
The Constitution of 1-α-Amyradiene (α-Amyradiene-III).

In 1891, Vesterberg (75) reported the preparation of this hydrocarbon, C_{30}H_{46}, by treatment of α-amyrin with phosphorus pentoxide in benzene at room temperature. It has subsequently been obtained by Ewer, Gillam, and Spring (76) by treatment of α-amyrin or its acetate with hydriodic-acetic acid mixture, and by Noller and Hearst (77) by thermal decomposition of α-amyrin methanesulphonate.

1-α-Amyradiene is not reduced by sodium and amyl alcohol or by catalytic hydrogenation (78). In addition, it does not react with maleic anhydride, and is inert towards the oxidizing agents, potassium permanganate, selenium dioxide and osmic acid (76,79).
Ewen et al. showed that the "1-diene" had the characteristic light absorption at a conjugated heteroannular diene chromophore, and tentatively suggested the partial formulation (VII). Subsequent work showing that the ionic-type dehydrations of 3β-hydroxytriterpenoids involve contraction of ring A led to the proposal (VII) rendered this proposal untenable.

Evidence is now available that ring A in the "1-diene" is indeed five-membered. The non-conjugated diene, α-amyradiene-I has been identified (73) as 8:10:14-trimethyl-5β-novurane-3(4):12-diene (III), and has been isomerised by boron trifluoride into 1-α-amyradiene, indicating that the latter has a five-membered ring A with attached isopropyl group. This conclusion has been supported by preparation of
the "1-diene" from 5:8:14-trimethylnovursa-9(10):12-diene (VIII) by treatment with hydrochloric-acetic acid mixture (73). The latter diene (VIII) has been prepared (73) from 5:8:14-trimethyl-11-oxonovursa-9(10):12-diene (α-amyradienone-III) (IX) by Wolff-Kishner reduction or prolonged treatment with lithium aluminium hydride. α-Amyradienone-III was, in turn, prepared either by ionic dehydration (76) of 11-oxonovursa-12-en-3β-ol (X) or by isomerisation (33,73) of 8:10:14-trimethyl-11-oxonovursa-3(5):12-diene (α-amyradienone-II) (XI). Since Allan et al. (73) have, moreover, shown that α-amyradienone-III has the structure (IX) in which a methyl group is located at C(5), the retention of this feature in the "1-diene" appears extremely probable.
With the nature of ring A in $\text{1-\alpha-amyradiene}$ established as described above, it remains to locate the positions of the two double bonds. Although $\text{1-\alpha-amyradiene}$ appeared to be singularly unamenable to oxidation or reduction (being inert towards hydrogenation, various reducing agents, selenium dioxide, osmic acid), an examination of the action of chromic acid has proved to be significant.

When treated with chromic acid (ca. 1.5 atoms of oxygen), $\text{1-\alpha-amyradiene}$, $C_{30}H_{48}$, yielded a compound isomerisation of the parent compound, which is a $\beta$-unsaturated ketone.
C₉₀H₄₆O, which does not exhibit any high intensity ultraviolet light absorption above 2200 Å. The presence of an isolated ethylenic linkage in this compound was revealed by the yellow colour it gave with the tetranitromethane in chloroform and the ultraviolet maximal absorption at 2050 Å, the intensity of which (ε = 3,500) suggested that the double bond is of the type >C = CH-. The compound, therefore, must have been formed by the oxidation of one of the two double bonds in the "1-diene", but it is not an oxide, since the infra-red absorption spectrum of the compound, C₉₀H₄₆O, contained a strong band at 1698 cm⁻¹, due to an isolated ketone group in a six-membered ring. This non-conjugated unsaturated ketone has been shown to be stable to mineral acid, being recovered unchanged after treatment with hydrochloric-acetic acid mixture for 1 hour.

When treated with alkali (5% methanolic sodium hydroxide) however, the compound, C₉₀H₄₆O, yielded an isomer, the ultraviolet spectrum of which showed a maximum at 2600 Å. (ε = 9,000). This compound is an αβ-unsaturated ketone, formed by the alkali-induced isomerisation of the parent compound, which is a βγ-unsaturated ketone.
More drastic oxidation of the "1-diene" using chromic acid yielded a compound, $C_{20}H_{20}O_2$, the ultraviolet spectrum of which showed a maximum at 2500 Å ($\lambda = 10,500$). This product must, therefore, contain an $\alpha\beta$-unsaturated ketone system together with an isolated carbonyl group. The formation of this compound can be explained by assuming that the new ketonic group has been introduced by the oxidation of a methylene group adjacent to the double bond in the $\beta\gamma$-unsaturated ketone. As expected, the diketone, $C_{20}H_{20}O_2$, was also obtained by chromic acid oxidation of the $\beta\gamma$-unsaturated ketone, $C_{20}H_{20}O$. The "1-diene" and its oxidation products are, therefore, represented by the following partial formulae:

\[
\begin{align*}
\text{1-}\alpha\text{-amy neitherene, } & C_{20}H_{20} \\
\text{Diketone, } & C_{20}H_{20}O_2 \\
\beta\gamma\text{-unsaturated ketone, } & C_{20}H_{20}O \\
\text{\&-unsaturated ketone, } & C_{20}H_{20}O
\end{align*}
\]
The position of the carbonyl group in the αβ-unsaturated ketone and the isolated carbonyl group in the diketone, C₆₀H₈₀O₂, was revealed by an examination of the action of hydriodic acid on 12-oxoursan-3β-yl acetate (XII, R = Ac) and its relatives. The preparations and interrelations of 12-oxoursan-3β-yl acetate (XII, R = Ac), 12-oxo-13α-ursan-3β-yl acetate (XIII, R = Ac) and 3β:12-diacetoxyurs-12-ene (XIV, R = Ac) have recently been described (81). Treatment of each of these acetates and of 12-oxo-13α-ursan-3β-yl benzoate (XIII, R = Bz) with hydriodic-acetic acid mixture under reflux gave, in variable yields, an αβ-unsaturated ketone which was identical with that
obtained as described above from \( \text{1-\( \alpha \)-amyrdiene} \) via the \( \beta \)-unsaturated ketone.

These important reactions demonstrate conclusively that the ketonic function in the \( \beta \gamma \)-unsaturated ketone, and the isolated ketonic group is the diketone, \( C_{30}H_{46}O_2 \), is located at \( C(12) \) and thus one of the two double bonds in the "1-diene" must include \( C(12) \) as an unsaturated centre.

The fact that acid-induced isomerisation of both \( 5:8:14\)-trimethylnovursa-9(10):12-diene (VIII) and \( 8:10:14\)-trimethyl-5\( \gamma \)-novursa-3(4):12-diene (III) lead to the "1-diene" together with the established relationship between the last compound and the \( \alpha\beta \)-unsaturated ketone, \( C_{30}H_{46}O \), indicates that the conversion of 12-oxo-ursan-3\( \beta \)-yl acetate (XII, \( R = \text{Ac} \)) and its relations (XIII and XIV, \( R = \text{Ac} \)) into the \( \alpha\beta \)-unsaturated ketone must involve the contraction of ring A, the movement of the methyl group at \( C(10) \) to \( C(8) \) followed by conjugation of the introduced double bond with the carbonyl group at \( C(12) \). The simplest representation of this conversion includes the intermediate formation of \( 8:10:14\)-trimethyl-12-oxo-novursa-
-3(4)-ene (XV). Approach of a proton to the double bond of (XV) with the synchronous (i) movement of the C(5)-hydrogen to C(5), (ii) movement of the C(10)-methyl group (β) to C(5), (iii) movement of the C(6)-hydrogen (α) to C(10) and finally (iv) loss of a proton from C(11) then leads to the αβ-unsaturated ketone (XVI).
If the reaction mechanism depicted above is correct, the βγ-unsaturated ketone will be represented by (XVII), the diketone, C₆H₄O₂ by (XVIII) and 1-α-amyradiene by (XIX).

Several considerations, however, show that the related representations (XVI), (XVII), (XVIII) and (XIX) are incorrect. Firstly, the intensity of absorption in the ethylenic region of the spectrum precludes the possibility that the double bond in the βγ-unsaturated ketone is tetrasubstituted and exocyclic to two rings as in (XVII). Secondly, the αβ-unsaturated ketone shows maximal absorption in the ultra-violet light at 2600Å, whereas by analogy with other 12-oxo-9(11)-enes, in both the α- and β-
amyris series, a compound of structure \((\text{XVI})\) should show maximal absorption at approximately \(2500\ \text{Å}\). Thirdly, the ultraviolet spectrum of the diketone \(\text{C}_{30}\text{H}_{56}\text{O}_{2}\) shows a maximum at \(2500\ \text{Å}\), characteristic of \(\alpha\beta\)-unsaturated ketones in which the double bond is trisubstituted. Fourthly, the ultraviolet spectrum of the "1-diene" shows a triple-peaked maximal absorption, the principal maximum of which is at \(\text{ca.} 2410\ \text{Å}\). Such absorption is characteristic of the general type of heteroannular diene chromophore in which both double bonds are trisubstituted as in exemplified by eupha-7:9(11)-dien-3β-ol \((\text{XX})\) (62), which has an ultraviolet absorption spectrum identical with that of the "1-diene". Further, the infra-red spectrum of the "1-diene" shows bonds at \(801\text{(s)}\) and \(789\text{(ms)}\) cm\(^{-1}\) characteristic of a trisubstituted double bond (67). In contrast, structure \((\text{XIX})\) for the "1-diene" would be expected to show triple maximal absorption at \(\text{ca.} 2500\ \text{Å}\), by analogy with the known heteroannular 11:13(18)-dienes \((\text{XXI})\) (46, 56, 83) in the \(\alpha\)- and the \(\beta\)-amyris series where one double bond is tetrasubstituted while the other is disubstituted.
Finally, and more important, the oxidation of the αβ-unsaturated ketone with chromic acid gave, in high yield, a bright yellow coloured compound, 
\[\text{C}_{26}\text{H}_{44}\text{O}_{2}\], which shows the ultraviolet spectrum of the fully transoid system:  
\[\begin{array}{ccc}
\text{C} & \text{C} & \text{C} \\
\hline
\text{X} & \text{X} & \text{X}
\end{array}\]  
\((\lambda_{\text{max}} = 2760 \text{ Å}, \epsilon = 8000)\). The formation of this "ene-dione" cannot be accommodated on the basis of structure (XVI) for the αβ-unsaturated ketone, as it proves that a methylene group is adjacent to the double bond.

It is therefore concluded that the αβ-unsaturated ketone cannot be represented by (XVI) and that the double bond in this compound is between \(\text{C}(1\alpha)\) and \(\text{C}(1\alpha)\); i.e., that during the formation of the αβ-unsaturated ketone from 1\(2\)-oxoursanyl acetate, the methyl group at \(\text{C}(1\alpha)\) has migrated. The mechanism of the reaction
may now be represented as including the formation of the intermediate (XV) followed by attack by a proton at the double bond in (XV) thus allowing the fully synchronous (i) movement of the hydrogen at C(3) to C(4), (ii) movement of the C(10)-methyl group (β) to C(11), (iii) movement of the C(11)-hydrogen (α) to C(10), (iv) movement of the C(8)-methyl group (β) to C(9), (v) movement of the C(10)-methyl group (α) to C(9) and (vi) loss of a proton f^2^2^2^2m C(11) to give a double bond between C(11) and C(12).

The αβ-unsaturated ketone, C_{30}H_{40}O, is therefore 5:8α:9β-trimethyl-12-oxo-10α-novurs-13-ene (XXII). Accordingly, the β-unsaturated ketone is 5:8α:9β-trimethyl-12-oxo-10α-novurs-14-ene (XXIII); the diketone C_{30}H_{40}O_{2}, is 5:8α:9β-trimethyl-12:16-dioxo-10α-novurs-14-ene (XXIV); 1-α-amyradiene is 5:8α:9β-trimethyl-10α-novursa-12:14-diene (XXV), and the transoid "ene-dione", C_{30}H_{40}O_{2}, is 5:8α:9β-trimethyl-12:15-dioxo-10α-novurs-15-ene (XXVI) (108).

The concerted reaction detailed above leads to a conformation in which the stereochemistry at C(3),
$O(10)$, $C(a)$ and $C(b)$ coincides with that at $C(18)$, $O(14)$, $C(a)$ and $C(5)$ in cholestane (XXVII) and it is suggested that the urge to adopt this conformation is at least part of the force motivating the reaction (XII) $\rightarrow$ (XXII).

As will be shown later, an essential motivating force for this reaction is the cis-$\beta$-locking of rings D and E.

The decisions made above have been supported by experimental evidence relating the $\alpha\beta$-unsaturated ketone (XXIII) with the "isomers" (XIV). Reaction of the 9,10-dimethyl-10-carboxyl-dihydrosqualene (XII) on lithium aluminium hydride in absolute alcohol (the reaction is almost quantitative), from which one pure pinene exhibiting a maximum absorption at 3180 $\AA$ ($\varepsilon = 6200$) has been isolated. Treatment of the mixture with ethanolic hydrochloric acid yielded, after hydrolysis, $\alpha\beta$-acetic acid mixtures. The $\alpha\beta$-acetic acid mixtures are identical with those from 7-$\alpha$-oxyxurin obtained by dehydration of 7-$\alpha$-oxyxurin with phosphorus pentoxide with hydrochloric-acetic acid mixture.

$(\text{XII}, \text{XIII}, \text{XIV}, R = H)$
The decisions made above have been supported by experimental evidence relating the αβ-unsaturated ketone (XXII) with the "1-diene" (XXV). Reduction of 5:8α:9β-trimethyl-12-oxo-10α-novurs-13-ene (XXII) with lithium aluminium hydride in ether gave a mixture of epimeric allylic alcohols (XXVIII), from which one pure epimer exhibiting a maximal absorption at 2160 Å (λ = 5300) has been isolated. Treatment of the mixture with either acetic anhydride and pyridine or hydrochloric-acetic acid mixture gave 5:8α:9β-trimethyl-10α-novursa-12:14-diene (XXV), identical with 1-α-amyradiene obtained by dehydration of α-amyrin with phosphorus pentoxide or with hydriodic-acetic acid mixture.
A mechanism similar to that described above for the formation of the αβ-unsaturated ketone (XXII) is postulated for the conversion of α-amyrin (urs-12-en-3β-ol) (II) into 1-α-amyradiene (XXV), with the difference that final proton elimination occurs from C(15). The full mechanism of the conversion is represented in the following sequence:
The conversion of α-amyrin (II) into the "1-diene" (XXV) by shaking with phosphorus pentoxide in benzene at room temperature is considered to be a fully concerted reaction; both 8:10:14-trimethyl-5-novursa-3(4):12-diene (III) and the 3(5):12-isomer (XXIX), are recovered unchanged after the same treatment (84).
Recently, Béton and Halsall (67) proposed structure (XXX) for 1-α-amyra dien e involving the migration of the methyl groups at C(3) and C(19) to the positions indicated. They attributed this postulated group migration to a conformational driving force resulting from certain stereochemical features present in α-amy rin, but not in β-amy rin (which does not give an analogous 1-β-amyra diene).

The structure of α-amy rin providing such a conformational driving force, they conclude, is that which has the D/E ring junction trans and the C(17)-methyl group α-orientated (XXXI):
Apart from the stereochemical assignments given to the D/E ring junction in α-amyrin, their formulation of 1-α-amyrdiene cannot be correct; this follows from the experiments described above.

Reference has been previously made to the oxidation of the αβ-unsaturated ketone (XXII) with chromic acid to give the transoid "ene-dione" formulated as (XXVI). This compound, C_{30}H_{44}O_{2}, identified as 5:8α:9β-trimethyl-12:15-dioxo-10α-novurs-13-ene, was isolated as yellow needles, exhibiting ultraviolet maximal absorption at 2260 and 2760 Å. (λ = 3400 and 8000). It was isolated by chromatography from a mixture containing other oxidation products. These included two isomeric compounds, C_{30}H_{44}O_{2}. One, isolated as flat orange needles, exhibited maximal
absorption at 2220 and 2990 Å. (λ = 4600 and 5600). The other, had a slightly different spectrum, 
λ max. 2220 and 2960 Å. (λ = 3500 and 6000) and was isolated as orange-yellow needles. These isomeric 'ene-triones' are considered to be 5:6α:9β-trimethyl-12:15:16-trioxo-10α-novur-13-ene (XXXII) and 5:6α:9β-trimethyl-11:12:15-trioxo-10α-novur-13-ene (XXXIII).

No distinction between these two structures can be made at present.

Since a characteristic reaction of a conjugated enedione is its reduction by zinc dust to yield a saturated 1:4-diketone, -CH = CH - 0 - 0 - 
-CH - CH - 0 - , the reduction of the enedione
(XXVI) was investigated.

Using activated zinc dust in neutral solvent the starting material was recovered. Treatment with zinc dust in acetic acid, however, yielded a laevo-rotatory compound ([α]_D -39°), which gave a positive reaction with tetranitromethane and exhibited light absorption in the ethylenic region (λ_{max} 2080 Å, ε = 6500) and for which analysis indicated the molecular formula C_{36}H_{46}O_{12}. Acetylation of this compound readily gave an acetate, C_{36}H_{46}O_{12} preserving the laevo-rotation of the alcohol ([α]_D -37°), and which, again, gave a position that with tetranitromethane and exhibited maximal absorption at 2080 Å (ε = 3700).

A satisfactory explanation of this reaction is not apparent; the simplest representation of the reduction product and its acetate, according to the analytical and spectroscopical determinations, would be (XXXIV, R = H) and (XXXIV, R = Ac) respectively.

Infra-red examination of the alcohol and the acetate, however, provided information which is difficult to reconcile with the above formulation.
The infra-red spectrum of the alcohol showed peaks at 3300 cm\(^{-1}\) (hydroxyl group) and at 1690 cm\(^{-1}\) (carbonyl group). Two possible explanations for this low frequency of carbonyl absorption, as compared with a six-membered ring ketone, are (i) hydrogen-bonding between carbonyl and hydroxyl groups, observed in 17\(\alpha\)- and 17\(\beta\)-hydroxy-20-keto steroids (85), and (ii) the presence of a cyclopropane bridge in conjugation with the ketone, as observed in 3\(\beta\)-cyclo-6-keto steroids (86, 87). The infra-red spectrum of the acetate contained peaks at 1754 and 1720 cm\(^{-1}\) (acetoxy group and carbonyl groups) and at 1240 cm\(^{-1}\) (acetoxy group). This displacement towards higher frequency for the acetoxy and carbonyl groups is attributable to dicarbonyl interaction as is observed...
in 17β-acetoxy-20-keto steroids (85). These observations, consequently indicate the presence of an α-ketol group in the reduction product, in which case the hydroxyl group should be tertiary, notwithstanding its ease of acetylation. Three possible formulations, therefore, emerge on the basis of the infra-red observations: (XXXV), (XXXVI) and (XXXVII), where R = H for the alcohol and Ac for the acetate.

Formula (XXXVIII), possible on the infra-red spectrum of the alcohol would appear to be precluded by the change of carbonyl frequency on acetylation.

alternative formulations (XXXIX) and (XL) tentatively proposed for the mineral acid product from the alcohol and the acetate. A more detailed examination of the infrared of the two will be required to enable the structure of the product to be determined.
Attempts to locate the hydroxyl group by chemical methods have given results difficult to reconcile with formulations (XXXV - XXXVII).

Surprisingly, chromic acid oxidation of the alcohol (1 mole of oxygen) gave back the enedione (XXVI), as did alkaline hydrolysis of the acetate. Mild treatment of both the alcohol and the acetate with hydrochloric-acetic acid mixture gave a dextro-rotatory product ([\(\alpha\])\(_D^0\) + 18\(\circ\)), which exhibited a remarkable maximal absorption at 3220 A. ([\(\varepsilon\] = 5500). This absorption is in fair agreement for a diene, 

\[ \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \]

chromophore, as shown in the alternative formulations (XXXIX) and (XL) tentatively proposed for the mineral acid product from the alcohol and the acetate. A more detailed examination of the reduction of the ene-dione will be required to enable the structure of the product to be determined.
In the opinion of the author this interesting behaviour of the ene-dione with zinc dust is well worthy of further study.

In high yield by treatment of e-amyrin at room temperature with methanesulphonyl chloride. These authors reported that whilst the treatment of methyl e-amyrin with methanesulphonic acid gave a glassy solid treatment with pyridine under reflux gave a hydrocarbon, C₃₈H₆₄, colorless in the ultraviolet light above 3200 Å, and which they called e-amyridione-IV. Since no experimental details were reported for the preparation, and no proposals made for the constitution of this dione, the reaction was reinvestigated.

Experiments were carried out with a view to finding the optimal conditions for the preparation of e-amyridione-IV. It was found that treatment of methyl e-amyrin (XII) under reflux in pyridine solution for six days gave the best yield (ca. 80%) of e-amyridione-IV. Although heating methyl e-amyrin in pyridine in an autoclave at 110°C for 15 hours gave a slightly lower yield (ca. 65%), this method was preferred.
The Constitution of \( \alpha \)-Amyradiene-IV.

Noller and Hearst (77) have reported the preparation of mesyl \( \alpha \)-amyrin (\( \alpha \)-amyrin methanesulphonate) in high yield by treatment of \( \alpha \)-amyrin at room temperature with methanesulphonyl chloride. These authors reported that whilst the treatment of mesyl \( \alpha \)-amyrin with methanolic hydrochloric acid gave "a glossy solid", treatment with pyridine under reflux gave a hydrocarbon, \( \text{C}_{6}\text{H}_{12} \), which was transparent to the ultraviolet light above 2200 A., and which they called \( \alpha \)-amyradiene-IV. Since no experimental details were reported for the preparation, and no proposals made for the constitution of this diene, the reaction was reinvestigated.

Experiments were carried out with a view to finding the optimum conditions for the preparation of \( \alpha \)-amyradiene-IV. It was found that treatment of mesyl \( \alpha \)-amyrin (XLI) under reflux in pyridine solution for six days gave the best yield (ca. 50%) of \( \alpha \)-amyradiene-IV. Although heating mesyl \( \alpha \)-amyrin in pyridine in an autoclave at 210° for 18 hours gave a slightly lower yield (ca. 43%), this method was preferred.
a-Amyradiene-IV, like all the other diene hydrocarbons derived from α-amyrin except the "1-diene", is dextrorotatory (table 1). The ultraviolet absorption spectrum exhibits an apparent maximum at 2070 Å, showing that the diene system is not conjugated; the low intensity of absorption (ν = 3800) is, however, noteworthy.

The elucidation of the structure of α-amyradiene-IV has been considerably facilitated by the observation that 1-α-amyradiene (5:8a:9β-trimethyl-10a-novursa-12:14-diene) (XXV) is obtained, in low yield, when α-amyradiene-IV was refluxed with hydrochloric-acetic acid mixture. This conversion suggests, in the first place, that the diene-IV possesses a novursane skeleton with an isolated double bond, located probably at positions 2:3 or 4:25, since the hydrocarbons with double bond at 3:4 and 3:5 are known and differ from the diene-IV. The possibility of the presence of a cyclopropane system was ruled out by the results of ozonolysis of α-amyradiene-IV. Thus from low temperature treatment with ozone, formaldehyde, isolated as its dimedone derivative and a ketone, C_{20}H_{30}O, were isolated. This proves that the new double bond
in α-amyradiene-IV lies between C(4) and C(23). The compound is, therefore, considered to be 8:10:14-trimethyl-5\(^\beta\)-novursta-4(25):12-diene (XLII) and the methyl ketone is represented by (XLIII).
Treatment of α-amyradiene-IV with mild acidic reagent (trichloro-acetic acid) did not yield a homogeneous product. A final experiment in this series was the investigation of the action of heat, (100°), on solid mesyl α-amyrin. This gave, in a very high yield, 1-α-amyradiene (XXV). This reaction is considered to have proceeded via α-amyradiene-IV (XLIII), formed as a discrete intermediate, which was then isomerised to the "1-diene" (XXV) under the influence of methanesulphonic acid produced by thermal elimination.

<table>
<thead>
<tr>
<th>Hydrosarcon</th>
<th>Tp.</th>
<th>[α]D</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-Amyradiene-I</td>
<td>167-172°</td>
<td>+210°</td>
</tr>
<tr>
<td>8-Amyradiene-II</td>
<td>130-136°</td>
<td>+138°</td>
</tr>
<tr>
<td>8-Amyradiene-III</td>
<td>102°</td>
<td>+120°</td>
</tr>
</tbody>
</table>
B. The Constitution of the Products obtained by Dehydration of \( \beta \)-Amyrin and Related Alcohols.

1. Dehydration of \( \beta \)-Amyrin.

Dehydration experiments analogous to those carried out on \( \alpha \)-amyrin have been performed on \( \beta \)-amyrin (I). Three hydrocarbon dienes derived from \( \beta \)-amyrin, namely \( \beta \)-amyadiene-I, \( \beta \)-amyadiene-II, and \( \beta \)-amyadiene-III, have been described in the literature \((68,71,72)\). Of these hydrocarbons, the physical constants of which are listed (table 2), the structure of only \( \beta \)-amyadiene-II has been established \((88)\).

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>m.p.</th>
<th>([\alpha]_D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )-Amyadiene-I</td>
<td>167-172°</td>
<td>+110°</td>
</tr>
<tr>
<td>( \beta )-Amyadiene-II</td>
<td>148-150°</td>
<td>+139°</td>
</tr>
<tr>
<td>( \beta )-Amyadiene-III</td>
<td>102°</td>
<td>+120°</td>
</tr>
</tbody>
</table>

The investigation described in this section is concerned with the elucidation of the structures of
\( \beta \)-amyrdiene-I and \( \beta \)-amyrdiene-III. In addition, two further dienes have been prepared, the novursane counterparts of which are known and have been dealt with in the previous section. As a system of naming the \( \beta \)-amyrin dehydration products, the hydrocarbon, \( C_{97}H_{16} \), having the constitution and stereochemistry represented by (II) is called novoleanane.

The Constitution of \( \beta \)-Amyrdiene-II.

This compound, the analogue of \( \alpha \)-amyrdiene-II, was first prepared by Winterstein and Stein (72) by heating \( \beta \)-amyrin benzoate (III) at 270-300\(^\circ\), and later by Dieterle, Brass and Schaal (92) by heating \( \beta \)-amyrin with \( p \)-toluenesulphonyl chloride in pyridine at 100\(^\circ\).
The compound is considered to have been formed by cis-elimination of benzoic acid and p-toluene-sulphonic acid respectively, without involving any further rearrangements (86). Noller and Hearst (77) reported that β-amyra diene-II could be prepared by heating β-amyrin methanesulphonate (IV) in pyridine. In the author's hands, however, the compound has been obtained directly by treatment of β-amyrin with methanesulphonyl chloride. β-Amyra diene-II, consequently, is oleane-2:12-diene (V).

Catalytic hydrogenation of oleane-2:12-diene (V) affords β-amyrone-II (72), formed by the saturation of the 2:3-double bond, and identical with the product prepared by Wolff-Kishner reduction of 3-oxo-olean-12-ene (VI).

In β-amyrone-II the centre of unsaturation must be regarded to be the same as in the parent amyrin since under the reduction conditions leading to its formation, it is unlikely that isomerisation has taken place. β-Amyrone-II was therefore formulated as oleane-12-ene (VII) (53).
The Constitution of $\beta$-Amyradiene-I.

This hydrocarbon, the counterpart of $\alpha$-amyradiene-I and first obtained by Vesterberg in 1887 (68), is prepared by treatment of $\beta$-amyrin (I) with phosphorus pentachloride in light petroleum (68,70,71,72); it is also referred to in the literature as $\beta$-amyrilene-I. The presence of two double bonds is apparent from the
observations of Bauer and Starke (89) and Ruzicka (70,90) who obtained a monoepoxide and diepoxide, although the constants reported are not in good agreement. Various reduction products of \( \beta \)-amyraidene-I have also been described, as summarised below:

\[
\begin{align*}
\beta \text{-Amyraidene-I} & \quad \text{H}_2/\text{Pt} \quad \text{Na}/\text{AmOH} \quad (91) \\
& \quad (70,72,90) \\
& \quad \beta \text{-Amyrene-I} \quad \text{m.p.93° or 92°} \\
& \quad \beta \text{-Amyrene-Ia} \quad \text{m.p.209°, [\( \alpha \)]_D +115°} \\
& \quad (72) \\
& \quad \beta \text{-Amyrene-V} \quad \beta \text{-Amyrene-Ib} \\
& \quad \text{m.p. 84°,} \quad \text{m.p.104°} \quad (72) \\
& \quad [\( \alpha \)]_D +83° \quad (70,90,91) \\
\end{align*}
\]
β-Amyradiene-I exhibits selective absorption in the ultraviolet region at 2080 Å of high intensity ($\lambda = 9,200$). By analogy with the product, α-amyradiene-I, obtained in a similar way from α-amyrin (68,69,70,71,72) it was believed that β-amyradiene-I was formed by a similar ring-A contraction. The high intensity of the absorption spectrum of β-amyrilene-I suggests that one of the isolated double bonds is highly substituted. Ozonolysis of β-amyrilene-I yielded acetone, which was identified as its 2:4-dinitrophenylhydrazone, and a ketone, C$_{97}$H$_{13}$O, which closely resembles in physical properties, the isomeric ketone obtained in the same way from 8:10:14-trimethyl-5-$\delta$-novursa-3(4):12-diene (IXa) (73), and was shown to contain a carbonyl group in a five-membered ring by infra-red examination. The double bond between C$_{18}$ and C$_{18}$ is not affected in the course of ozonolysis, the ketone giving a yellow colour with tetranitromethane. The ketone, therefore, is formulated as (VIII) and its formation shows that the double bond in β-amyrilene-I is exocyclic to ring A and consequently, β-amyradiene-I has the constitution represented by (IX).
The cis-β-fusion assigned to rings A and B in the ketone (VIII) is based on the observation that the change in the value of molecular rotation (+470°) accompanying the conversion of β-amyrin (I) into the ketone (VIII) accords well with the values observed for comparable reactions (50). The configuration of the hydrogen atom at C(8) in β-amyrlene-I is uncertain. β-Amyrlene-I is, therefore, named systematically.
Treatment of \( \beta \)-amyrydene-I (IX) with boron trifluoride-acetic acid, under conditions which isomerise the analogous novursa-3(4):12-diene (IXa) to \( \Delta \)-amyrydene (73), gave an oil, the ultraviolet spectrum of which indicated the presence of only a small proportion of a conjugated diene (ill-defined maxima at 2130 and 2500 Å). This difference is significant and will be discussed later.

The Constitution of \( \beta \)-Amyrydene-III.

This compound, also known as \( \beta \)-amricalene-III was prepared by Dieterle, Brass, and Schaal (92) by prolonged treatment of \( \beta \)-amyrin with phosphorus pentachloride. In this investigation, it was readily obtained by isomerisation of \( \beta \)-amyrydene-I (IX) with trichloroacetic acid. This diene exhibits maximal absorption at 2090 Å. (\( \epsilon = 9000 \)), and a comparison (table 3) of the physical properties of the various dehydration products from \( \alpha \)- and \( \beta \)-amyrin and related alcohols, supports the view that \( \beta \)-amricalene-III is the counterpart of 8:10:14-trimethylene-3(5):12-diene (Xa), which has been obtained by a similar
isomerisation procedure. \( \beta \)-Amyrilene-III is, therefore, 8:10:14-trimethylnovolena-3(5):12-diene \( \text{(X)} \).

Treatment of 14-ace-8-en-12-yl acetate \( \text{(XI)} \), \( \text{C}_{13} \text{H}_{24} \text{O} \), with hydrochloric-acetic acid mixture under reflux yielded a compound, \( \text{C}_{29} \text{H}_{46} \text{O} \), which gave a negative test for an estradiol ether. Spectroscopic analysis and mass spectrometry showed it contained no conjugated double bonds. The ultraviolet spectrum suggested in the literature. The ultraviolet spectrum of 12:13-double bond does not migrate during the conversion of \( \beta \)-amyrin into the dienes \( \text{(IX)} \) and \( \text{(X)} \), the double bond in \( \alpha \)-amyrin being known to be stable to strong acid conditions \( \text{(32, 53)} \). Again, attempted isomerisation of the 3(5):12-diene \( \text{(X)} \) with hydrochloric-acetic acid mixture, under various conditions, gave oily products, the ultraviolet spectra of which revealed the presence of only small quantities of conjugated heteroannular dienes (triplet max. at \( 2420, 2480 \) and \( 2580 \) \( \text{A} \)).
2. Dehydration of 11-Oxo-olean-12-en-3β-ol.

(Oxonovoleanadiene Products)

Treatment of 11-oxo-olean-12-en-3β-yl acetate (XI), R = Ac with hydriodic-acetic acid mixture under reflux yielded a compound, C₃₀H₄₂O₂, which gave a negative test with tetranitromethane. The ultraviolet spectrum of the compound contained three maxima: 2060 Å (c = 6,900), and 2560 Å (c = 10,700) and 2870 Å (c = 9,300).

Several compounds containing the conjugated "enonene" chromophore \( \text{C} = \text{C} - \text{C} = \text{C} - \text{C} = \text{C} \) have been reported in the literature. The ultraviolet spectra of many di-transoid conjugated enones have been described 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. On the other hand, a few compounds containing the chromophore \( \text{C} = \text{C} = \text{C} - \text{C} = \text{C} \) in which the geometry is cisoid-transoid, are known, and they show characteristic absorption spectra containing three separate maxima. Thus, 12-oxo-oleana-9(11):13(18)-dien-3β-yl acetate (XII) (93) exhibits a triple maxima absorption spectrum \( \lambda_{\text{max}} \) 2080, 2600
and 2950 A, (e = 9000, 9250 and 8450) which is almost identical with that exhibited by 12-oxoursa-9(11):13(16)-dien-3β-yl acetate (XIII) (94) (table 5). Further, a novursane enonene has been prepared from 11-oxoursa-12-en-3β-ol (XIV), R = H) by dehydration with hydriodic-acetic acid mixture (76) and has been shown to contain a similarly constrained chromophore and has been identified as 5:8:14-trimethyl-11-oxonovursa-9(10):12-diene (XV) (73). It is, therefore, concluded that the novoleanane derivative obtained by dehydration of the acetate (XI), R = Ac) with hydriodic-acetic acid mixture, must contain the same conjugated cisoid-transoid enonene chromophore. It is formulated as 5:8:14-trimethyl-11-oxo-18α-novoleana-9(10):12-diene (XVI). The C(18)-hydrogen is α-orientated, i.e., inversion at this centre to the more stable (α) configuration has occurred during the reaction. Such inversion of the C(18)-hydrogen, when adjacent to an αβ-unsaturated ketone system, is a familiar process, since 11-oxo-olean-12-en-3β-yl benzoate (XI), R = Bz) is known to yield the more stable 18α-epimer (XVII, R = Bz) by treatment with strong alkali (59) and it is, therefore, likely that hydriodic acid had brought...
about the same result at C(1a). This has been conclusively verified by the preparation of the same oxo-18α-novoleanadiene (XVI) by similar treatment of 11-oxo-18α-cleane-12-en-3β-yl acetate (59) (XVII, R = Ac) with hydriodic-acetic acid mixture.
The action of hydriodic acid on 11-oxo-clean-12-ene-3β-ol (XI, R = H) must, therefore, have led to the contraction of ring A, the migration of the methyl group attached to C(10) to C(8) with the subsequent conjugation of the introduced double bond in position 9:10 and the inversion at C(18). This conversion is outlined in the following sequence:-

The method described for the conversion of 3β-synmyrin into the conjugated oexene (XVI) duplicates that used for the conversion of α-synmyrin into the enone (XIV). The methyl-11-oxene (XV) is free from unsaturation at C(18) in contrast to the oexene (XVIII) apart from the physical properties (tables 3 and 4). For example, treatment with lithium aluminium hydride at 0°C, gave, in both cases, analogous products which behaved similarly when treated with mineral acid. Again reduction of the oexene (XV) and (XVI) by the Wolff-Kishner method afforded products which showed no conjugation of the double bond.
The oxonovoleanadiene (XVI) has also been prepared by a similar treatment of 11-oxo-cleane-12:18-dien-3β-yl acetate (XVIII) (84, 96, 96) a reaction which must have involved the reduction of the 18:19-double bond, the C(18)-hydrogen adopting the α-configuration, besides the above-outlined contraction of ring A and migration of the C(18)-methyl group to C(α).

The method described for the conversion of 6-amyrin into the conjugated enonene (XVI) duplicates that used for the conversion of α-amyrin into the isomeric 5:8:14-trimethyl-11-oxonovursa-9(10):12-diene (XV) apart from inversion at C(18) in the former case. There is again, therefore, a general similarity between the reactions of the conjugated enonenes (XV) and (XVI) apart from the physical properties (tables 3 and 4). For example, treatment with lithium aluminium hydride at 0°C, gave, in both cases, analogous products which behaved similarly when treated with mineral acid. Again reduction of the enonenes (XV) and (XVI) by the Wolff-Kishner method gave analogously constituted products, (see later).
### Table 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maxima Å (ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-oxo-oleana-9(11):13(18)-dien-3β-ol acetate (44)</td>
<td>2080(9000), 2600</td>
</tr>
<tr>
<td></td>
<td>(9250), 2950(8450)</td>
</tr>
<tr>
<td>12-oxo-oleana-9(11):13(18)-dien-3β-ol (44)</td>
<td>2100(7500), 2600</td>
</tr>
<tr>
<td></td>
<td>(8600), 2950(8100)</td>
</tr>
<tr>
<td>12-oxoursa-9(11):13(18)-dien-3β-y1 acetate (45)</td>
<td>2070(9000), 2610</td>
</tr>
<tr>
<td></td>
<td>(9700), 2940(8100)</td>
</tr>
<tr>
<td>12-oxoursa-9(11):13(18)-dien-3β-ol (45)</td>
<td>2080(8050), 2630</td>
</tr>
<tr>
<td></td>
<td>(9600), 2950(7400)</td>
</tr>
<tr>
<td>5:8:14-Trimethyl-11-oxonovursa-9(10):12-diene (29)</td>
<td>2040(9900), 2560</td>
</tr>
<tr>
<td></td>
<td>(10,000), 2900(10,200)</td>
</tr>
<tr>
<td>5:8:14-Trimethyl-11-oxo-18α-novoleana-9(10):12-diene (39)</td>
<td>2060(6,900), 2560</td>
</tr>
<tr>
<td></td>
<td>(10,700), 2870(9300).</td>
</tr>
</tbody>
</table>


Ewen, Gillam and Spring (76) reported that dehydration of ursa-9(11):12-dien-3β-ol (XIX) with phosphorus pentachloride in light petroleum at room temperature yielded strongly characteristic ultraviolet spectra of which should be introduced by dehydration of ursa-9(11):12-dien-3β-ol.
phosphorus pentachloride gave a triene, "d-a-amyra-triene", the constitution of which, 8:10:14-trimethyl-novursa-3(4):9(11):12-triene (XX), has been established (73).

Treatment of β-amyradienol-I (oleana-9(11):12-dien-3β-ol) (95) (XXI) with phosphorus pentachloride in light petroleum at room temperature yielded a strongly dextro-rotatory hydrocarbon, C₃₀H₄₈ \([\alpha]_D^o + 356^\circ\), the ultraviolet spectrum of which showed that the double bond introduced by dehydration is remote from the homoannular conjugated system in ring C, (max. at 2060 and 2800 Å, \(\epsilon = 8300\) and 8000). This triene is considered to have been formed by the contraction of ring A and the formation of an ethyleni
Linkage situated either between C(3) and C(4) or between C(4) and C(3), i.e., it is considered to be 8:10:14-trimethyl-5α-novoleana-3(4):9(11):12-triene (XXII) or the 3(5):9(11):12-triene isomer (XXII a). Its method of formation and its strong dextrorotation, in comparison with the novursa-3(4):9(11):12-triene isomer, (table 3) favours the 3:4-position for the isolated double bond.

Treatment of 8:10:14-trimethyl-5α-novoleana-3(4):9(11):12-triene (XXII) with trichloroacetic acid, in the expectation that the double bond at 3:4 might isomerise to the 3:5 position, yielded a strongly laevorotatory isomeric triene ([α]_D^20 -400°) which gave a deep red-brown colour with tetranitromethane and which exhibited a triple absorption spectrum (λ_{max} 286c, 2950 and 3080 Å, ε = 31,000, 36,000 and 25,400). The properties are in agreement with the postulated structure 5:8:14-trimethylnovoleana-9(10):11:13(18)- triene (XXIII). A satisfactory mechanism involving the synchronous (i) protonation of the double bond from the rear (α) side, (ii) movement of the C(3)-hydrogen to C(3), (iii) movement of the C(18)-methyl group (β) to C(3), and (iv) loss of a proton from
C(18), is proposed. Rearrangement of the methyl groups at C(9) and C(18) is not involved. This triene has also been obtained directly from ckey-
9(11):12-dien-3β-ol (XXI) by shaking with phosphorus pentoxide in benzene at room temperature (84, 95).
Dehydration of oleana-11:13(18)-dien-3β-ol (XXIV) with phosphorus pentoxide in benzene at room temperature also afforded 5:8:14-trimethylnovolena-9(10):11:13(18)-triene (XXIII). The transoid triene (XXIII) has analogous properties to 5:8:14-trimethylnovursa-9(10):11:13(18)-triene (1-α-amyraatriene) (XXV) obtained by phosphorus pentoxide dehydration of ursa-9(11):12-dien-3β-ol (XIX) at room temperature (73, 76) (see table 3).
A compound having an analogously constituted triene system, ergosta-4:6:8(14):22-tetraene (XXIIIa) contains a chromophore comparable with that in (XXIII) and (XXV) and exhibits a triple maxima absorption spectrum, the principal band of which is at 2630 Å. (ε = 33,000) (97). The value (2940 Å) calculated for the location of the principal band in the spectrum of the heteroannular triene (XXV) using Woodward’s empirical rules, is in excellent agreement with the observed value.

Treatment of either oleana-9(11):12-dien-3β-ol (XXI) or the novoleana-3(4):9(11):12-triene (XXII) with hydriodic-acetic acid mixture under reflux gave an oil which exhibited no absorption above 2200 Å.

### Table 4.

<table>
<thead>
<tr>
<th>Dehydration of oleana-11(13) 2-oxytrienol-II</th>
<th>[α]_P (in chloroform)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydration of oleana-11(13) 2-oxytrienol-II</td>
<td>[α]_P (in chloroform)</td>
</tr>
<tr>
<td>Novoursane Derivative</td>
<td>+110°</td>
</tr>
<tr>
<td>Novoleanane Derivative</td>
<td>+110°</td>
</tr>
<tr>
<td>8:10:14-Trimethyl-5-</td>
<td>+123°</td>
</tr>
<tr>
<td>-3(4):12-diene</td>
<td>+120°</td>
</tr>
<tr>
<td>8:10:14-Trimethyl-3(5):12-</td>
<td>+210°</td>
</tr>
<tr>
<td>-diene</td>
<td>+215°</td>
</tr>
<tr>
<td>Ketone, C_{27}H_{42}O</td>
<td></td>
</tr>
</tbody>
</table>
Dehydration of oleana-11:13(18)-dien-3β-ol (β-amyradienol-II) (XXIV) (46,56,83) using phosphorus pentachloride in light petroleum at room temperature gave a laevorotatory hydrocarbon, C_{36}H_{40}, ([α]_D^{29} -49°), the ultraviolet spectrum of which revealed the presence of an isolated ethylenic bond together with the

<table>
<thead>
<tr>
<th>Compound</th>
<th>Novursane Derivative</th>
<th>Novoleanane Derivative</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:8:14-Trimethyl-11-oxo--9(10):12-diene</td>
<td>+170°</td>
<td>+122°(18a)</td>
</tr>
<tr>
<td>5:8:14-Trimethyl--9(10):12-triene</td>
<td>-358°</td>
<td>-450°(18a)</td>
</tr>
<tr>
<td>5:8:14-Trimethyl--9(10):11:13(18)-trienes</td>
<td>-450°</td>
<td>-400°</td>
</tr>
<tr>
<td>5:8:14-Trimethyl-12-diene</td>
<td>+120°</td>
<td>+103°(18a)</td>
</tr>
<tr>
<td>5:8a:9β-Trimethyl-12-oxo--13-ene</td>
<td>-41°</td>
<td>-32°(18ξ)</td>
</tr>
<tr>
<td>5:8a:9β-Trimethyl-10α--12:14-diene</td>
<td>-111°</td>
<td>-83°(18ξ)</td>
</tr>
<tr>
<td>5:8a:9β-Trimethyl-12:15-dioxo-10α--13-ene</td>
<td>+86°</td>
<td>-7°(18ξ)</td>
</tr>
</tbody>
</table>
original heteroannular diene system. As with the analogous reaction (XXI) \(\rightarrow\) (XXII), the isolated double bond in the new triene can be accommodated either in position 3:4 or position 3:5 in the basic novoleanane skeleton. This compound is therefore considered to be 8:10:14-trimethyl-5\(\frac{5}{2}\)-novoleana-3(4):11:13(18)-triene (XXVI) or the -3(5):11:13(18)-isomer (XXVIa). No corresponding triene has yet been prepared in the novursane series. Contrary to expectation, the triene (XXVI) or (XXVIa) was recovered unchanged after treatment with trichloroacetic acid at room temperature or with hydrochloric-acetic acid mixture under reflux and thus failed to isomerise to a fully conjugated triene.

Reference has already been made to the similarity between the oxo-diene (XV) and (XVI) with respect to physical properties, and origin. There is, moreover, a similarity between the reactions of these two compounds, whereby analogously constituted trienes are formed. Thus, treatment of 5:8:14-trimethyl-11-oxonovursa-9(10):12-diene (XV) and of 5:8:14-trimethyl-11-oxo-18\(\alpha\)-novoleana-9(10):12-diene (XVI) with lithium aluminium hydride in ether at 0°C gave strongly laevo-
-rotatory trienes ([α]_D -358° and -450° respectively) which exhibited maximal absorption in the ultraviolet at 3200 Å (ε = 15,000) and 3150 Å (ε = 14,000) respectively for the two products. These have been formulated as 5:8:14-trimethylnovusene-1(10):9(11):12-triene (XXVII) and 5:8:14-trimethyl-18α-novolena-1(10):9(11):12-triene (XXVIII) respectively (73, 84, 95). Further, mineral-acid isomerisation of the trienes (XXVII) and (XXVIII) gave the analogous transoid trienes.
5:8:14-trimethylnovursa-9(10):11:13(18)-triene (XXV)
and 5:8:14-trimethylnovoleana-9(10):11:13(18)-triene (XXIII) respectively (73,84,95).

In all the reactions described in this section, it is to be observed that the methyl groups attached to
C(9) and C(14) are unaffected, and that only the methyl

A final reaction in this series has been carried
out. Reduction of 5,8:14-trimethyl-11-endo-13-exo-novolena-
-9(10) gave the dione, m.p. 230° (62). 

(6 = 10,000). These properties and the origin of the
compound show that it is an unconjugated diene formed
A final reaction in this series has been carried out. Reduction of 5:8:14-trimethyl-11-oxo-18α-novolane-9(10):12-diene (XVI) by the Wolff-Kishner method, afforded a product, C_{30}H_{38}, which gave a strong tetranitromethane reaction and exhibited strong selective absorption in the ethylenic region at 2080 Å. (ε = 10,500). These properties and the origin of the compound show that it is an unconjugated diene formed...
by reduction of the carbonyl group at C(11) in the enonene (XVI). This compound, therefore, is considered to be 5:8:14-trimethyl-18α-novoleana-9(10):12-diene (XXIX). It has also been formed by treatment of the enonene (XVI) with lithium aluminium hydride in ether under reflux, together with the triene (XXIII) presumably formed by rearrangement of the triene (XXVI) produced as an intermediate. This behaviour of the oxonovoleanadiene (XXVI), again, finds a counterpart in the novuransane series. When 5:8:14-trimethyl-11-oxonovursa-9(10):12-diene (XXV) was reduced by refluxing with lithium aluminium hydride or by the Wolff-Kishner method, it gave an analogously constituted diene which has been formulated as 5:8:14-trimethylnovursa-9(10):12-diene (XXX) (73).
It may be generally concluded that the 3(4):12-, 3(5):12- and 9(10):12-dienes, the 11-oxo-9(10):12-dienes and the three 3(4 or 5):9(11):12-, 1(10):9(11):12- and 9(10):11:13(18)-triines in both the novursane and the novoleanane series prepared by comparable methods, have analogous structures (apart from the 18a-configuration in the oxo-novoleanadiene and its derivative) similar physical properties (see tables 3 and 4) and generally similar reactions. In the course of these dehydration reactions the only methyl group migration involved is from C(10) to C(5). These observations of parallel behavior lead to the conclusion that there is no difference in the stereochemistry of the ring-juncti between α- and β-amyrins.
There are, however, certain differences in the behaviour of some of the compounds in the novursane and novoleanane series. Thus, while 8:10:14-trimethyl-5\textsuperscript{\*$}$-novursa-3(4):12-diene (IX\textsubscript{a}), upon treatment with borontrifluoride, readily isomerised to 1-\textalpha--amyradiene (73), the analogous novoleanane diene (IX) failed to undergo a similar reaction. The behaviour of the nonconjugated 9(10):12-dienes (XXIX) and (XXX) towards mineral acid will be discussed in the following section and it will be found that these differences are capable of throwing further light on the stereochemistry of the D/E-ring junction in \textalpha--amyrin.
C. The Stereochemistry of the D/E-Ring Junction in a-Amyrin.

In the previous section, it has been emphasised that while there is a general similarity between the novursane and novoleanane derivatives, with respect to origin, properties and reactions, there was, however, an instance in which a marked difference was observed, i.e., the behaviour of the isomeric 3(4):12-dienes (I) and (II) towards boron trifluoride. Another significant difference was found in the behaviour of the nonconjugated dienes (IV) and (VII) which were obtained by reductive removal of the carbonyl groups in the oxodienes (III) and (VI) respectively.

Allan, Spring, Stevenson and Strachan (73) reported that treatment of 5:8:14-trimethylnovursa-9(10):12-diene...
(IV) with hydrochloric-acetic acid mixture readily gave, in a high yield, the conjugated 5:8α:9β-trimethyl-10α-
novursa-12:14-diene (1α-amyrdiene) (V), which had previously been prepared by treatment of α-amyrin with phosphorus pentoxide (75) or with hydriodic-acetic acid mixture (76). The constitution of the "1-diene" as (V) has been discussed (Section A) and it has been shown that its formation includes the migration of the methyl groups attached to $C(10)$, $C(8)$ and $C(14)$ to $C(10)$, $C(8)$ and $C(14)$ respectively. In remarkable contrast, however, it was found that treatment of the nonconjugated 5:8:14-trimethyl-18α-novoleana-9(10):12-diene (VII) with hydrocholoric-acetic acid mixture, under the same conditions used for the novursadiene (IV), gave an uncrystallizable gum, the ultraviolet spectrum of which revealed the absence of "1-diene" type of absorption.

This difference in behaviour is, in the author's opinion, of great significance. In the novursane case, the diene (IV) undergoes a reaction involving the migration of the methyl groups attached to $C(8)$ and $C(14)$ to $C(8)$ and $C(14)$ respectively, while in the 18α-novoleane case, the diene (VII) did not undergo this reaction.
The stability of the C\(_{18}\)-hydrogen atom in \(\alpha\)-amyrin and its derivatives is established \((32, 46, 53)\). The instability of the C\(_{18}\)-hydrogen atom and its tendency to invert to the \(\alpha\)-configuration, in \(\beta\)-amyrin derivative, is equally well established \((52, 59)\). The fact that the double bond and cis-\(\beta\)-locking of rings D and E in \(\beta\)-amyrin are both unstable in acid media will form the subject of discussion in the following section.

It appears probable, therefore, that the driving force responsible for the migration of the C\(_3\)- and C\(_9\)-methyl groups, an "1-diene" type reaction, reposes in a conformational constraint imposed by the stable locking
of the rings D and E in \( \alpha \)-amyrrin [cf. Beton and Halsall (67)], a condition which must be absent in the 18a-
oleanane system where the D/E-ring junction has the
17\( \beta \):18\( \alpha \)-arrangement. This same driving force is, again,
probably responsible for the final stages of the conversion
of \( \alpha \)-amyrrin into 5:8\( \alpha \):9\( \beta \)-trimethyl-10\( \alpha \)-novursa-12:14-diene
(V). With \( \beta \)-amyrrin, however, a different situation exists.
\( \beta \)-Amyrrin, in contrast with \( \alpha \)-amyrrin, does not give an
"1-diene" upon treatment with phosphorus pentoxide in
benzene at room temperature or with hydriodic-acetic acid
mixture under reflux. The difference in behaviour
between \( \alpha \)- and \( \beta \)-amyrrins towards phosphorus pentoxide and
hydriodic acid can, therefore, be defined as the inability
of the 18\( \alpha \)-oleanane derivatives, formed under the iso-
merising effect of these acidic reagents, to undergo
a reaction involving the migration of the methyl groups
attached to \( C(\alpha) \) and \( C(\alpha \alpha) \) to \( C(\alpha) \) and \( C(\alpha) \) respectively.
If this postulation is correct, then it should be
possible to achieve an "1-diene" type reaction, starting
from a \( \beta \)-amyrrin derivative in which the \( \text{cis}(\beta) \)-junction
of rings D and E is "locked". This locking can be
secured by using compounds in which there are no double
bonds or carbonyl groups immediately adjacent to \( C(\alpha \alpha) \).
It has been shown (Section A) that treatment of 12-oxoursan-3β-yl acetate (VIII) with hydriodic-acetic acid mixture gave an αβ-unsaturated ketone, which was proved to be 5:8α:9β-trimethyl-12-oxo-10α-novurs-13-ene (IX), a reaction analogous to the conversion of α-amyrin into 5:8α:9β-trimethyl-10α-novursa-12:14-diene (V), since it included ring-A contraction and the synchronous movement of the axial methyl groups from C(10), C(α) and C(14) to C(α), C(α) and C(α) respectively. The relation between the αβ-unsaturated ketone (IX) and the conjugated diene (V) was confirmed by their inter-conversion.

\[
\begin{align*}
\text{VIII} & \quad \rightarrow \quad \text{IX} \\
& \quad \downarrow \\
\text{V} & \quad \rightarrow \quad \text{XIII}
\end{align*}
\]
12-Oxo-oleanan-3β-yl benzoate (X) is a model compound in which the possibility of inversion at C(1α) under the influence of acidic reagents is prevented and should, therefore, undergo a reaction similar to that of 12-oxoursan-3β-yl acetate (VIII).

Treatment of 12-oxo-oleanan-3β-yl benzoate (X) with hydriodic-acetic acid mixture under reflux yielded a compound, C₃₀H₄₈O, which gave a negative reaction with tetranitromethane and which exhibited a maximal absorption in the ultraviolet light at 2600 Å (ε = 9700) identical with that exhibited by the novursane αβ-unsaturated ketone (IX) and, therefore contains an ααββ-tetrasubstituted αβ-unsaturated ketone chromophore. This compound, in complete analogy, is formulated as 5:8α:9β-trimethyl-12-oxo-10α:18β-novolean-15-ene (XI).

Reduction of (XI) with lithium aluminium hydride followed by treatment of the product with hydrochloric-acetic acid mixture afforded, in a very good yield, a conjugated diene, C₃₀H₄₈, which gave an orange-brown colour with tetranitromethane and exhibited a triple-maximal absorption at 2340, 2410 and 2490 Å (ε = 15,000, 16,000 and 10,700). This conjugated diene was laevo-rotatory ([α]D = -83°) and by a consideration of its properties and its method of preparation, it is obvious
that it is the \( \beta \)-amyryin analogue of \( \text{I-}\alpha \)-amyryadiene (V). It is, therefore, formulated as 5:8\( \alpha \):9\( \beta \)-trimethyl-10\( \alpha \):18\( \beta \)-novoleana-12:14-diene (XII) i.e., an \( \text{I-}\beta \)-amyryadiene.

It has been previously mentioned that 5:8\( \alpha \):9\( \beta \)-trimethyl-12-oxo-10\( \alpha \)-novurus-15-ene (IX) gave, upon chromic acid oxidation, a yellow enedione formulated as (XIII).

Similarly, 5:8\( \alpha \):9\( \beta \)-trimethyl-12-oxo-10\( \alpha \):18\( \xi \)-novolean-12-ene (XI) has been oxidised to a yellow transoid enedion 5:8\( \alpha \):9\( \beta \)-trimethyl-12:15-dioxo-10\( \alpha \):18\( \xi \)-novolean-13-ene (XIV), which showed a maximum at 2780 Å. \( \lambda \) = 8000).

[Diagram of structures A, XI, XII, XIV]
By reference to table 4, it will be noted that there is a general correspondence in the specific rotations of the analogous novoleanane and novursane derivatives (XI) and (IX); (XII) and (V). The negative rotation of the dioxonovoleanane (XIV), however, as compared with the dioxonovursane (XIII) led to the consideration that inversion at C(13) might have occurred during the conversion of the saturated keto-benzoate (X) into the αβ-unsaturated ketone (XI) or during the chromic acid oxidation of the latter into the enedione (XIV). It is for this reason that no configuration has been assigned at C(13) in (XI), (XII) and (XIV).

This similarity in behaviour of β-amyrin (when possibility of inversion at C(13) is excluded) to α-amyrin, and difference in behaviour of 18α-novoleanane derivatives to novursane derivatives strongly suggests that α-amyrin has the same stereochemistry at C(13) and C(17) as β-amyrin and that the rings D/E are consequent cis-β-fused. It appears therefore, that this cis-β-fusion is an essential feature of the driving force necessary to cause an "1-diene"-type reaction. Further support for this view was obtained by an examination of 12-oxo-18α-oleanan-3β-yl acetate (XV) (59).
Treatment of the 18α-saturated keto-acetate (XV) with hydriodic-acetic acid, under the conditions which convert (X) to (XI), gave an αβ-unsaturated ketone which exhibited selective absorption in the ultraviolet region at 2440 Å. (ε = 11,200), characteristic of αβ-tribsubstituted αβ-unsaturated ketones. Moreover, this compound is dextro-rotatory ([α]D + 99°), and in its properties it differs markedly from the αβ-unsaturated ketones (IX) and (XI). Since the only position which can accommodate the double bond in this compound is between C(9) and C(11), it is formulated as 5:8:14-trimethyl-12-oxo-10α:18α-novolen-9(11)ene (XVI).

The formation of this compound must, therefore, have included ring-A contraction, migration of the methyl group at C(18) to C(9) with the subsequent conjugation of the introduced double bond with the carbonyl group at C(12) without either of the methyl groups at C(8) or C(14) being involved.

The formation of the αβ-unsaturated ketone (XVI) from the keto-acetate (XV) by dehydration with hydriodic acid was accompanied by another compound, C38H48O, which gave a positive tetranitromethane test and exhibited selective absorption in the ethylenic region at 2100 Å.
The structure of the αβ-unsaturated ketone (XVI) was confirmed by its reduction with lithium aluminium hydride, followed by treatment of the product with
acetic anhydride and sodium acetate to yield a hydrocarbon, C_{30}H_{48}, which gave a dark-brown colour with tetranitromethane and exhibited a triple maximal absorption at 2450, 2520 and 2600 Å. (ε = 24,600, 27,000 and 26,000). This absorption spectrum resembles that characteristic of many heteroannular dienes in which one double bond is tetrastubstituted and the other is trisubstituted, such as ursa- or oleana-11:13(18)-dien-3β-yl acetate (λ_{max} = 2420, 2500 and 2600 Å. (ε = 23,500, 26,500 and 16,800) (XXI) (36,37,38). The product is, therefore, regarded as either 5:8:14-trimethyl-9β:10β-novoleana-11:13(18)-diene (XIX) or the isomeric 5:8:14-trimethyl-18α-novoleana-9(10):11-diene (XX).
It remains, in conclusion, to summarise the more important implications of the comparison of the behaviour of the analogous oleanane and ursane derivatives made above. The cis-locking of rings D and E in β-amyrrin 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 can occur. It is postulated that a reaction strictly analogous to the conversion of α-amyrrin into the "1-diene" is not observed with β-amyrrin, because the 12:13-double bond in this compound is not stable to strong acid. This instability also affords a possible reason for the failure to isolate pure products from such reactions (e.g. phosphorus pentoxide and hydriodic acid on β-amyrrin, boron trifluoride on the nonconjugated diene (II) and hydrochloric acid on the nonconjugated dienes (VII) and (XXI gave impure products).
On the other hand, the locking of rings D and E in α-amyrin and its derivatives is stable to strong acid treatment. Davy, Halsall and Jones (53) recovered urs-12-en-3-one after vigorous treatment with mineral acid, in contrast with the corresponding oleanane derivative. Recently, Beaton, Spring, Stevenson and Strachan (52) found that treatment of 11-oxo-urs-12-en-3β-yl acetate (XXIII) with strong alkali does not change the configuration at C(10a), in contrast with 11-oxo-olean-12-en-3β-yl benzoate (XXIV) which is easily isomerised by similar treatment to give the 18α-epimer (XXV) (59).

The conversion of 12-oxo-oleanan-3β-yl acetate (I), but not its 18α-epimer (XV) into a 12-oxo-13:14-ene (XI) shows that the cis-locking of rings D and E is the driving force supporting the "1-diene" type reaction.
The similar behaviour of 12-oxoursean-3β-yl acetate (VIII) to give the 12-oxo-13:14-ene (IX) and 12-oxooleananyl acetate, when treated with hydriodic-acetic acid mixture, leads to the conclusion that the junctions of rings D and E in α-amyrin and β-amyrin (XXVI) are the same, i.e., that α-amyrin has the 17β:18β-configuration.

This conclusion is in agreement with the findings of Spring et al. (32) which were based, among other reasons, upon the conversion of an α-amyrin derivative into a β-amyrin derivative, thus conclusively establishing that the C(17)-methyl group in α-amyrin is β-orientated (see introductory section).

It is concluded that α- and β-amyrins have identical configurations at all ring junctions and that the constitution and stereochemistry of α-amyrin must be represented by either (XXVII) or proposed by Spring et al. (32,54) or (XXVIII) as proposed by Corey et al. (58).
D. The Behaviour of Olean-12-ene, 18α-Olean-12-ene, Olean-13(13)-ene and Olean-13-ene with Mineral Acid.

In the previous section, it has been shown that the locking of rings D and E in α- and β-amyrin and their derivatives is a determining factor controlling the reaction which involve rearrangements of the skeletal structure. The relative stability of the D/E-ring junction and the double bond in α- and β-amyrin and derivatives is responsible, in the author's opinion, for many of the hitherto inexplicable differences in their behaviour towards acidic reagents. This section discusses the relative stability of olean-12-ene, 13α-olean-12-ene, olean-13(13)-ene, and olean-13-ene (germane) under acid conditions. Hydrocarbons were chosen for this study to obviate secondary reactions attributable to the presence of functional groups. The four hydrocarbons were prepared as shown below; their physical constants are listed in Table 5.

Table 5.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>$[\alpha]_D$</th>
<th>m.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olean-12-ene (I)</td>
<td>$+94^\circ$</td>
<td>160-1$^\circ$</td>
</tr>
<tr>
<td>13α-Olean-12-ene (III)</td>
<td>$+37^\circ$</td>
<td>136-3$^\circ$</td>
</tr>
<tr>
<td>Olean-13(19)-ene (VI)</td>
<td>$+5.5^\circ$</td>
<td>163-9$^\circ$</td>
</tr>
<tr>
<td>Olean-13(13)-ene (VIII)</td>
<td>$-48^\circ$</td>
<td>136-7$^\circ$</td>
</tr>
</tbody>
</table>
(i) Olean-12-ene (β-amyrene-II) (I) was prepared by Wolff-Kishner reduction of 3-oxo-olean-12-ene (II) (53).

(ii) 18α-Olean-12-ene (III) was prepared by treatment of 11-oxo-olean-12-en-3β-yl acetate (IV) with strong alkali (59) to yield the 18α-epimer (V) which was then converted to the hydrocarbon as shown below:
(iii) Olean-18(19)-ene (Germanicene) (VI) (98) was prepared from lupeol (VII) by the method described by Halsall, Jones and Meakins (99), viz:

\[
\begin{align*}
\text{HCl} & \quad \rightarrow \quad \text{OH} \\
\text{Ac}_2\text{O} & \quad \rightarrow \quad \text{AcO}
\end{align*}
\]

In 1935, Winterstein and Stein (72) reported that treatment of olean-12-ene (β-amyrene-II)(I) with hydrochloric acid and amalgamated zinc yielded a hydrocarbon "β-amyrene-III", m.p. 187-189°, [α]_D -22°, also formed by similar treatment of 3-oxo-olean-12-ene (β-amyrenone (II). These workers also reported the formation of a hydrocarbon, β-amyrene-IV, m.p. 162-163°, [α]_D +51°,
by treatment of \( \beta \)-amyrene-II with zinc and hydrochloric acid. Nazicka, Schellenberg and Goldberg (106) also described the preparation of a hydrocarbon identical with \( \beta \)-amyrene-IV by Wolff-Kishner reduction of 3-oxo-olean-12-ene (II). \( \beta \)-Amyrene-IV is said to have been converted into \( \beta \)-amyrene-III by treatment with amalgamated zinc in hydrochloric acid (72).

\[ \begin{align*}
\beta \text{-amyrene-II} & \quad \text{Zn/Hg - HCl} \quad \beta \text{-amyrenone} \\
& \quad \text{HCl or Zn/HCl} \\
& \quad \text{Zn/Hg - HCl} \\
& \quad \beta \text{-amyrene-IV} \\
& \quad \text{Zn/Hg - HCl} \\
& \quad \text{Zn/Hg - HCl} \\
& \quad \beta \text{-amyrene-III}
\end{align*} \]

In the course of a reinvestigation of the findings outlined above, Davy, Halsall and Jones (53) discovered that the isomerisation of \( \beta \)-amyrene-II in hydrochloric-acetic acid mixture in the presence or absence of zinc or mercury, if carried to completion, gave \( \beta \)-amyrene-III as the sole product (for which they quoted an \( [\alpha]_D -33^\circ \) and attributed the difference from Winterstein and Stein's value to their preparation being purer). If, however,
the isomerisation were not carried to completion, products of variable rotation were obtained, corresponding to those reported for \( \beta \)-amyrene-IV. They showed that the \( \beta \)-amyrene-IV of Winterstein and Stein (72) is a mixture of \( \beta \)-amyrene-II and \( \beta \)-amyrene-III. Davy et al. also showed that Wolff-Kishner reduction of \( \beta \)-amyrenone, using the procedure of Ruzicka et al. (100), gave \( \beta \)-amyrene-II and not \( \beta \)-amyrene-IV. On the basis of this reinvestigation, Davy et al. concluded that treatment of olean-12-ene (\( \beta \)-amyrene-II) with mineral acid resulted in double bond isomerisation and, when carried to completion, the product, olean-13(18)-ene (\( \beta \)-amyrene-III) (VIII) had m.p. 190-191°, and \([\alpha]_D \) -33°.

\[
\text{VIII}
\]

Other preparations of olean-13(18)-ene have been reported. In a study of the naturally occurring compound taraxerone (skimmione) (1,101,102,103), Takeda (104,105) prepared a hydrocarbon, skimmione-II, m.p. 189-190°, \([\alpha]_D \) -20.5°, by Clemmenson's reduction of skimmione,
which he showed to be identical with Winterstein and Stein's β-amyrrene-III (72). In 1953, Brooks (20) showed that skimmene-III is in fact olean-13(18)-ene (VIII). In 1960, Koller et al. (106) reported that catalytic hydrogenation of oleana-11:13(18)-dien-3β-yl acetate (X) into olean-13(18)-en-3β-yl acetate (δ-amyrin) (XI) (107).
In this laboratory, olean-13(18)-ene (VIII) has been prepared by Messrs. G. Brownlie and W. S. Strachan (private communication) by the alternative non-equilibrating methods outlined below. Using either method, the hydrocarbon obtained had $[\alpha]_D -48^\circ$. It is apparent, therefore, that the substance, $[\alpha]_D -33^\circ$, prepared by Davy et al. under equilibrating conditions is not pure olean-13(18)-ene.
Treatment of the hydrocarbons, oleane-12-ene (I), 18α-oleane-12-ene (III), oleane-18-ene (VI) and oleane-13(18)-ene (VIII) with concentrated hydrochloric acid in acetic acid solutions under reflux for 17 hours afforded in each case a product, m.p. 185-187°, and $[\alpha]_D$ $-18^\circ$ to $-20^\circ$ which showed no depression in m.p. when mixed with each other, and which exhibited identical absorptions in the ethylenic region of the ultraviolet light ($\lambda_{max}$ 2080 Å, $\epsilon$ = 6500). This observation is significant since the properties of this product, are in good agreement with those reported for β-amylene-III by Winterstein and Stein (72), Takeda (104,105) and Brooks (20), and indicates conclusively that β-amylene-III, prepared under mineral acid equilibrating conditions is a mixture. It was appreciated that the hydrocarbon $[\alpha]_D$ $-18$ to $-20^\circ$ might be a mixed crystal containing any of the four oleane isomers (I), (III), (VI) and (VIII), with (III) and (VII) being the most likely pair. Mixtures of pairs of the homogeneous hydrocarbons were prepared and recrystallized as anticipated, only oleane-13(18)-ene (VIII) and 18α-oleane-12-ene (III) (in the ratio 2:1 respectively) yielded a clearly defined product, m.p. 186-187°, $[\alpha]_D$ $-20^\circ$, $\lambda_{max}$ 2080 Å, ($\epsilon$ = 6400), which was identical with the
product obtained by mineral acid treatment of the isomeric oleananes (I), (III), (VI) and (VIII).

It follows, therefore, that olean-13(18)-ene (VII) and 18α-olean-12-ene (III) are both more stable than olean-18-ene (VI) and olean-12-ene (I) and that there is produced an equilibrium mixture from which a mixed

[Diagram showing molecular structures of (I), (III), (VII), (VI), and labeled as Mixed Crystal.]

These findings suggest that when treated with mineral acid reagent, 18α-olean-12-ene (III) isomerizes to olean-13(18)-ene (VII) and 18α-olean-12-ene (III).
crystal consisting of the two former hydrocarbons can be isolated, whenever any of the four isomeric oleanenes is treated with mineral acid.

It can be stated in conclusion that β-amyrene-III (53,72), or skimmene-III (20,104, 105), is in fact an equilibrium mixture of olean-13(18)-ene (VIII) and 18α-olean-12-ene (III), and that neither zinc nor mercury is essential for the acid-induced isomerisation of olean-12-ene (β-amyrene-II) (I) to β-amyrene-III (cf. 53,72)

A more important conclusion is that treatment of β-amyrin (olean-12-en-3β-ol) with acid reagents is likely to produce mixtures in which the -13(18)- and 18α-12-en-3β-ol isomers are present. It is suggested, therefore, that when treated with an acidic reagent, β-amyrin isomerises to a mixture of δ-amyrin (olean-13(18)-en-3β-ol)(XII) and 18α-olean-12-en-3β-ol (XIII).
This behaviour might partly explain the enigmatic fact that $\beta$-amyrin fails to give an "$\alpha$-diene" when treated with phosphorus pentoxide or with hydriodic acid, only uncrystallisable gums being formed. This conclusion probably also applies to the corresponding novooleanene derivatives.

An instance is available in which strong mineral acid treatment is likely to have produced an analogous equilibrium mixture in the novooleanane series. Reduction of 8:10:14-trimethyl-$5\xi$-novoleana-5(4):12-diene (XIV) (see Section B) either catalytically with hydrogen (70, 72, 90), or with sodium in amyl alcohol (91) gave a monoo-ethylenic compound, $\beta$-amyrene-I, which can be formulated as 8:10:14-trimethyl-$5\xi$-novolean-12-ene (XV). Wintersteiner and Stein (72) reported that treatment of $\beta$-amyrene-I with concentrated hydrochloric acid and amalgamated zinc gave a product, $\beta$-amyrene-Ib. It is now suggested, on the basis of the above argument, that $\beta$-amyrene-Ib is in fact an equilibrium mixture of novooleanane derivatives of analogous constitution and composition to the equilibrium mixture [(III) + (VII)].
Recently, Brownlie, Spring, Stevenson and Strachan (23,26) have reported the rearrangement of friedelene (XVI) with hydrochloric-acetic acid to a product (m.p. 186-187°, [α]D -20°), identified as the equilibrium mixture of olean-13(18)-ene (VII) and 18α-olean-12-ene (III); an infra-red spectrum comparison has further established the identity. An analogous rearrangement has been effected by Corey and Ursprung (25) by dehydration of friedelanol (XVII) with hydrogen chloride in phenol at 110°.

The latter authors give m.p. 186-187°, [α]D -12.5° for their product, which they call olean-13(18)-ene, having obtained a product of similar constants by acid isomerisation of olean-12-ene. Dutler, Jeger and Ruzicka (24) have also reported that treatment of
friedel-2-ene (XVIII) with freshly fused zinc chloride in acetic acid under reflux yielded a product, m.p. 183-184°, \([\alpha]_D^{18} -18°\), which they call olean-13(18)-ene. In view of the work described in this section, the products obtained by Corey and Ursprung (25) and by Dutler et al. (24) must similarly be equilibrium mixtures of (VIII) and (III) in different proportions.
Melting points were determined using a standard B.P.I. thermometer.

Specific rotations were determined in chloroform solution in a 1 dm. tube at room temperature.

Colour reactions with tetranitromethane were done in chloroform solution.

Ultraviolet absorption spectra were measured in absolute ethanol solution with a Unicam SP.500 spectrophotometer, and (4) denoted molecular extinction coefficient.

For chromatography, alumina (Brockmann Grade I-II) was used.

"Stabilised acetic acid" denotes acetic acid which has been distilled over and distilled from glacial acetic anhydride. The phrase "in the usual way" generally, drying with ether, extraction with ether, washing successively with aqueous sodium hydroxide, water, dilute hydrochloric acid, aqueous sodium hydrogen carbonate, followed by drying of the ethereal extract over anhydrous sodium sulphate, filtration and evaporation to dryness under reduced pressure.

The microanalyses were carried out by Mr. W. McCorkindale; the ultraviolet spectral measurements were by Misses J. Adams, N. Carrawa and D. MacMullen under the direction of Dr. A. C. Sine, the Royal Technical College, Glasgow, and the infra-red spectra were determined by Dr. G. Forster, Manchester, to whom are due best thanks.
Melting points were determined using a standard N.P.L. thermometer.
Specific rotations were determined in chloroform solution in a 1 dm. tube at room temperature.
Colour reactions with tetranitromethane were done in chloroform solution.
Ultraviolet absorption spectra were measured in absolute ethanol solution with a Unicam SP.500 spectrophotometer, and (\(\varepsilon\)) denoted molecular extinction coefficient.
For chromatography, alumina (Brockmann Grade I-II) was used.
"Stabilised acetic acid" denotes acetic acid which has been refluxed over and distilled from chromic anhydride. The phrase "in the usual way" implies, in general, dilution with water, extraction with ether, washing successively with aqueous sodium hydroxide, water, dilute hydrochloric acid, aqueous sodium hydrogen carbonate, followed by drying of the ethereal extract over anhydrous sodium sulphate, filtration and evaporation to dryness under reduced pressure.
The microanalyses were carried out by Mr. Wm. McCorkindal.
the ultraviolet spectral measurements were by Misses, P. Adams, N. Caramando and S. MacKenzie under the direction of Dr. A.C. Syme, the Royal Technical College, Glasgow, and the infra-red spectra were determined by Dr. G. Eglinton, Manchester, to whom are due best thanks.
5:8α:9β-Trimethyl-10α-novursa-12:14-diene, (1-α-Amyradiene). - a) A solution of α-amyrin (urs-12-en-3β-ol) (m.p. 176-178°, 2.0 g.) in acetic acid (20 c.c.) was refluxed for 4 hours with hydriodic acid (8 c.c.). Water was then added and the mixture extracted with ether, washed with aqueous sodium thiosulphate and worked up in the usual way. The product was crystallised from chloroform-methanol to give 5:8α:9β-trimethyl-10α-novursa-12:14-diene (1-α-amyradiene) as long plates (900 mg.), m.p. 195-196°, [α]D -110° (c, 3.5). It gives an orange-brown colour with tetranitromethane. Light absorption: \( \lambda_{max} \) 2560, 2410 and 2500 nm. (β = 13,000, 14,500 and 8550).

b) A solution of α-amyrin (m.p. 176-178°, 4 g.) in benzene (100 c.c.) was treated with phosphorus pentoxide (9 g.), added portionwise with shaking. Shaking was continued for 24 hours at room temperature. The product, worked up in the usual manner, was dissolved in light petroleum (b.p. 40-60°, 100 c.c.), filtered through alumina and crystallised from chloroform-methanol to give 5:8α:9β-trimethyl-10α-novursa-12:14-diene (1-α-amyradiene) as long plates (1.1 g.); m.p. 193-195° (no depression), [α]D -109° (c, 1.9).
For 1-α-amyradiene, Vesterberg (75) gives m.p. 193-194°, 
\([\alpha]_D^\text{[a]} = -105°;\) Ewen, Gillam and Spring (76) give m.p. 193-
194°, \([\alpha]_D^\text{[a]} = -101°.

Oxidation of 5:8α:9β-Ttrimethyl-10α-novursa-12:14-
diene with Chromic Acid. - (a) A solution of chromium
trioxide (540 mg., 1.5 mols.) in 90% acetic acid (15 c.c.
was added portionwise with stirring to a solution of
5:8α:9β-trimethyl-10α-novursa-12:14-diene (1-α-amyradiene
(m.p. 194°C; 2.0 g.) in benzene (20 c.c.) and stabilised
glacial acetic acid (60 c.c.), and the mixture maintained
at 100° for 1 hr. Methanol was then added to destroy
excess chromic acid and the solution evaporated to dryness
to give a gummy solid. The product was then worked up
in the usual manner through water and ether. Five re-
crystallisations from chloroform-methanol gave 5:8α:9β-
-Ttrimethyl-12-oxo-10α-novursa-14-ene as needles (760 mg.),
m.p. 218-219°, \([\alpha]_D^\text{[a]} = -62° (c, 2.2).\) It gives a yellow
colour with tetranitromethane. Light absorption:
\[\lambda_{\text{max}} = 2050 \text{ Å} \quad (t = 3,500).\] The ultraviolet spectrum
showed the presence of ca. 5% of αβ-unsaturated ketone
impurity, which could not be removed by crystallisation
or chromatography. (Found: C, 84.86; H, 11.36%.
C₈₀H₄₄O requires: C, 84.84; H, 11.39%). Infra-red
absorption (in chloroform solution): Strong band at 1696 cm$^{-1}$

(b) Chromium trioxide (3.0 g., ca. 6 mols.) in glacial acetic acid solution (stabilised, 150 c.c.) was added dropwise with stirring to a solution of 5:8a:9β-trimethyl-10α-novursa-12:14-diene (m.p. 194°C, 3.0 g.) in glacial acetic acid (stabilised, 1.5 l.) at 100°C, over a period of 1½ hours. Stirring was continued for a further 5½ hours at 100°C, and the solution was left to stand at room temperature overnight. Methanol was then added to destroy excess of the oxidant and the solution evaporated to dryness. Water and ether were then added and the product worked up in the usual manner. Crystallisation of the residue from chloroform-methanol yielded needles (900 mg.), m.p. 216-220°C, $\lambda_{\text{max.}}$ 2500 Å ($\epsilon = 7500$), which were dissolved in benzene-light petroleum (360 c.c.; 1:1) and chromatographed on alumina (100 g.). The product, eluted with the same solvent (600 c.c.), crystallised from chloroform-methanol to give 5:8a:9β-trimethyl-12:16-dioxo-10α-novursa-14-ene as needles (320 mg.), m.p. 224-225°C, $[\alpha]_D$ -134° (c,1.2). It does not give a colour with tetranitromethane.

Light absorption: $\lambda_{\text{max.}}$ 2500 Å ($\epsilon = 10,500$). (Found: C, 81.85; H, 10.4%. $\text{C}_{30}\text{H}_{40}\text{O}_{2}$ requires C, 82.2; H, 10.5%).
Attempted acid rearrangement of 5:8a:9β-Trimethyl-12-oxo-10α-novurs-14-ene. - The βγ-unsaturated ketone (m.p. 218-219°C, 45 mg.) was dissolved in chloroform (2 c.c.) and acetic acid (5 c.c.), and heated at 40°C for 1 hour with concentrated hydrochloric acid (1 c.c.). The solution was then diluted with water and extracted with chloroform and the extract repeatedly washed with water, NaHCO₃ solution and dried (Na₂SO₄). Upon evaporation of the solvent, a solid residue was obtained which crystallised from chloroform-methanol as needles, m.p. 217-218°C. It gave a yellow colour with tetranitromethane. The product gave no depression in m.p. when mixed with the starting material and showed no appreciable ultraviolet absorption above 2200 Å.

Action of Alkali on 5:8α:9β-Trimethyl-12-oxo-10α-novurs-14-ene. - The βγ-unsaturated ketone (5:8α:9β-trimethyl-12-oxo-10α-novurs-14-ene) (m.p. 218-219°C, 250 mg.) in 5% methanolic sodium hydroxide solution (200 c.c.) was refluxed for 3 hours. Addition of water precipitated a solid which was recrystallised from aqueous methanol to give 5:8α:9β-trimethyl-12-oxo-10α-novurs-13-ene as needles, m.p. 155-157°C, depressed upon admixture...
with a sample of the product obtained from the treatment of 12-oxo-13α-ursan-3β-yl acetate with hydroiodic acid (see later), \([\alpha]_D^{2600} -38^\circ (c, 0.9)\). Light absorption: \(\lambda_{\text{max}}\) 2600 Å. (\(\epsilon = 8600\)).

**Oxidation of 5:8α:9β-Trimethyl-12-oxo-10α-novursa-14-ene with Chromic Acid.** - Chromium trioxide (112 mg. in 90% acetic acid solution (5 c.c.) was added dropwise to a solution of 5:8α:9β-trimethyl-12-oxo-10α-novursa-14-ene (m.p. 218-219°C, 224 mg.) in benzene (5 c.c.) and acetic acid (stabilised, 1.8 c.c.) and the mixture heated at 100°C for 1 hour. Methanol was added to destroy excess CrO₃, and the solution evaporated to dryness, and worked up in the usual way. Crystallisation of the residue from chloroform-methanol gave 5:8α:9β-trimethyl-12:16-dioxo-10α-novursa-14-ene as fine needles (93 mg.), m.p. 220-222°C, [α]_D^{2600} -130° (c, 0.8) undepressed upon admixture with a specimen of the product obtained by oxidation of 5:8α:9β-trimethyl-10α-novursa-12:14-diene with excess chromic acid. Light absorption: \(\lambda_{\text{max}}\) 2600 Å. (\(\epsilon = 1000\)).

**12-Oxo-13α-ursan-3β-yl acetate.** - (McLean, Silverstone, and Spring (111)). - A solution of α-amyrin acetate (224-225°C, 5 g.) in glacial acetic acid (250 c.c.-
was treated at 100° with a mixture of hydrogen peroxide (100 vols., 30 c.c.) and glacial acetic acid (30 c.c.) added dropwise during 30 mins. with stirring. Stirring was continued for 2 further hours at 100° when more hydrogen peroxide (20 c.c.) in acetic acid (20 c.c.) was added during 15 mins. The solution was maintained at 100° for a further 1 hr. and then diluted with water until faintly opalescent; a crystalline solid deposited upon standing overnight which was collected. After three crystallisations from methanol-chloroform, it gave 12-oxo-13α-ursan-3β-yl acetate as small plates, m.p. 208-210°, (no depression), [α]_D^2 = 118° (c, 1.9).

12-Oxo-13α-ursan-3β-yl benzoate was prepared by a similar treatment of α-amyrin benzoate (111). It crystallised from methanol-chloroform as needles (52% yield m.p. 218-219°, [α]_D^2 = 150° (c, 1.1).

3β:12-Diacetoxyurs-12-ene. - A mixture of 12-oxo-13α-ursan-3β-yl acetate (m.p. 208-210°, 1 g.) and fresh fused sodium acetate (1.0 g.) was refluxed in acetic anhydride (redistilled, 20 c.c.) for 24 hours. Most of the solvent was evaporated and the residue treated with water, ether and worked up as usual. After 3 crystallis
ations from methanol-chloroform, 3β:12-diacetoxyurs-
-12-ene was obtained as needles, m.p. 254-256 (no
depression with authentic specimen), [α]D + 50° (g,1.3).

12-Oxoursan-3β-yl Acetate. - A solution of 12-oxo-
-13α-ursan-3β-yl acetate (m.p. 206-210°, 3.0 g.) in
chloroform (15 c.c.) and acetic acid (60 c.c.) was
treated with concentrated hydrochloric acid (3 c.c.) at
40° for ½ hr. The product, worked up as usual, cry-
stallised from methanol-chloroform to give 12-oxoursan-
-3β-yl acetate as plates (1.2 g.), m.p. 280-282° (un-
derpressed), [α]D + 13° (g,1.4).

5:8α:9β-Trimethyl-12-oxo-10α-novura-13-ene. -
(a) A solution of 12-oxo-13α-ursan-3β-yl acetate
(m.p. 206-210°C, 2.0 g.) in glacial acetic acid (25 c.c.)
was refluxed for 16 hours with hydriodic acid (7 c.c.;
d,1.7). The mixture was diluted with water and extracted
with ether, the extract washed with sodium thiosulphate
solution, and evaporated. The residue was crystallised
from aqueous methanol to give 5:8α:9β-trimethyl-12-oxo-
-10α-novura-13-ene as flat needles (400 mg.), m.p. 157-
-168.5°C, [α]D -41° (g,1.6). Light absorption: λmax
2600 Å. (1 D,000). (Found: C,84.91; H,11.71%.
C38H56O requires: C,84.84; H,11.39%). It does not
give a colour with tetranitromethane.

(b) A solution of 12-oxo-13α-ursan-3β-yl benzoate (m.p. 218-219°C, 45 g.) in glacial acetic acid (2 l.) was refluxed for 16 hours with hydriodic acid (150 c.c.; d, 1.7). The mixture was concentrated, diluted with water, and the product isolated as described in the previous experiment. A solution of the product in benzene-light petroleum (300 c.c.; 1:2) was chromatographed on alumina (1000 g.). Elution with the same solvent (4 l.) gave a fraction which after four recrystallisations from aqueous methanol gave 5:6α:9β-trimethyl-12-oxo-10α-novurs-13-ene (10.0 g.) as flat needles, m.p. 155-157° alone or when mixed with a sample of the product prepared in the previous experiment [α]_D -38° (c, 1.0). Light absorption: λ_max 2610 Å. (4 8,600).

(c) A solution of 36:12-diacetoxyurs-12-ene (m.p. 254-256°C, 1.0 g.) in glacial acetic acid (18 c.c.) was treated with hydriodic acid (3.5 c.c.; d, 1.7) and the mixture refluxed overnight. The product was worked up through water and ether as described before. The residue (a pale yellowish gum) was then dissolved in light-petroleum (40-60°C) and filtered through a short column of alumina, from which the solid product was
eluted with benzene-light petroleum mixture (3:7). The product was crystallised three times from aqueous methanol to give 5:8α:9β-trimethyl-12-oxo-10α-novurs-13-ene (550 mg.) as flat needles, m.p. 167-168°C which was not depressed by the product described under (a), [α]_D -41° (c, 1.8).

(d) A solution of 12-oxo-ursan-3β-yl acetate (m.p. 280-282°C, 900 mg.) in glacial acetic acid (18 c.c.) was treated with hydriodic acid (3.5 c.c.; d, 1.7) under reflux for 16 hours. The product was worked up as described under (a). The residue (a pale yellowish gum) was then dissolved in light petroleum (40-60°C) and filtered through alumina from which a solid product (0.22 g.) was eluted with benzene-light petroleum mixture (3:7). After four recrystallisations from aqueous methanol, 5:8α:9β-trimethyl-12-oxo-10α-novurs-13-ene was obtained as flat needles, m.p. 158-159°C undepressed upon admixture with a sample of the product prepared under (a); [α]_D -39° (c, 1.5).

Oxidation of 5:8α:9β-Trimethyl-12-oxo-10α-novurs-13-ene with Chromic Acid. - Chromium trioxide (4.8 g.) in 90% acetic acid solution (56 c.c.) was added in portions to a solution of 5:8α:9β-trimethyl-12-oxo-10α-novurs-13-
-ene (m.p. 155-157°C, 8.0 g.) in glacial acetic acid (stabilised, 580 c.c.), and the mixture stirred at 95°C for 1 hour. Methanol was then added and the solution evaporated to dryness. Water and ether were then added and the product worked in the usual way. The residue (a reddish gum) was then dissolved in benzene-light petroleum (40-60°, 3:7) and chromatographed on an alumina column (1" x 12"):

<table>
<thead>
<tr>
<th>Volume</th>
<th>Eluent</th>
<th>Residue</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 ml</td>
<td>Benzene-Light Petroleum (3:7)</td>
<td>2.6 g.</td>
<td>1</td>
</tr>
<tr>
<td>500 ml</td>
<td>Benzene-Light Petroleum (1:1)</td>
<td>0.84 g.</td>
<td>4</td>
</tr>
<tr>
<td>200 ml</td>
<td>Benzene-Light Petroleum (1:1)</td>
<td>0.09 g.</td>
<td>9</td>
</tr>
<tr>
<td>300 ml</td>
<td>Benzene-Light Petroleum (4:1)</td>
<td>0.12 g.</td>
<td>16</td>
</tr>
</tbody>
</table>

Fractions 1 and 2 were combined and crystallised from methanol to give yellow needles which, upon repeated recrystallisation from the same solvent gave 5:8a:9β-trimethyl-12:15-dioxo-10α-novur-13-ene as flat yellow needles, m.p. 176-177°C, [α]_D + 85° (c, 2.7). Light absorption: \( \lambda_{\text{max}} = 2250 \text{ Å} \) (\( \epsilon = 3400 \)) and \( \lambda_{\text{max}} = 2760 \text{ Å} \) (\( \epsilon = 8000 \)). (Found: C, 82.14; H, 10.51%. C_{38}H_{42}O_{16} requires: C, 82.13; H, 10.57%).
Fractions 4-8 were combined and crystallised from aqueous methanol to give orange flat needles which required several recrystallisations from the same solvent to give pure 5:8α:9β-trimethyl-11(or 16):12:15-trioxo-10α-novur-13-ene as long flat orange needles, m.p. 182-183°C, [α]D + 214° (c, 1.8). Light absorption: 
\[\lambda_{\text{max}} = 2220 \text{ Å} \quad (\epsilon = 4600) \text{ and } \lambda_{\text{max}} = 2990 \text{ Å} \quad (\epsilon = 5600).\]
(Found: C, 79.40; H, 9.93%; C59H44O8 requires: C, 79.60; H, 9.80%).

Fractions 9 and 10 were combined and crystallised from aqueous methanol to give dark yellowish needles. After six recrystallisations from the same solvent was obtained 5:8α:9β-trimethyl-12:15:16(or 11)-trioxo-10α-novur-13-ene yellow-orange needles, m.p. 228-230°C, [α]D + 376° (c, 0.2). Light absorption: 
\[\lambda_{\text{max}} = 2220 \text{ Å} \quad (\epsilon = 3500) \text{ and } \lambda_{\text{max}} = 2960 \text{ Å} \quad (\epsilon = 6000).\]
(Found: C, 79.90; H, 10.08%. C59H44O8 requires: C, 79.60; H, 9.80%).

From fractions 16-18 was obtained a very small quantity of crimson-red prisms, m.p. 192-194°C, after crystallisation from aqueous methanol, and which were not further examined.
**Oxidation of 5:8α:9β-Trimethyl-12:15-dioxo-10α-novurs-13-ene with Chromic Acid.**

Chromium trioxide (200 mg.) in acetic acid (5 c.c.) was added portionwise to a solution of 5:8α:9β-trimethyl-12:15-dioxo-10α-novurs-13-ene (m.p. 172-174°C, 120 mg.) in glacial acetic acid (stabilised, 20 c.c.) and the mixture stirred at 95°C for 1 hour. The product was isolated in the manner described in the previous CrO₃-oxidation experiments, dissolved in benzene-light petroleum (1:1) and filtered through a short column of alumina. Crystallisation of the residue from aqueous methanol gave 5:8α:9β-trimethyl-11(or 16):12:15-trioxo-10α-novurs-13-ene as flat orange needles (30 mg.), m.p. 178-180°C. (no depression).

**Treatment of 5:8α:9β-Trimethyl-12-oxo-10α-novurs-13-ene with Alkali.**

(a) A solution of 5:8α:9β-trimethyl-12-oxo-10α-novurs-13-ene (m.p. 155-155°C, 100 mg.) in 5 methanolic solution of sodium hydroxide (100 c.c.) was refluxed for 3 hours. The product was then worked up in the usual way through water and ether to give a gummy residue which produced a small amount of a yellowish-white amorphous solid upon treatment with aqueous methanol. When the mother-liquors were concentrated, flat needles (32 mg.) were obtained, m.p. 144-148°C. After three
recrystallisations from aqueous methanol flat needles were obtained, m.p. 155-156°C undepressed by the starting material.

(b) A solution of 5:8a:9β-trimethyl-12-oxo-10α-novur-13-ene (m.p. 153-155°C. 200 mg.) in 10% ethanolic potassium hydroxide solution (150 c.c.) was refluxed for 3 hours. The product, isolated in the usual way, crystallized from aqueous methanol as flat yellow needles (104 mg.), m. p. 155-160°C. which, after 3 recrystallisations from the same solvent gave flat yellow needles, m.p. 170-172°C., \([\alpha]_D^+ (c, 2.4)\). Light absorption: \(\lambda_{\text{max}} 2260 \text{ Å} \ (\epsilon = 2800)\) and \(\lambda_{\text{max}} 2750 \text{ Å} \ (\epsilon = 7000)\).

The product gave no depression in m.p. when mixed with a specimen of 5:8a:9β-trimethyl-12:15-dioxo-10α-novurs-13-ene.

(c) Repetition of the above experiment using 20% ethanolic potassium hydroxide solution, gave the same result.

Reduction of 5:8a:9β-Trimethyl-12-oxo-10α-novurs-13-ene with Lithium Aluminium Hydride. — A solution of 5:8a:9β-trimethyl-12-oxo-10α-novurs-13-ene (m.p. 154-156°C. 1.0 g.) in dry ether (200 c.c.) was added dropwise to a suspension of lithium aluminium hydride (1.0 g.) in dry
ether (200 c.c.), the mixture refluxed on the steam-bath for 2 hours, and allowed to stand overnight at room temperature. Water was then cautiously added and the product worked up in the usual manner. Upon evaporation of the dry ethereal extract a colourless gum-solid mass (0.68 g.) was obtained, which upon crystallisation from chloroform-methanol gave needles and prisms m.p. 142-143°. A portion of this product (300 mg.) was purified by chromatography whereby a fraction (158 mg.) was eluted with benzene-light petroleum mixture (1:1). After several recrystallisations from chloroform-methanol small prisms (changing into needles upon standing) were obtained m.p. 155-156°, [α]D -77° (c 2.0). This product gave a yellow colouration with the tetranitromethane reagent.

Light absorption: \( \lambda_{max} \) 2160 Å. (t = 5300). (Found: C, 83.7; H, 11.73%. \( \text{C}_{30}\text{H}_{30}\text{O} \) requires: C, 84.44; H, 11.81%). \( \text{C}_{30}\text{H}_{30}\text{O} \cdot \text{MeOH} \) requires: C, 83.65; H, 11.75%.

5:8a:9β-Trimethyl-10a-novurase-12:14-diene from the Product of Lithium Aluminium Hydride Reduction of 5:8a:9β-Trimethyl-12-oxo-10a-novurase-13-ene. (a) The mixture obtained in the previous experiment by lithium aluminium hydride reduction of the αβ-unsaturated ketone (100 mg.) was dissolved in chloroform (2 c.c.) and glacial acetic
acid (20 c.c.), then heated on the steam-bath for 2 hours, with concentrated hydrochloric acid (1 c.c.). On cooling, a crystalline solid separated, which was collected, washed and dried (80 mg.). After two recrystallisations from chloroform-methanol it gave plates, m.p. 195-197°C. which were shown to be 5:8α:9β-trimethyl-10α-novuras-12:14-diene (1-α-amyradiene) (no depression in m.p.); [α]$_D$ -112° (c, 2.5). It gives an orange-brown colouration with tetranitromethane. Light absorption: $\lambda_{max}$ 2340, 2410 and 2500 A. (4 = 15,200, 16,400 and 10,000).

(b) The mixture of alcohols obtained by lithium aluminium hydride reduction of the αβ-unsaturated ketone (66 mg.) was treated with pyridide (2 c.c.) and acetic anhydride (2 c.c.) and heated on the steam-bath for 1 hour. The product, isolated by working up in the usual manner, was crystallised several times from chloroform-methanol to yield 5:8α:9β-trimethyl-10α-novuras-12:14-diene (50 mg.) m.p. 194-196°C. (undepressed); [α]$_D$ -111° (c, 2.2).

Light absorption: $\lambda_{max}$ 2340, 2410 and 2500 A. (4 = 13,300, 15,000 and 8,800).

175-176°C. 90 mg.) in ethanol (10 c.c.) was refluxed with freshly activated zinc dust (0.5 g.) for 5 hours. The solution was filtered and evaporated to give a residue which crystallised from methanol to give yellow needles (72 mg.), m.p. 170-173°C., [α]D + 84° (c,1 l). The product showed no depression in m.p. upon admixture with the starting material.

Reduction of 5:8a:9β-Trimethyl-12:16-dioxo-10α-novulen-13-ene with Zinc in Acetic Acid: The Alcohol C₃₀H₄₈O₅

(a) A solution of 5:8a:9β-trimethyl-12:16-dioxo-10α-novulen-13-ene (m.p. 175-176°C. 400 mg.) in glacial acetic acid (10 c.c.) was refluxed with freshly activated zinc (2.0 g.) for 30 minutes. The colourless solution was then filtered off, treated with water and ether in the usual manner. Upon evaporation of the dry ethereal extract, a pale yellowish gum was obtained which yielded a crop of rhombic plates (260 mg.), m.p. 199-204°C., on crystallisation from aqueous methanol. After eight recrystallisations from the same solvent rhombic plates were obtained, m.p. 214-217°C. [α]D -39° (c,2.1) giving a yellow-brown colour with tetranitromethane in chloroform. Light absorption: λ max. 2080 (ε = 6000). (Found: C,61.53; H,11.04%. C₃₀H₄₈O₅.
requires: C, 81.76; H, 10.98%. Infra-red spectrum in Nujol showed bands at 3300 and 1690 cm.\(^{-1}\)

(b) The above experiment was repeated in an atmosphere of nitrogen. The product was identical with that described above.

**Acetylation of the Product from Zinc-Acetic Acid Reduction of 5:8α:9β-trimethyl-12:15-dioxo-10α-novur-13-ene**: The Acetate \(\text{C}_{53}\text{H}_{46}\text{O}_3\). The alcohol (m.p. 212-214°C., 70 mg.), obtained as described in the previous experiment was dissolved in pyridine (1 c.c.) and treated with acetic anhydride (1 c.c.) at room temperature overnight. The reaction mixture was then diluted with water, extracted with ether and worked up in the usual manner. The residue was crystallised from aqueous methanol to give needles, m.p. 130-134°C., which, after several recrystallizations from the same solvent, yielded the acetate \(\text{C}_{53}\text{H}_{46}\text{O}_3\), m.p. 143-144°C., \([\alpha]_D \approx -38^\circ \ (c \ 0.98)\). It gives a faint yellow colour with tetrainitromethane.

Light absorption: \(\lambda_{\text{max}} \approx 2060\ \text{Å} \ (\epsilon = 4800)\). (Found: C, 79.7; H, 10.6%. \(\text{C}_{53}\text{H}_{46}\text{O}_3\) requires: C, 79.62; H, 10.44%). Infra-red spectrum in Nujol showed bands at 1754, 1720 and 1240 cm.\(^{-1}\).
Oxidation of the Product from Zinc-Acetic Acid

Reduction of 5:8a:9β-trimethyl-12:15-dioxo-10a-novurs-13-ene. — A solution of the alcohol (m.p. 212-214°C, 480 mg.), in glacial acetic acid (50 c.c.), was treated with chromium trioxide (100 mg.; 1 oxygen atom) in a 90% acetic acid solution (5 c.c.), and left at room temperature overnight and then heated on the steam-bath for 15 minutes. Isolation of the product in the usual manner followed by three crystallisations of the residue from aqueous acetone gave 5:8a:9β-trimethyl-12:15-dioxo-10a-novurs-13-ene (125 mg.) as yellow needles, m.p. and mixed m.p. 175-176°C. Light absorption: \( \lambda_{\text{max}} \) 2760 Å. (\( \varepsilon = 8000 \)).

Treatment of the Acetate C\(_{38}\)H\(_{54}\)O\(_{5}\) with Alkali. —

The acetate (m.p. 143-144°C., [\( \alpha \)] \(-38^{\circ}\), 230 mg.) obtained by acetylation of the reduction product from 5:8a:9β-trimethyl-12:15-dioxo-10a-novurs-13-ene was refluxed in an ethanolic potassium hydroxide solution (1%, 100 c.c.) for 1 hour. Isolation of the product in the usual manner, followed by two crystallisations from aqueous methanol gave 5:8a:9β-trimethyl-12:15-dioxo-10a-novurs-13-ene (136 mg.) as yellow needles, m.p. and mixed m.p. 174-175°C., [\( \alpha \)] \(+85^{\circ}\) (c.1.3). Light absorption: Max. at 2760 Å. (\( \varepsilon = 8000 \)).
Treatment of the Alcohol $\text{C}_9\text{H}_{18}\text{O}_2$ with Hydrochloric Acid. - The alcohol (m.p. 212-214°C, $[\alpha]_D$ -39°, 80 mg. obtained by zinc-acetic acid reduction of 5:8α:9β-trimethyl-12:15-dioxa-10α-novura-13-one was dissolved in chloroform (2 c.c.) and glacial acetic acid (10 c.c.) and treated with concentrated hydrochloric acid (2 c.c.) at 100°C. for 2 hours. The product was isolated in the usual manner, to give yellow needles (33 mg.), m.p. 146-148°C., on crystallisation from aqueous methanol. Five recrystallisations from the same solvent gave the dienone $\text{C}_9\text{H}_{16}\text{O}_2$, as yellow needles, m.p. 154-155°C., $[\alpha]_D$ +18° (c,2.2). It gives a yellow colour with tetranitromethane.

Light absorption: $\lambda_{\text{max}}$ 2080 and 3220 Å. (ε = 6250 and 5500). (Found: C,84.63; H,11.2%. $\text{C}_9\text{H}_{16}\text{O}_2$ requires: C,85.2; H,11.0%).

Treatment of the Acetate $\text{C}_9\text{H}_{16}\text{O}_2$ with Hydrochloric Acid. - The acetate $\text{C}_9\text{H}_{16}\text{O}_2$ (m.p. 143-144°C., $[\alpha]_D$ -38° 120 mg.) was dissolved in chloroform (2 c.c.) and acetic acid (15 c.c.) then heated on the steam-bath for two hours with concentrated hydrochloric acid (4 c.c.). The product, isolated in the usual manner, was crystallised from aqueous methanol to give yellow needles (40 mg.), m.p. 149-151°C. which, after several recrystallisations
gave the dienone C_{26}H_{40}O, m.p. 154-155°C. (no depression) 
[a]_{D}^{+}18° (c,1.1).

\(a\)-Amyrin Methanesulphonate. - To a solution of 
\(a\)-amyrin (3.0 g.) in dry pyridine (17 c.c.) was added 
methanesulphonyl chloride (redistilled, b.p. 163°, 
1.7 c.c.) and the mixture allowed to stand overnight. 
The dark-reddish product was treated cautiously with a 
little water, then poured into excess water. The gummy 
precipitate, which hardened upon standing for approximat 
15 min., was filtered and washed with water and methanol. 
It was then repeatedly recrystallised from methanol to 
give \(a\)-amyrin methanesulphonate as hexagonal plates, 
m.p. 120° (decomp.), [a]_{D}^{+}71.5 (c,3.0). For mesyl \(a\)- 
-amyrin, Moller and Hearst (77) give m.p. 116-118°. It 
gives a yellow colour with tetrinitromethane.

Treatment of \(a\)-Amyrin Methanesulphonate with 
Pyridine. - (a) A solution of \(a\)-amyrin methanesulphonate 
(m.p. 120°, 1.0 g.) in pyridine (50 c.c.) was refluxed 
for 2 hours. The solution was then evaporated to drynes 
under reduced pressure, the residue treated with water 
and extracted with benzene. The extract washed with 
water, dried (Na_{2}SO_{4}) and evaporated. The residue was
repeatedly recrystallised from methanol to give plates, m.p. 119-120°, \([a]_D^\text{m} +72^\circ (c,2.2)\), undepressed by the starting material. In another experiment, in which the reflux time was extended to 6 hours, starting material was again obtained.

(b) \(\alpha\)-Amyrin methanesulphonate (1.0 g.) was refluxed in pyridine (50 c.c.) for 17 hours and the product was worked up as in (a) to give a colourless gum which upon standing for several days under methanol-acetone, gave an amorphous solid which, in view of its intractable nature was not further investigated.

(c) \(\alpha\)-Amyrin methanesulphonate (0.5 g.) was dissolved in pyridine (25 c.c.) and the solution refluxed for 48 hours, then worked up as in (a) to give a gummy residue which was dissolved in light petroleum (b.p. 40-60°) and chromatographed on alumina. A fraction (70 mg., 14% yield) was eluted with light petroleum and after crystallisation from acetone gave 8:10:14-trimethyl-8\(\chi\)-novurana-4(23):12-diene (\(\alpha\)-amyradiene-IV), as prismatic needles, m.p. 125-126°, \([a]_D^\text{m} +149^\circ (c,1.7)\). It gives a yellow colour with tetranitromethane. Light absorption, \(\lambda_{\text{max}}\) 2070 A., \(\epsilon = 3800\) (Found: C, 88.2; H, 11.9%). Calculated for C\(_{38}\)H\(_{48}\): C, 88.2; H, 11.8%). For \(\alpha\)-amyradiene-IV, Noller and Hearst (77)

(d) Refluxing α-amyrin methanesulphonate in pyridine for 72 hours and for 6 days, and working up as described before, gave respectively 34 and 50% yields of 8:10:14-trimethyl-5α-novursee-4(23):12-diene.

(e) A solution of α-amyrin methanesulphonate (300 mg in pyridine (30 c.c.) was heated in an autoclave at 210° for 18 hours. The product, worked up as described above gave α-amyradiene-IV (130 mg., 43%), m.p. 119-121°, which after 3 recrystallisations from acetone gave a pure specimen, m.p. 125-127°, [α]D +147° (c, 1.1).

Treatment of 8:10:14-Trimethyl-5α-novursee-4(23):12-diene (α-amyradiene-IV) with Hydrochloric Acid. - A solution of α-amyradiene-IV (m.p. 124-126°, 200 mg.) in chloroform (5 c.c.) and glacial acetic acid (60 c.c.) was treated with concentrated hydrochloric acid (10 c.c. under reflux overnight. The product, worked up in the usual way, gave a brown gum which was dissolved in light petroleum (40-60°) and chromatographed on alumina. Light petroleum eluted a fraction (58 mg.) which was crystallised from methanol-chloroform to give needles, m.p. 148-160°.

After 5 recrystallisations from the same solvent, it gave 5:8α:9β-trimethyl-10α-novursee-12:14-diene (1-α-
-amyradiene) as small flat needles, m.p. 190-192°, (undepressed), [α]D -108° (c, 0.8). It gives an orange colour with tetranitromethane. Light absorption:
λmax: 2340, 2410 and 2500, ε = 15,000, 16,2000 and 10,000

Treatment of α-amyradiene-IV (100 mg.) with trichloroacetic acid (100 mg.) in chloroform (2 c.c.) at room temperature, gave a yellow gum, which failed to give a solid after chromatography.

Ozonolysis of 8:10:14-Trimethyl-5ξ-novursea-4(23):12-diene. - A solution of α-amyradiene-IV (m.p. 124-5°, 0.1 g.) in dry chloroform (100 c.c.) was treated at -40° with ozone (1.2 mol.). After attaining room temperature, the mixture was stirred with zinc dust (1.5 g.) and acetic acid (25 c.c.) for 1 hour. The filtered solution was washed with water (3 x 250 c.c.; see later), the chloroform removed under reduced pressure, and the residue dissolved in light petroleum (40-60°) and chromatographed. Light petroleum (100 c.c.), eluted unchanged α-amyradiene-IV (113 mg.). The fraction (118 mg.) eluted with benzene-light petroleum (1:4, 250 c.c.) was recrystallised six times from methanol or aqueous methanol to give the methyl ketone, C8H8O, as flat needles or hexagonal plates, m.p. 151-152°, [α]D +139.5° (c, 0.95). It gives
a yellow colour with tetranitromethane. Light
absorption: $\lambda_{\text{max}}$ 2060 Å, $\epsilon = 4500$. (Found: C, 84.55;
H, 11.47%. C$_{30}$H$_{46}$O requires: C, 84.8; H, 11.3%).

The water washings (above) were adjusted to pH 7
by addition of sodium bicarbonate, and the solution
distilled. The first fraction (150 cc.) was treated
with a cold saturated solution of dimerdone in water and
the mixture allowed to stand at 0°C overnight. The solid
deposited was isolated and recrystallised from aqueous
methanol to give dimerdone formaldehyde as needles,
(44 mg.) m.p. 186-189° (no depression with an authentic
preparation).

Action of Heat on α-Amyrin Methanesulphonate. -
Dry α-amyrin methanesulphonate (m.p. 119-120°, 0.5 g.)
was heated on the steam-bath for 3½ hours. The dark
red-brown mass was then taken up in ether, repeatedly
washed with water, dried and evaporated. The residue
crystallised from methanol-chloroform to give 5α:8α:9β-
trimethyl-10α-novursa-12:14-diene, (l-α-amyradiene)
(410 mg.), as long plates, m.p. 185-188°, which after
one crystallisation gave a pure specimen, m.p. 194-195°
(no depression), $[\alpha]_D -112° \left( \epsilon, 1.9 \right)$. It gives an orange
colour with tetranitromethane.
Treatment of α-amyrin with Methanesulphonyl Chloride. - To a solution of dry β-amyrin (3.0 g.) in dry pyridine (17 c.c.) was added methanesulphonyl chloride (redistilled, b.p. 163°, 1.7 c.c.). The red solution was allowed to stand at room temperature overnight, treated with a little water to destroy excess reagent and then poured into a large excess of water. The brown gum quickly transformed into a white solid which was separated by filtration, repeatedly washed with water and dried. A solution of the product (2.79 g.) in benzene-light petroleum (1:9, 100 c.c.) was chromatographed. A fraction (950 mg.) eluted with the same solvent, was given seven recrystallisations from acetone to yield oleane-2:12-diene (β-amyradiene-II) as flat needles, m.p. 146-148°, [α]D +136° (c, 2.0). It gives a yellow colour with tetranitromethane. Light absorption:

\[ \lambda_{\text{max}} \approx 2070 \text{ A. (c = 4400).} \]

(Found: C, 88.33; H, 11.66%). Calculated for C₃₆H₄₆: C, 88.16; H, 11.84%). For β-amyradiene-II, Winterstein and Stein (72) give, m.p. 148-150°, \([\alpha]_D +139°\).

Treatment of β-amyrin with Phosphorus Pentoxide. - (a) β-Amyrin (0.5 g.) was dissolved in benzene (25 c.c.) and an excess of phosphorus pentoxide was added with
swirling. The solution quickly assumed a reddish-orange colour and hardened into a gel. After standing for 24 hours at room temperature, the mixture was diluted with water, the layers separated, and the washed benzene solution dried (Na$_2$SO$_4$) and evaporated. A yellow gum which failed to give any crystalline material was obtained. Light absorption: $\lambda_{\text{max}}$ 2070 and 2420 Å. ($\varepsilon$ = 4500 and 4400).

(b) β-Amyrin (0.5 g.) in dry ether (30 c.c.) was shaken with phosphorus pentoxide (0.5 g.) for 24 hours and allowed to stand at room temperature for a further 16 hours. The product, worked up in the usual manner, gave a gum which, upon chromatography, gave most of the starting material (benzene-ether, 1:1) and a small quantity of an uncrystallisable gum.

Treatment of β-Amyrin with Hydriodic Acid. - A solution of β-amyrin (2 g.) in glacial acetic acid (25 c.c.) was refluxed for 2 hours with hydriodic acid (8 c.c.; d,1.7; freshly distilled from hypophosphorous acid). The mixture was then diluted with water, extracted with ether and the extract repeatedly washed with water, sodium thiosulphate solution, sodium bicarbonate solution, dried (Na$_2$SO$_4$) and evaporated under reduced pressure. The
residue, an uncrystallisable gum, showed a single maximal absorption at 2070 Å, in the ultraviolet region.

Repetition of the experiment for 4 hours gave a gum, the ultraviolet spectrum of which revealed a maximum at 2160 Å, and a triplet maximum at 2420, 2500 and 2580 Å.

Repetition of the experiment for 6 hours gave again an uncrystallisable gum which showed a single maximal absorption at 2070 Å, in the ultraviolet region.

Repetition of the experiment for 16 hours yielded an amorphous solid, m.p. 110-145°C., which failed to give a pure product upon repeated crystallisation or upon chromatography and was not further examined.

Light absorption: Max. at 2100 Å.

8:10:14-Trimethyl-5ξ-novoleana-3(4):12-diene (β-Amyrilene-I). - β-Amyrin (5.0 g.) was added portionwise to a suspension of phosphorus pentachloride (3.2 g.) in dry light petroleum (b.p. 60-80°C., 40 c.c.), the mixture shaken for 30 minutes and filtered. The filtrate was washed with warm water, dried (Na₂SO₄), evaporated, and the residue crystallised from acetone to give 8:10:14-trimethyl-5ξ-novoleana-3(4):12-diene (β-amyradiene-I), m.p. 167-170°C., [α]D +110° (c,1.8). Light absorption: λmax 2080 Å (ε = 9200). It gives a yellow colour with
tetranitromethane. (Found: C, 86.8; H, 12.0%. Calc. for C₈₀H₄₆: C, 86.2; H, 11.8%).

For β-amyrilene-1, Vesterberg (68) gives m.p. 175-178°C., [α] +110° (in benzene); Ruzicka, Silbermann and Furter (70) give m.p. 173-175°C., and Winterstein and Stein (72) give m.p. 170-175°C.

Ozonolysis of 8:10:14-Trimethyl-5α-novolean-3(4):12-diene. - A solution of 8:10:14-trimethyl-5α-novolean-3(4):12-diene (m.p. 167-172°C., 1.0 g.) in chloroform (200 c.c.) was treated at -40°C. with ozone (1.2 mols.). After attaining room temperature, the mixture was stirred with zinc dust (3.0 g.) and glacial acetic acid (50 c.c.) for 1 hour. The filtered solution was washed with water (3 x 500 c.c., see later), the chloroform removed under reduced pressure, and the residue dissolved in light petroleum and chromatographed. Light petroleum (100 c.c.) eluted unchanged starting material (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 C₉₇H₄₄O as plates, m.p. 192-194°C., [α] D +215° (c, 2.7). It gives a yellow colour with tetranitromethane.
Light absorption: \( \lambda_{\text{max}} = 2060 \text{ Å} \) (\( t = 5700 \)).

(Found:
C, 85.05; H, 10.83%. \( \text{C}_9\text{H}_8\text{O} \) requires: C, 84.75; H, 11.00%)

The water washings (above) were adjusted to pH7 by addition of sodium hydrogen carbonate, and the solution was distilled. The first fraction (250 c.c.) was treated with 2:4-dinitrophenylhydrazine hydrochloride solution to give acetone 2:4-dinitrophenylhydrazone (117 mg.) as long orange blades, m.p. 123-125°C., which was not depressed upon admixture with an authentic specimen of the compound.

**Treatment of 8:10:14-Trimethyl-5\( \xi \)-novoleana-3(4):12-diene with Boron Trifluoride.** — A solution of 8:10:14-Trimethyl-5\( \xi \)-novoleana-3(4):12-diene (m.p. 167-172°C., 250 mg.) in glacial acetic acid (200 c.c.) was refluxed with boron trifluoride-acetic acid (3 c.c.) for 72 hours. The solution assumed a light reddish-brown colour, which changed to deep green upon cooling. Water and ether were then added and the product, isolated in the usual manner, was a dark gum which failed to give any crystalline solid.

The ultraviolet spectrum showed ill-defined maxima at 2130 and 2500 Å.
8:10:14-Trimethyl-novolean-3(5):12-diene, (β-
Amyrilene-III). - (a) β-Amyrin (2.5 g.) was added
portionwise to a suspension of phosphorus pentachloride
(1.6 g.) in dry light petroleum (b.p. 60-80°C., 15 c.c.)
in a flask fitted with a drying-tube with continuous
shaking for 1 hour. After all the solid was in solution
the flask was stoppered and allowed to stand for 24 hour.
The solution was then treated with water and worked up in
the usual way. The dried (Na₂SO₄) solution was evaporated
to give a colourless gum which gave plates (1.1 g.) from
methanol-chloroform. After four recrystallisations from
the same solvent 8:10:14-trimethyl-novolean-3(5):12-diene
(β-amyrilene-III) was obtained as plates, m.p. 102-104°C
[a]₀ D +120° (c,1.8). It gives a yellow colour with
tetranitromethane. Light absorption: \(\lambda_{max} \text{2090 Å.}
(\epsilon = 9000).

For β-amyrilene-III, Dieterls, Brass and Schaal
(92) give m.p. 103°C.

(b) A mixture of 8:10:14-trimethyl-5ζ-novolean-
-3(4):12-diene (m.p. 167-172°C., 0.5 g.) and trichloro-
acetic acid (0.5 g.) was dissolved in dry chloroform
(5 c.c.) and allowed to stand at room temperature for 1
hour. The solvent was then removed under reduced pressu
without heating. The pale pink crystalline solid, which gave a deep violet melt upon heating on the steam-bath, was taken up in ether, repeatedly washed with water, dried (Na₂SO₄) and evaporated. The residue crystallised from chloroform-methanol to give 8:10:14-trimethylnovoleana-3(5):12-diene as plates (0.18 g.), m.p. 95-97°C. After several recrystallisations from the same solvent the pure compound was obtained, m.p. 102-104°C., (no depression), [α]D +116° (c,2.1).

Attempted Isomerisation of 8:10:14-Trimethylnovoleana-3(5):12-diene (β-Amyrilene-III). — (a) A solution of 8:10:14-trimethylnovoleana-3(5):12-diene (m.p. 100-112°C 1.0 g.) in chloroform (5 c.c.) and acetic acid (20 c.c.) was treated with concentrated hydrochloric acid (2 c.c.) at 100°C for periods of 2, 4 and 6 hours. After each treatment, the product was worked up in the usual manner and in all cases uncrystallisable gums were obtained, all of which gave a red brown colour with tetranitromethane. The ultraviolet spectrum showed, in all cases, maxima at 2070 Å, and triplet maxima at 2420, 2480 and 2580 Å. (b) A solution of the diene (above) (0.4 g.) in chloroform (12 c.c.) and acetic acid (120 c.c.) was refluxed overnight with concentrated hydrochloric acid (20 c.c.).
The product, isolated as usual, was a yellowish gum which failed to give any solid, gave a red-brown tetranitromethane test. Light absorption: Max. at 2070 Å, and a triplet max. at 2420, 2480 and 2580 Å.

(c) The gummy product from the previous experiment was again treated with concentrated hydrochloric acid in chlorform-acetic acid solution, under reflux for 24 hours with further addition of concentrated hydrochloric acid at intervals. Again an uncrystallisable gum was obtained, and the ultraviolet spectrum revealed a single maximal absorption at 2070 Å.

11-Oxo-olean-12-en-3β-yl Acetate. - A solution of β-amyrin benzoate (30 g.) in boiling acetic acid (stabilised 1.5 l.) was treated with a solution of chromic anhydride (30 g.) in 90% acetic acid (stabilised, 600 c.c.) added dropwise during 1 hr. Refluxing was continued for 1½ hr. and the solution then treated with boiling water added portionwise with stirring until a crystalline solid appeared. After standing overnight, the solid was collected, washed and dried (18 g.). Four crystallisations from methanol chloroform gave 11-oxo-olean-12-en-3β-yl benzoate as prismatic needles, m.p. 269-271° (undepressed), [α]_D

m.p. 182-184° from chloroform-methanol. After four
A solution of 11-oxo-olean-12-en-3β-yl benzoate (above, 12 g.) in benzene (100 c.c.) and ethanolic potassium hydroxide (14 g. KOH, 20 c.c. water and 230 c.c. ethanol) was refluxed overnight. The product isolated in the usual manner, was acetylated (100 c.c. each of pyridine and acetic anhydride) at room temperature overnight, worked up, and the product crystallised from methanol-chloroform to give 11-oxo-olean-12-en-3β-yl acetate as needles, m.p. 260-262° (undepressed), [α]_D^22 +118° (c, 0.74).

6°: 8°: 14°-Trimethyl-11-oxo-18α-novoleane-9(10):12-diene. — A solution of 11-oxo-olean-12-en-3β-yl acetate (m.p. 260-262°C., 2.75 g.) in glacial acetic acid (45 c.c.) was refluxed overnight with hydriodic acid (10 c.c.; d, 1.02). The resultant solution was then diluted with water, extracted with ether, and the extract repeatedly washed with sodium thiosulphate solution and water, dried (Na₂SO₄) and evaporated. The residue (yellow gum) was then dissolved in light petroleum (b.p. 40-60°C.) and filtered through an alumina column. Uncrystallisable gums were obtained before and after the product was eluted with benzene-light petroleum mixture (3:2) to give needles (0.7 g.), m.p. 182-186° from chloroform-methanol. After four re-
crystallisations from the same solvent, 5:8:14-trimethyl-11-oxo-18α-novoleana-9(10):12-diene was obtained as needles, m.p. 191-192°C., \([\alpha]_D^{+} +122^\circ \pm 2.7\). It gives no colouration with tetranitromethane. Light absorption:

\[ \lambda_{\text{max}}: 2060, 2560 \text{ and } 2870 \text{ Å.} \] (Found: C, 85.3; H, 11.3%. C\(_{30}H_{48}O_3\) requires: C, 85.2; H, 11.0%).

The product showed no depression in m.p. when mixed with a specimen of the product obtained by a similar treatment with hydriodic acid of 11-oxo-18α-olean-12-en-3β-y1 acetate (95).

**Reduction of 5:8:14-Trimethyl-11-oxo-18α-novoleana-9(10):12-diene with Lithium Aluminium Hydride.** — A solution of 5:8:14-trimethyl-11-oxo-18α-novoleana-9(10):12-diene (m.p. 188-190°C., 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 hours. The product was worked up in the usual manner, and the residue dissolved in light petroleum (b.p. 60-80°C.) and chromatographed on an alumina column:

<table>
<thead>
<tr>
<th>Volume</th>
<th>Eluent</th>
<th>Weight</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 ml.</td>
<td>Light petroleum</td>
<td>147 mg.</td>
<td>1 - 6</td>
</tr>
<tr>
<td>100 ml.</td>
<td>&quot;</td>
<td>33 mg.</td>
<td>7 and 8</td>
</tr>
<tr>
<td>650 ml.</td>
<td>Benzene-light petroleum (1:9)</td>
<td>464 mg.</td>
<td>9 - 21</td>
</tr>
</tbody>
</table>
Fractions 1-6 were combined, and after repeated crystallisations from methanol-chloroform, 5:8:14-trimethyl-18α-novoleana-9(10):12-diene was obtained as matted needles, m.p. 161-162°C., [α]_D +101° (c, 0.85). It gives a yellow colour with tetranitromethane.

Light absorption: \( \lambda_{\text{max}} \) 2080 Å (ε = 10,500). (Found: C, 88.0; H, 12.0%. C_{30}H_{46} requires: C, 88.2; H, 11.8%).

Fractions 7 and 8 were not further examined.

Fractions 9-21 were combined and after several crystallisations from chloroform-methanol, 5:8:14-trimethyl-novoleana-9(10):11:13(18)-triene was obtained as needles, m.p. 135-136°C., [α]_D -400° (c, 1.8).

It gives a red-brown colour with tetranitromethane.

Light absorption: \( \lambda_{\text{max}} \) 2860, 2950 and 3080 Å (ε = 51,000, 36,000 and 25,400). (Found: C, 88.9; H, 11.7%.

C_{30}H_{46} requires: C, 88.6; H, 11.4%).

The product was not depressed in m.p. when mixed with a specimen of 5:8:14-trimethyl-novoleana-9(10):11:13(18)-triene prepared by treatment of oleana-9(11):12-dien-3β-ol with phosphorus pentoxide in benzene (95).

Wolff-Kishner Reduction of 5:8:14-Trimethyl-11-oxo-18α-novoleana-9(10):12-diene. - The oxodiene (m.p. 188-190°C., 500 mg.) was treated with sodium methoxide
solution in methanol (from 0.5 g. sodium and 25 c.c. methanol) and hydrazine hydrate (100%, 5 c.c.) in an autoclave at 200° for 18 hours. The product was worked up in the usual manner to give a residue which was dissolved in light petroleum (40/60°) and chromatographed. A fraction (380 mg.), eluted with light petroleum gave, after five recrystallisations from chloroform-methanol, 5:8:14-trimethyl-18α-novolena-9(10):12-diene as matted needles, m.p. 160-161° (no depression), [α]_D +100° (c,1.2). It gives a yellow colour with tetranitromethane.

8:10:14-Trimethyl-5β-novolena-3(4 or 5):9(11):12-triene. - Oleana-9(11):12-dien-3β-ol (β-amyradienol-I) (0.8 g.) was added portionwise to a suspension of phosphorus pentachloride (0.42 g.) in light petroleum (b.p. 60-80°C., 25 c.c.), the mixture shaken until all the compound has passed into solution (1 hour) and then refluxed for 2 minutes. Water was then added and the product worked up as usual to give a residue which was crystallised five times from acetone to give 8:10:14-trimethyl-5β-novolena-3(4 or 5):9(11):12-triene as needles, m.p. 150-152°C., [α]_D +356° (c,2.7). It gives a deep red-brown colour with tetranitromethane. Light absorption: λ_max.
2060 and 2800 Å. (λ = 2300 and 8000). (Found: C, 88.24; H, 11.76%. C₆₀H₄₆ requires: C, 88.60; H, 11.40%).

Treatment of this triene (100 mg.) in glacial acetic acid solution (10 c.c.) with hydriodic acid (1 c.c.; d, 1.1) under reflux overnight yielded a colourless un-crystallisable gum, the ultraviolet spectrum of which revealed a single absorption maximum at 2060 Å. When treated in a similar manner, oleana-9(11):12-dien-3β-ol yielded a colourless gum which failed to give any crystalline solid and which exhibited a similar maximal absorption in the ultraviolet region at 2060 Å.

Treatment of 8:10:14-Trimethyl-5ξ-novoleana-3(4):9(11):12-triene with Trichloroacetic acid. - A solution of 8:10:14-trimethyl-5ξ-novoleana-3(4):9(11):12-triene (m.p. 150-152°C., 40 mg.) and trichloroacetic acid (40 mg. in dry chloroform (1 c.c.) was kept at room temperature for 1 hour after which the solvent was evaporated under reduced pressure without heating. The pink gummy residue was then taken up in ether and worked up in the usual manner to give needles (25 mg.), m.p. 120-123°C., from aqueous acetone. After two further recrystallisations from the same solvent, 5:8:14-trimethyl-novoleana-9(10):11:13(18)-triene was obtained as needles, m.p. 133-134°C.
Treatments of Oleaena-11:13(18)-dien-3β-ol with Phosphorus Pentoxide. - A mixture of oleaena-11:13(18)-dien-3β-ol (β-amyradienol-II) (m.p. 226-227°, 0.5 g.) and phosphorus pentoxide (1.0 g.) in benzene (30 c.c.) was shaken for 24 hours. The resultant orange gelatinous mass was treated with water and benzene and worked up as usual. Evaporation of the dry benzene extract gave a yellowish gum which was dissolved in light petroleum (40/60°, 50 c.c.) and filtered through an alumina column. A fraction (350 mg.) eluted with light petroleum was given 3 crystallisations from methanol to yield 5:8:14-trimethyl-novoleana-9(10):11:13(18)-triene, as flat needles, m.p. 133-134° (no depression), [α]_D D-394° (ε, 2.9). It gives deep brown colour with tetranitromethane. Light absorption: λ_{max} 2840, 2960 and 3080 Å. (ε = 31,000, 37,000 and 26,000).

Treatments of oleaena-11:13(18)-dienyl acetate (0.5 g.) with a mixture of hydroiodic acid (d,1.7; 2 c.c.) and acetic acid (25 c.c.) under reflux overnight, gave an uncrystallisable yellow gum, λ_{max} 2080 Å. (ε = 10,500).
8:10:14-Trimethyl-5\textsuperscript{\textbeta}-novoleana-3(4 or 5):11:13(18)-triene. - Oleaenal-11:13(18)-dien-3\beta-ol (m.p. 226-227\textdegree, 1.0 g.) was shaken for 1 hour with a suspension of phosphorus pentachloride (1.0 g.) in light petroleum (dry, b.p. 60/90\textdegree, 30 c.c.). After evolution of hydrogen chloride had ceased, the solution was filtered, washed with water, dried (Na\textsubscript{2}SO\textsubscript{4}) and evaporated. The residue was crystallised from acetone to give needles (0.68 g.), m.p. 121-126\textdegree. After four recrystallisations from the same solvent, or from methanol, 8:10:14-trimethyl-5\textsuperscript{\textbeta}-novoleana-3(4 or 5):11:13(18)-triene was obtained as needles, m.p. 130-131\textdegree, [\alpha]\textsubscript{D} -49\textdegree (c,1.4). It gives a dark orange-brown colour with tetrinitromethane.

Light absorption: Max. at 2080 \textmu m (\epsilon = 8500), and a triple max. at 2430, 2510 and 2600 \textmu m (\epsilon = 30,500, 32,500 and 21,000). (Found: C,68.41; H,11.66\%. C\textsubscript{36}H\textsubscript{26} requires: C,68.60; H,11.40%).

Attempted Acid Isomerisation of 8:10:14-Trimethyl-5\textsuperscript{\textbeta}-novoleana-3(4 or 5):11:13(18)-triene. - (a) A solution of the 3(4 or 5):11:13(18)-triene (m.p. 129-130\textdegree, 140 mg.) and trichloroacetic acid (140 mg.) in chloroform (2 c.c.) was kept at room temperature for 1 hour. The solvent was then removed under reduced pressure and the
residue worked in the usual manner. The product, after a few crystallisations from methanol, gave needles (105 mg.), m.p. 150-151°, undepressed by the starting material.

(b) A solution of the triene (100 mg.) in chloroform (5 c.c.) and acetic acid (25 c.c.) was treated with concentrated hydrochloric acid (5 c.c.) on the steam-bath for 1 hour. The product was shown to be the starting material (60% recovery).

(c) A solution of the triene (200 mg.) in acetic acid (80 c.c.) was refluxed overnight with concentrated hydrochloric acid (10 c.c.). The product (22 mg.) isolated by chromatography, was again starting material.

Attempted Isomerisation of 5:8:14-Trimethyl-18α-novoleana-9(10):12-diene. — (a) A solution of 5:8:14-trimethyl-18α-novoleana-9(10):12-diene (m.p. 161-162°C, 72 mg.) in chloroform (2 c.c.) and glacial acetic acid (25 c.c.) was treated with concentrated hydrochloric acid (1 c.c.) at room temperature for 48 hours. The fluorescent green solution was then worked up in the usual manner, to give a residue which was dissolved in light petroleum (b.p. 40-60°C.) and filtered through alumina. The residual remainder allowed to stand overnight. The crystalline
crystallised from chloroform-methanol as matted needles, m.p. 160-161°C. undepressed by the starting material. 

(b) The above experiment was repeated, in approximate the same proportions, refluxing the mixture overnight. The product, isolated in the usual manner, was a yellowish gum which failed to give any solid and which gave a light red-brown colour with tetraniotromethane. Light absorption: Max. at 2070 Å. and a triplet max. at 2420, 2480 and 2560 Å.

(c) The gummy residue from the above experiment was further treated with concentrated hydrochloric acid in acetic acid-chloroform solution under reflux for 24 hours with addition of hydrochloric acid at intervals. Again an uncrycstallisable gum was obtained, the ultraviolet spectrum of which revealed a single maximum at 2150 Å. 

12-Oxo-olean-3β-yl Benzoate. - A solution of β-amyrin benzoate (20 g.) in ethyl acetate (1.4 l.) was treated at 50-55° with a mixture of hydrogen peroxide (100 vols., 100 c.c.) and formic acid (98%, 300 c.c.) added dropwise during 2 hr. with stirring. Stirring was then continued for 4 hr., at the end of which period, about half the solvent was removed by distillation and the remainder allowed to stand overnight. The crystalline
solid deposited was collected and crystallised twice from acetone to give 12-oxo-cleanan-3β-yl benzoate as glistening plates (12 g.), m.p. 255-258° (no depression), \([\alpha]_D = \,^o (c, 0.9)\).

and exhibited ultraviolet light absorption at 300 A. 158 158

5:8a:9β-Trimethyl-12-oxo-10α:18β-novolean-13-ene. - Hydric acid (4 c.c., d, 1.7) was added to a solution of 12-oxo-cleanan-3β-yl benzoate (m.p. 255-258°C., 1.0 g.) in acetic acid (20 c.c.), the mixture refluxed for 16 hours, diluted with water, and extracted with ether. The extract was repeatedly washed with sodium thiosulphate solution, sodium hydrogen carbonate solution and water, dried (Na₂SO₄) and evaporated. The crude product (0.36 g., m.p. 155-159°C.) was crystallised three times from aqueous methanol to give 5:8α:9β-trimethyl-12-oxo-10α:18β-novolean-13-ene as long plates, m.p. 171-172°C., \([\alpha]_D = -32° (c, 2.5)\). It does not give a colour with tetranitromethane.

Light absorption: \(\lambda_{\text{max}} \) 2050 and 2600 Å. \((\epsilon = 3800\) and 9700). (Found: C, 84.64; H, 11.56%. C, H requires C, 84.84; H, 11.40%).

5:8α:9β-Trimethyl-10α-18β-novolean-12:14-diene. - A solution of 5:8α:9β-trimethyl-12-oxo-10α-18-novolean-13-ene (m.p. 166-168°C., 1.0 g.) in dry ether (200 c.c.)
was added dropwise to a suspension of lithium aluminium hydride (1.0 g.) in dry ether (200 c.c.) and the mixture refluxed for 2 hours. The product (680 mg.), isolated in the usual way, gave a yellow colour with tetranitromethane and exhibited ultraviolet light absorption at 2130 Å.

A portion of the product (100 mg.) in a solution of chloroform (3 c.c.) and glacial acetic acid (25 c.c.) was treated with concentrated hydrochloric acid (2 c.c.) and the mixture heated on the steam-bath for 30 minutes. On cooling, a crystalline solid deposited which was collected and recrystallised from chloroform-methanol to give 5:8c:9β-trimethyl-10α-18β-novolean-12:14-diene (75 mg.) as needle, m.p. 155-156°C., [α]_D^25 -83° (c, 2.5). It gives an orange-brown colour with tetranitromethane.

Light absorption: λ_max 2340 (shoulder), 2410 and 2490 (shoulder) Å. (ε = 15,000, 16,000 and 10,700).

(Found: C, 88.09; H, 11.74%. C_{30}H_{34} requires: C, 88.16; H, 11.84%).

5:8c:9β-Trimethyl-12:15-dioxo-10α:18β-novolean-13-ene

(a) Chromium trioxide (0.6 g.) in 90% acetic acid (7 c.c.) was added portionwise to a solution of 5:8c:9β-trimethyl-12-oxo-10:18β-novolean-13-ene (m.p. 168-170°C., 1.0 g.) in acetic acid (72 c.c.), and the mixture stirred on the
steam-bath for 1 hour. Methanol was then added and the solution evaporated under reduced pressure. Water was then added and the mixture extracted with ether and worked up in the usual manner. The product was dissolved in benzene-light petroleum (3:7) and chromatographed on alumina. Elution with the same solvent mixture (200 c.c.) yielded a solid (600 mg.), m.p. 139-143°C. After four recrystallisations from aqueous methanol, it gave 5:8a:9β-trimethyl-12:15-dioxo-10α:18ξ-novolean-13-ene as yellow needles, m.p. 145-146°C., [α]D -8°, -7° (c,2.2, l.9). It does not give a colour with tetraniitromethane. Light absorption: λmax 2220 and 2780 Å. (ţ = 3100 and 800 (Found: C,82.27; H,10.74%. C30H46O2 requires: C,82.13; H,10.57%). From the chromatography column was also eluted a small quantity (41 mg.) of an amorphous orange solid which did not give any satisfactorily crystalline material and was not further examined.

(b) A solution of 5:8a:9β-trimethyl-12-oxo-10α:18ξ-novolean-13-ene (m.p. 168-170°C., 120 mg.) in 10% ethanolic potassium hydroxide (100 c.c.) was refluxed for 2 hours. The reaction mixture was then worked up in the usual manner and the ethereal extract dried (Na2SO4)
and evaporated to give a yellow solid (70 mg.), m.p. 138-142°C. After four recrystallisations from aqueous methanol, 5β:8α:9β-trimethyl-12:15-dioxo-10α-18ξ-novolean-13-ene was obtained as yellow needles, m.p. 145-146° (no depression), $[\alpha]_D -7^\circ$ (c, 2.4).

Light absorption: $\lambda_{max}$ 2220 and 2770 A. ($\varepsilon = 3,200$ and 7,700).

**11-Oxo-18α-olean-12-en-3β-yl Acetate.** A solution of 11-oxo-olean-12-en-3β-yl benzoate (m.p. 269-271°, 30 g) in ethanolic potassium hydroxide (15%, 2.4 l.) was refluxed for 52 hr. The brown solution was then concentrated to half bulk, diluted with hot water (1 l.) and allowed to stand overnight, whereby a crystalline solid deposited which was collected and dried (26 g.). This product was then acetylated (120 c.c. pyridine and 80 c.c. acetic anhydride) on the steam-bath for 1 hr., and worked up as usual, to give 11-oxo-18α-olean-12-en-3β-yl acetate (11.5 g.) as small prisms from methanol-chloroform, m.p. 270-272° (no depression), $[\alpha]_D +73^\circ$ (c, 2.5).

**18α-Olean-12-en-3β-yl Acetate.** A solution of 11-oxo-18α-olean-12-en-3β-yl acetate (m.p. 270-272°, 11.5 g) in stabilised acetic acid (1.5 l.) was added to a suspens
of freshly reduced platinum (from 4.5 g. of PtO₂) in acetic acid (500 c.c.) and shaken with hydrogen for 72 hours. The product, isolated in the usual way, was crystallised from methanol-chloroform to give 18α-olean-12-en-3β-yl acetate as plates (7 g.), m.p. 237-239° (undepressed), [α]D +51° (c, 2.5).

**12-Oxo-18α-oleanan-3β-yl Acetate.** - A solution of 18α-olean-12-en-3β-yl acetate (m.p. 237-239°, 7.0 g.) in ethyl acetate (500 c.c.) was treated, at 50-60°, with a mixture of hydrogen peroxide (30%, 30 c.c.) and formic acid (98%, 100 c.c.) added dropwise during 1 hr. with stirring. Stirring was continued, at 50-60°, for further 6 hr., and the solution concentrated to a small bulk. The solid separated was collected (2.3 g.) and crystallised 4 times from methanol-chloroform to give 12-oxo-18α-oleanan-3β-yl acetate as prismatic needles, m.p. 287-288°C (undepressed), [α]D +74° (c, 2.8).

**Action of Hydriodic Acid on 12-oxo-18α-oleanan-3β-yl Acetate.** - Hydriodic acid (4 c.c., d, 1.7) was added to a solution of 12-oxo-18α-oleanan-3β-yl acetate (m.p. 287-288°C., 1.0 g.) in glacial acetic acid (20 c.c.) and the mixture refluxed overnight. The product was then
worked up in the usual manner to give a residue which was dissolved in light petroleum (b.p. 40-60°C.) 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°C., [α]_D^20 +50° (c, 2.5). It gives a yellow colour with tetranitromethane.

Light absorption: \(\lambda_{\text{max}} \approx 2100\text{ Å} \quad (\varepsilon = 6200)\). (Found: C, 84.96; H, 11.56\%. C_{30}H_{40}O requires: C, 84.84; H, 11.40%) 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-10\(\alpha\)-18α-novolean-9(11)-ene as needles, m.p. 247-248°C., [α]_D^20 +99° (c, 0.89). It gives no colouration with tetranitromethane.

Light absorption: \(\lambda_{\text{max}} \approx 2440\text{ Å} \quad (\varepsilon = 11,200)\). (Found: C, 85.06; H, 11.57\%. C_{30}H_{40}O requires: C, 84.84; H, 11.40%)

Lithium Aluminium Hydride Reduction of 5:8:14-trimethyl-12-oxo-10\(\alpha\)-18α-novolean-9(11)-ene, followed by Dehydration. - A solution of 5:8:14-trimethyl-12-oxo-
-10\(\xi\):18\(\alpha\)-novolean-9(11)-ene (m.p. 242-244°C., 55 mg.) in dry ether (50 c.c.) was added to a suspension of lithium aluminium hydride (100 mg.) in dry ether (50 c.c.) and the mixture refluxed for 2 hours. The product, isolated by working up in the usual manner, was a gum which exhibited a maximal absorption in the ultraviolet light at 2060 Å. A solution of the residue in acetic anhydride (20 c.c.), containing freshly fused sodium acetate (100 mg.) was refluxed for 2 hours. The resultant solution was evaporated under reduced pressure, water added and extracted with ether. The ethereal extract, washed with water and dried (Na\(\text{2}SO_4\)), gave, upon evaporation, a residue which crystallised from chloroform-methanol (30 mg.), m.p. 167-169°C. Four recrystallisations from the same solvent gave 5:8:14-trimethyl-9\(\xi\):10\(\xi\)-novoleana-11:13(18)-diene or 5:8:14-trimethyl-18\(\alpha\)-novoleana-9(10):11-diene as plates, m.p. 178-179°C., \([\alpha]_D^\circ+30^\circ\) (c, 0.5). It gives a dark brown colour with tetraniitromethane.

Light absorption: \(\lambda_{\text{max}}\) 2450 (shoulder), 2520 and 2600 Å (shoulder).

(Found: C, 88.07; H, 12.16%. C\(_{39}\)H\(_{44}\) requires: C, 88.16; H, 11.94%).
Attempted Rearrangement of 8:10:14-Trimethyl-12-oxo-18a-novolean-3(4 or 5)-ene with Alkali and Acid. - (a)

A solution of 8:10:14-trimethyl-12-oxo-18a-novolean-3(4 or 5)-ene (m.p. 177-179°C., 170 mg.) in 5% ethanol solution of potassium hydroxide (100 c.c.) was refluxed for 1 hour. The solution was then diluted with water, extracted with ether and worked up in the usual manner. The product crystallised from chloroform-methanol as long plates (150 mg.) m.p. 165-170°C. which, upon repeated crystallisation from the same solvent, gave the starting material, m.p. and mixed m.p. 180-181°C., [α]$_D$ +49° (c)

(b) The unconjugated "enone" recovered from the previous experiment was dissolved in a mixture of concentrated hydrochloric acid (2 c.c.), chloroform (4 c.c.), and glacial acetic acid (20 c.c.) and the solution heated on the steam bath for 1 hour. The product, isolated in the usual manner, was shown to be the starting material.

(c) A solution of 8:10:14-trimethyl-12-oxo-18a-novolean-3(4 or 5)-ene (m.p. 177-179°C., 130 mg.) in acetic acid (20 c.c.) was refluxed with hydroiodic acid (4 c.c.) overnight. The product, isolated in the usual manner in a poor yield, was again the starting material.
3-Oxo-olean-12-ene. - A solution of β-amyrin (olean-12-en-3β-ol) (5 g.) in acetic acid (stabilised, 250 c.c. and benzene (30 c.c.) was treated with a solution of chromic anhydride (0.9 g.) in 90% acetic acid (stabilised 27 c.c.) at room temperature overnight. The product, isolated in the usual way, crystallised from methanol-chloroform to give 3-oxo-olean-12-ene as needles, m.p. 178-180°, [α]D +112° (c, 3.2).


Olean-12-ene. - A mixture of 3-oxo-olean-12-ene (β-amyrenone) (m.p. 177-179°, 1.0 g.), sodium methoxide solution in methanol (from 1 g. sodium and 50 c.c. methanol and hydrazine hydrate (100%, 10 c.c.) was heated at 200° in an autoclave for 18 hours. The product, worked up in the usual manner, after three crystallisations from methanol-chloroform, gave olean-12-ene (β-amyrene-II) as needles (0.71 g.), m.p. 160-161°, [α]D +94° (c, 1.9). It gives a yellow colour with tetranitromethane.

Light absorption: λmax 2070 Å (ε = 3100). For β-amyrene-II, Winterstein and Stein (72) give m.p. 162°, [α]D +94°.
18α-olean-12-en-3β-ol. - A solution of 18α-olean-12-en-3β-yl acetate (m.p. 237-239°, 1 g.) in dry ether (400 c.c.) was refluxed with lithium aluminium hydride (1 g.) for 20 min. The product, isolated in the usual manner, was crystallised from methanol to give 18α-olean-12-en-3β-ol as fibrous needles (0.8 g.), m.p. 211-212°, [α]_D +45° (c, 2.2).

Allan and Spring (60) give m.p. 213-214°, [α]_D +60°.

3-Oxo-18α-olean-12-ene. - Chromic anhydride (0.8 g.) was added portionwise to pyridine (pure redistilled, 8 c.c.) with occasional cooling, and the mixture vigorously shaken until a deposit of the yellow chromic-acid-pyridine complex formed a thick slurry. To this, was added a solution of 18α-olean-12-en-3β-ol (m.p. 211-212°, 0.8 g.) in pyridine (8 c.c.) and the mixture allowed to stand at room temperature for 18 hours. The resultant thick suspension was then filtered and the filtrate worked in the usual manner. The product was crystallised five times from methanol-chloroform to give 3-oxo-18α-olean-12-ene (0.48 g.) as plates, m.p. 209-210°, [α]_D +80°. It gives a yellow colour with tetranitromethane.

Light absorption: λ_max. 2060 Å, ε = 3600. (Found: C, 84.48; H, 11.62%. C_{30}H_{48}O requires: C, 84.84; H, 11.39%).
18a-Olean-12-ene. - A mixture of 5-oxo-18a-olean-12-ene (m.p. 207-209°, 450 mg.), sodium methoxide (from 450 mg. sodium and 25 c.c. methanol) and hydrazine hydrate (100%, 5 c.c.) was heated at 200° in an autoclave for 18 hours. The product was worked up as usual to give a residue, which after 6 recrystallisations from methanol-chloroform gave 18a-olean-12-ene (210 mg.) as plates, m.p. 186-188°, [a]_D +37° (c, 3.5). It gives a yellow colour with tetranitromethane.

Light absorption: \( \lambda_{\text{max}} = 2070 \, \text{Å} \) (\( \epsilon = 2500 \)). (Found: C, 87.7; H, 12.27%. C_{30}H_{50} requires: C, 87.73; H, 12.27%).

Lupeol Hydrochloride. - [cf. Halsall, Jones and Meakins (99)]. - Dry ethanol (800 c.c.) which had been saturated with dry hydrogen chloride gas at 0°, was added to a solution of lupeol (10 g.) in dry ethanol (500 c.c.) and the mixture allowed to stand at room temperature for 5 days. The mixture was then treated with water, extracted with chloroform and the extract washed with sodium bicarbonate solution and water, dried (Na_2SO_4) and evaporated.

Crystallisation of the residue from ethanol gave lupeol hydrochloride (4.0 g.) as fibrous needles, m.p. 204-206°, (decomp.), [a]_D -30° (c, 2.1).

Halsall et al. give m.p. 211-212°, [a]_D -31°.
Olean-18-en-3β-yl Acetate (Germaniceryl Acetate). - A solution of lupeol hydrochloride (m.p. 204-206°, 2.8 g.) in acetic anhydride (50 c.c.) was refluxed for 24 hours. Upon cooling, a crystalline solid deposited which was collected, dried, and dissolved in benzene-light petroleum (1:9, 100 c.c.) and chromatographed. The main fraction, (1.7 g.), eluted with the same solvent, was crystallised from ethanol-chloroform to give olean-18-en-3β-yl acetate (germaniceryl acetate), as plates, m.p. 276-277°, [α]D +18° (c.2.3).

Halsall et al. (99) give m.p. 279-280°, [α]D +18°.

Olean-18-en-3β-ol (Germanicol). - A solution of olean-18-en-3β-yl acetate (m.p. 276-277°, 1.1 g.) in dry ether (500 c.c.) was treated with lithium aluminium hydride (1.0 g.) and the suspension refluxed for 10 minutes. The product, worked up as usual, gave, on crystallisation from methanol, olean-18-en-3β-ol (germanicol) (0.9 g.) as fine needles, m.p. 177-178°, [α]D +6° (c.3.08).

Halsall et al. (99) give m.p. 180-181°, [α]D +7°.

3-Oxo-olean-18-ene. - A solution of olean-18-en-5β-ol (m.p. 177-178°, 680 mg.) in acetic acid (110 c.c.) and chloroform (27 c.c.) was added to a solution of chromic acid (110 c.c.) was refluxed with concen
anhydride (250 mg.) in 95% acetic acid (20 c.c.) and the mixture kept at room temperature for 2 days. Excess methanol was then added and the product worked up as usual, the residual product, after evaporation, was dissolved in light petrol (40-60°, 80 c.c.) and chromatographed using benzene-light petrol mixture (3:7) to elute the product (410 mg.). Three recrystallisations from methanol-chloroform gave 3-oxo-olean-18-ene as lustrous plates, m.p. 183-184°, [α]_D +38° (c, 2.3).

Halsall et al. (99) give m.p. 188-190°, [α]_D +37°.

**Olean-18-ene (Germanicene).** - A mixture of 3-oxo-olean-18-ene (m.p. 183-184°, 240 mg.), sodium methoxide (from 250 mg. sodium and 15 c.c. methanol) and hydrazine benzoate (100%, 3 c.c.) was heated at 200°, in an autoclave for 18 hours. The product, isolated as usual, was crystallised five times from methanol-chloroform to give olean-18-ene (germanicene) as plates, (0.16 g.), m.p. 168-169°, [α]_D +5.5° (c, 1.1).

Simpson (98) gives m.p. 171-172°, [α]_D +3°.

**Treatment of Olean-12-ene, 18α-Olean-12-ene, Olean-13(18)-ene and Olean-18-ene with Hydrochloric Acid.** - (a) A solution of olean-12-ene (m.p. 158-160°, 200 mg.) in acetic acid (110 c.c.) was refluxed with concentrated
hydrochloric acid (44 c.c.) for 16 hours. The solution was worked up in the usual manner to give a residue which crystallised from methanol-chloroform as small blades, (110mg.), m.p. 168-175°. After four further recrystallisations from the same solvent, the "mixed crystal" (see Theoretical section D) was obtained as flat needles, m.p. 184-185°, \([\alpha]_D\) -19° (c,1.0). It gives a strong yellow colour with tetranitromethane.

(b) A solution of 16α-olean-12-ene (m.p. 186-188°, 150 mg.) in acetic acid (120 c.c.) was refluxed overnight with concentrated hydrochloric acid (20 c.c.). The product isolated as usual, was crystallised four times from methanol-chloroform to give the "mixed crystal" as flat needles (70 mg.), m.p. 185-186°, \([\alpha]_D\) -18° (c,2.3). It gives a deep yellow colour with tetranitromethane and was undepressed in m.p. when mixed with the preparation under (a). Light absorption: \(\lambda_{max} = 2090\text{ A, } \epsilon = 6400\).

(c) A mixture of olean-13(18)-ene (m.p. 186-187°, 100 mg.) (kindly supplied by Mr. G. Brownlie, this Department), acetic acid (66 c.c.) and concentrated hydrochloric acid (15 c.c.) was refluxed overnight. The product required seven recrystallisations from methanol-chloroform to give the "mixed crystal", as flat needles, m.p. 186-188°, (no depression), \([\alpha]_D\) -19.5° (c,1.3).
(d) A solution of olean-18-ene (m.p. 167-168°, 100 mg.) in acetic acid (60 c.c.) and concentrated hydrochloric acid (28 c.c.) was refluxed overnight. Upon cooling and standing for several hours, a crystalline solid deposited which was collected (66 mg.) and crystallised seven times from methanol-chloroform to give blades, m.p. 182-183°, [α]_D^-12.5° (c,1.6). After further four recrystallisations from the same solvent, the "mixed crystal" was obtained as blades, m.p. 186-187° (no depression), [α]_D^-18.5° (c,1.3). It gives a yellow colour with tetranitromethane.

Light absorption: \( \lambda_{\text{max}} \) 2080 Å. (*) = 6400.

Synthesis of the "Mixed Crystal". - A mixture of 18aolean-12-ene (m.p. 186-188°, [α]_D^+57°, 20 mg.) and olean-13(18)-ene (m.p. 186-187°, [α]_D^-48°, 40 mg.) was repeatedly crystallised from methanol-chloroform to give the "mixed crystal" (see Theoretical section D) as blades, m.p. 186-187°, [α]_D^-21° (c,3.1). It was not depressed in m.p. upon admixture with any of the preparations described above. It gave a yellow colour with tetranitromethane.

Light absorption: \( \lambda_{\text{max}} \) 2080 Å. (*) = 6500.

When mixtures were prepared consisting of pairs of the four oleanenes described in the previous experiment, other than 18a-olean-12-ene and olean-13(18)-ene (above),
either ill-defined products melting over a large range of temperature were obtained, or one of the components was isolated in a pure state.
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