PART-II

OXIDATIVE TRANSFORMATIONS OF THE TRITERPENOIDS OF THE URSANE AND OLEANANE SKELETA

INTRODUCTION OF 11,12-DOUBLE BOND AND 13(28)-OXIDE MOIETY IN THE URSANE SYSTEM
Isomeric pentacyclic triterpenes of the α- and β-amyrin series differ only in the nature of methyl substitution patterns in their E ring. The former contain two vicinal methyls at C-19 and C-20, while these methyls are geminal at C-20 in the latter. From a naive consideration of structural similarity it appears that they would exhibit identical chemical properties. While this is true for reactions at some of the reactive sites of their molecules, a careful examination of their conformations (CCLXVII) and (CCLXIX) suggests that there may be significant differences in the reactivities of the α-amyrins at the sites which are within the steric influence of the 19-methyl group. This would be particularly manifested in reactions which are initiated by the 12,13-double bond of
these compounds.

Although a number of such reactions were studied \(^{52-54, 95-97}\) earlier, the possible role of the 19-methyl group in the \(\alpha\)-amyrins in remarkably changing the course of reactions in certain cases has not been clearly indicated. The first two extreme examples of this effect were observed in the laboratory of the present investigator in course of re-investigation of the action of hydrogen peroxide on ursolic acid acetate (CXXII), a reaction earlier studied by Jeger et al.\(^{52}\) in 1946. The three oxidation products (CXXIII), (CXXIV) and (CXXV) [Scheme 67] were reisolated and their structures were established\(^{51}\) by spectral and chemical evidences. Unlike the corresponding epoxide (CXXVI) of the oleanane skeleton, undergoing smooth acid-catalysed rearrangement to the 12-keto derivative

\[\text{(CXXII)} \xrightarrow{\text{H}_2\text{O}_2/\text{HOAc}} \text{(CXXIII)}\]

\[\text{(CXXIV)} + \text{(CXXV)} \]

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(CXXVII), the ursane analogue (CXXIII) was found to be remarkably stable under identical reaction conditions. The latter was only partly converted to (CXXIX) on refluxing with 6N ethanolic sulphuric acid for a prolonged period (10 hr) \[\text{Scheme 68}\]. Further, the 12-keto ursane derivative (CXXIX), once formed under extremely stringent condition is smoothly converted to the enol-acetate (CXXX) on just warming with AcO/Py, as compared to the conversion of the 12-keto oleanane derivative (CXXVII) to the corresponding enol-acetate (CXXXI), requiring refluxing of (CXXVII) with AcO/Py for 3 hr.

\[
\begin{align*}
\text{(CXXVI)} & \xrightarrow{6N \text{ H}_2\text{SO}_4, \text{EtOH, reflux}} \text{(CXXIV)} \\
\text{(CXXIII)} & \xrightarrow{6N \text{ H}_2\text{SO}_4, \text{EtOH, 10 hr.}} \text{(CXXII)} \\
\text{(CXXIX)} & \xrightarrow{\text{AcO}_2/\text{Py, 3 hr.}} \text{(CXXX)} \\
\text{(CXXVII)} & \xrightarrow{\text{AcO}_2/\text{Py, reflux}} \text{(CXXXI)}
\end{align*}
\]

Such remarkable differences in the chemical reactivities of (CXXIII) and (CXXIX) bearing an ursane skeleton from the corresponding oleanane derivatives (CXXVI) and (CXXVII) are obviously due to steric effects of the 13-methyl group in the former compounds.

The possible mechanisms of formation of the three oxidation products (CXXIII), (CXXIV) and (CXXV) obtained from ursolic acid acetate (CXXII) by the action of \(\text{H}_2\text{O}_2\) in glacial HOAc have been examined\(^{51}\) taking into consideration of the various steric effects.
existing in the vicinity of the reacting sites C-13, C-12 and C-11. An examination of the conformation of \((\text{CXXII})\) expressed as \((\text{CCLXXa})\) shows that the above sites are considerably crowded both on the beta (by 8-methyl, 10-methyl and 17-carboxylic groups) and alpha (14-methyl group and 18-19 bond) sides giving an impression of an overall lower reactivities of these sites towards an attacking reagent from either side. While these factors are common in both \(\Delta^{12,13}\) -ursane and oleananes, the former may be characterised by an additional steric effect exerted by the 19-methyl group towards a reagent attacking these sites from the \(\alpha\)-side. Such differences in the steric effects in the ursane and oleanane systems would, therefore, be expected to trigger the same reactions involving these sites in the two systems in substantially different manners. In the case of ursolic acid acetate \((\text{CXXII})\), the formation of the three oxidation products was assumed to involve the intermediacy of a \(12\beta,13\beta\)-epoxide \((\text{CCLXXIA})\) \(\text{Scheme 69}\) \(\text{path 'a'}\) formed intermolecularly by the action of peracetic acid formed \text{in situ} on the 12,13-double bond of \((\text{CCLXXa})\) \(\text{path 'a'}\). The intermediate epoxide \((\text{CCLXXIA})\) may undergo acid-catalysed rearrangement involving hydride shift from C-12 to C-13 to give the 12-ketodihydro acid \((\text{CXXV})\) \(\text{path 'b'}\). Alternatively, the epoxide may open up by attack of a nucleophile \(\text{H}_2\text{O}\) at C-12 followed by lactonisation of the resultant 13-hydroxy group with 17-carboxyl function to give 12\(\alpha\)-hydroxy-\(\gamma\)-lactone \((\text{CCLXXIIa})\) \(\text{path 'c'}\). The formation of the latter may also be envisaged by the nucleophilic attack of the 17-carboxyl group on C-13 with concomitant hydroxylation at C-12 by peracetic acid approaching from the \(\alpha\)-side \(\text{path 'f'}\), although this route would involve a greater steric hindrance to the approaching peracetic acid from the \(\alpha\)-side. The formation of the epoxy \(\gamma\)-lactone \((\text{CCLXXIIIa})\) has been explained either by the intermediate formation of a 11-hydroperoxy derivative \((\text{CCLXXIV})\) followed by acid-catalysed rearrangement involving nucleophilic participation of the 17-carboxyl group \(\text{path 'e'}\) or by opening of the \(12\beta,13\beta\)-epoxide with concomitant elimination of a proton from C-11 and lactonisation of the resultant 13-hydroxyl function with 17-carboxyl group to form the 11,12-olefinic lactone \((\text{CCLXXVa})\) which on epoxidation with peracetic acid may give rise to \((\text{CCLXXIIIa})\) \(\text{path 'd'}\). Of these two alternative mechanisms, the route 'e' appears to be a less likely process in view of the poor availability of triplet
oxygen under the boiling reaction condition.

While considering the above mechanistic approaches, it appears that the steric effect of the 19-methyl group in \( \Delta^{12,13} \)-ursanes might play a significant role in the oxidative transformations of these compounds, which are initiated by the 12,13-double bond. Consequently, this would also suggest that in absence of the 19-methyl group in the \( \Delta^{12,13} \)-oleananes the same reaction might take up a different course. This idea prompted us to study the action of hydrogen peroxide on oleanolic acid acetate (CCLXXVI) with a view to examining how the presence or absence of the 19-methyl group in (CXXII) and (CCLXXVI) respectively governs the course of the above reaction in the two cases. The report of Barton et al.\(^97\) of the formation of 12\( \alpha \)-hydroxy-\( \gamma \)-lactone (CCLXXVII) as the sole product from (CCLXXVI) under essentially similar condition and the absence of the oleanane counterparts (CCLXXVIII) and (CXXV) of the isomeric ursane derivatives (CXXIII) and (CXXV), respectively, is a further point in support of our conjecture.

Accordingly, oleanolic acid acetate (CCLXXVI) was subjected to the action of hydrogen peroxide in boiling acetic acid following the condition used by Jeger et al.\(^52\) for ursolic acid acetate (CXXII). This has resulted in the isolation of two compounds, O-I, \( \text{C}_{32}\text{H}_{46}\text{O}_{5} \) (m\(^+\) 512), m.p. 295\(^\circ\), \( \int_{0}^{D} 342 \) (CHCl\(_3\)) and O-II, \( \text{C}_{32}\text{H}_{30}\text{O}_{5} \) (m\(^+\) 514), m.p. 277\(^\circ\), \( \int_{0}^{D} 368.8 \) (CHCl\(_3\)). The physical constants and the IR (Fig. 1) \( \gamma_{\text{max}} \) cm\(^{-1}\) 3540 (OH), 1770 (\( \gamma \)-lactone), 1730 and 1240 (\( \delta \)-acetate); NMR \( \int_{0}^{B} 4.4 \), 1H, m (\( \gamma \)-lacile), 3.80, 1H, m (\( \gamma \)-lacile) and 0.79-1.23 (7 \( \gamma \)-lactyls) (Fig. 2) and the mass \( \int_{0} \) significant peaks at m/e 514 (m\(^+\)), 496, 454, 436, 249, 246, 234, 205, 204, 203, 189, 175, 161, 147, 134, 133 and 119 (Fig. 3), Scheme 70\(^{77}\) spectral data of O-II compare excellently with those of 3\( \beta \)-acetoxo-12\( \alpha \)-hydroxy-olean-28-oic-13(28)-lactone (CCLXXVII) reported earlier\(^54,97\).

O-I shows in its IR spectrum (Fig. 4) bands for an acetoxo function (\( \gamma_{\text{max}} \) 1720 and 1240 cm\(^{-1}\)), a \( \gamma \)-lactone (\( \gamma_{\text{max}} \) 1765 cm\(^{-1}\)) and an epoxide moiety (\( \gamma_{\text{max}} \) 870 cm\(^{-1}\)). The presence of the latter is also indicated by the two-proton singlet at \( \delta 3.0 \) in its NMR spectrum (Fig. 5) which also reveals the signals at \( \delta 4.4 \) and 2.04 for a secondary
FIG-1 IR SPECTRUM OF 3β-ACETOXY-12α-HYDROXY-OLEAN-28-OIC-13(28)-LACTONE (O-II) IN KBr
FIG. 2 PMR SPECTRUM OF 3β-ACETOXY-12β-HYDROXY OLEAN-28-OIC-13(28)-LACTONE (O-II)
FIG. 4. IR SPECTRUM OF 3β-ACETOXY-11α,12ß-EPoxy-OLEAN-28-OIC-13(28)-LACTONE (0-1) IN KBr
Scheme 70
Mass fragmentation of O-II

\[ \text{m/e 514 (M+)} \]

O-II (CLXXVII)

\[ \text{m/e 454} \]

\[ \text{m/e 234} \]

\[ \text{m/e 496} \]

\[ \text{m/e 436} \]

\[ \text{m/e 246} \]

\[ \text{m/e 249} \]

\[ \text{m/e 189} \]

\[ \text{m/e 205} \]

\[ \text{m/e 204} \]

\[ \text{m/e 133} \]
acetoxy function and at 0.8-1.24 for seven C-methyls. The mass spectrum of O-I (Fig. 6) showing significant peaks at m/e 512 (M⁺), 477, 494, 484, 468, 452, 277, 263, 249, 235, 218, 217, 203, 189, 175, 135, 133, 121 and 119/Scheme 7/ strikingly resembles that of (CXXIII). The physical constants of O-I, and its above spectral data suggest its identity with 3β-acetoxy-l1x,12β-epoxy-olean-28-oic-13(28)-lactone (CCXXXVIII) earlier obtained by Kitagawa et al. in course of photochemical irradiation of oleanolic acid. The above structural assignment of O-I was finally confirmed by its chemical correlation with (CCXXXVII) /Scheme 7/. Thus treatment of O-I with 6N ethanolic sulphuric acid afforded the hydroxy-keto derivative (CCXXX) which on acetylation gave (CCXXXI) identical in all respects /m.p., m.m.p. and superimposable IR spectrum (Fig. 7)/ with the product of chromic acid oxidation of (CCXXXVII). The results of the above reaction thus conclusively establish the validity of our conjecture that the presence and absence of the 19-methyl group in (CXXII) and (CCCLXXVII) respectively can significantly alter the course of the above reaction with the two compounds. It is interesting to note that while oxidation of (CXXII) afforded, besides (CXXIII) and (CXXIV), the keto-dihydroderivative (CXXV), the corresponding oleanane analogue (CCXXXIX) is totally absent in identical oxidation of (CCLXXVII), although (CXXII) and (CCLXXVII) differ only in the alkyl substitution pattern in their E-ring. This difference in the chemical behaviour of (CXXII) and (CCLXXVII) may be attributed to the additional steric effect of the 19-methyl group in the former and its absence in the latter as evident from their conformational expressions (CCXXXa) and (CCXXXb), respectively. Based on the mechanism proposed at the beginning (Scheme 69), the formation of the keto-dihydro acid (CXXV) or (CCXXXIX) requires the intermediacy of a 12β,13β-epoxide (CCXXXIa) or (CCXXXIIb) which would rearrange presumably through hydride shift (Scheme 69, path 'b'); the formation of (CCXXXIIa) and (CCXXXIIb) may involve the alternative paths 'c' and 'f'. In the ursane series (as in 'CXXII) both these processes would be expected to involve a high activation energy due to steric
FIG-6 MASS SPECTRUM OF 3β-ACETOXY-11\alpha,12\alpha-EPOXY-OLEAN-28-OIC-13(28)-LACTONE (O-I)
Scheme 71

Mass fragmentation of 0-I

![Chemical structure diagrams with mass fragmentation reactions and ionization states](attachment:image.png)
interference of the 19-methyl group either to the nucleophile (HgO* path 'c') or to the peracid (path 'f') approaching from the alpha side. This makes the reaction leading to Scheme 72

(CXXV) a significantly competitive process. In the absence of such additional steric effect of the 19-methyl group in the oleanane system (as in CCLXXVI), the reaction leading to (CCLXXIIb) as well as (CCLXXXIIIb) becomes considerably less energetic and so
proceeds well before the path 'b' becoming a competing process to give (CCLXXIX).

On the basis of the foregoing mechanistic rationale, it was tempting to assume that $\Delta^{12,13}$-ursanes and oleananes bearing a hydroxymethyl group at C-17 might also undergo similar oxidative transformations with hydrogen peroxide, and that the 17-hydroxymethyl group might also undergo nucleophilic participation like the 17-carboxyl function in (CXXII) and (CCLXXVI). With this assumption, both uvaol (CCLXXXIIa) and erythrodiol (CCLXXXIIb) were treated with hydrogen peroxide in boiling acetic acid. This has resulted in the isolation of three crystalline compounds in each case. With uvaol (CCLXXXIIa), the three compounds were A, $\text{C}_{32}\text{H}_{52}\text{O}_3$ ($m^+ 484$), m.p. 159°, B, $\text{C}_{32}\text{H}_{52}\text{O}_3$ ($m^+ 484$), m.p. 242° and C, $\text{C}_{34}\text{H}_{54}\text{O}_4$ ($m^+ 526$), m.p. 151°. Similarly, with erythrodiol (CCLXXXIIb), the three products were the corresponding isomeric compounds, D, $\text{C}_{32}\text{H}_{52}\text{O}_3$ ($m^+ 484$), m.p. 191°, F, $\text{C}_{32}\text{H}_{52}\text{O}_3$ ($m^+ 484$), m.p. 155° and F, $\text{C}_{34}\text{H}_{54}\text{O}_4$ ($m^+ 526$), m.p. 182°. The IR spectrum of compound A (Fig. 8) shows bands for hydroxyl group ($\gamma_{\text{max}} 3620 \text{ cm}^{-1}$) and acetoxy function ($\gamma_{\text{max}} 1725$ and 1230 cm$^{-1}$). The presence of the same functionalities in compound B was also indicated by its IR spectrum (Fig. 9) ($\gamma_{\text{max}} 3560$ (OH), 1720 and 1265 (OAc) cm$^{-1}$). The IR spectrum of compound C (Fig. 10), on the other hand, is devoid of any hydroxyl absorption, but shows absorption for acetoxy group ($\gamma_{\text{max}} 1735$ and 1245 (OAc) cm$^{-1}$). All the three compounds are characterised by weak IR absorptions around 1650 cm$^{-1}$ for trisubstituted double bond. The PMR spectra of A (Fig. 11), B (Fig. 12) and C (Fig. 13) while showing some common features, viz., the presence of an olefinic proton ($\delta 5.10-5.19$) and seven C-methyls ($\delta 0.76-1.24$) differ essentially from each other in the nature and the number of acetyl groups present in their molecules. Thus, while the PMR spectrum of compound A is characterised by the presence of signals for secondary hydroxyl group ($\delta 3.28, 1\text{H}, \text{m}$) and an acetoxyethyl group attached to a quaternary carbon ($\delta 3.77, 2\text{H}$, ABq, J 10 Hz and $\delta 1.99, 3\text{H}, \text{s}$), that of compound B shows signals for a secondary acetate function ($\delta 4.4, 1\text{H}, \text{m}$ and 2.05, $3\text{H}, \text{s}$) and a hydroxymethyl group linked to a quaternary carbon atom ($\delta 3.35, 2\text{H}$, ABq, J 10 Hz). The signals in the spectrum of C, on the
FIG. 8  IR SPECTRUM OF 28-O-ACETYL UVAOL (A) IN KBr.

WAVELENGTH IN MICRONS

WAVENUMBER CM⁻¹
WAVELENGTH IN MICRONS

WAVENUMBER CM⁻¹

FIG. 10 IR SPECTRUM OF 3,28-O-DIACETYL UVAOL (C) IN KBr
FIG. 11 NMR SPECTRUM OF 28-O-ACETYL UDP-Ac (A)
other hand, correspond to those of a secondary acetate function (δ 4.33, 1H, ə) and an acetoxymethyl group (δ 3.83, 2H, ABq) along with a six proton singlet at δ 2.03 for two acetate methyl groups. The above spectral data coupled with the mass fragmentation of compound A (Fig. 14): Significant peaks at m/e 484 (M+424, 276, 221, 208, 207, 203, 189 and 133) typical of the α- or β-amyris suggest the structure (CXXXIIIa) for compound A and (CXXXIVa) and (CXXXVb) for compounds B and C, respectively. This has been finally confirmed by their chemical correlation with uvaol. Thus acetylation of either compound A or B with \( \text{Ac}_2\text{O}/\text{Py} \) afforded C, which, in turn, was identical in all respects and superimposable IR spectra (Fig. 15) with uvaol diacetate. Alternatively, alkaline hydrolysis of all the compounds afforded uvaol. Similarly, compounds D, E and F were shown to be 23-0-acetyl erythrodiol (CXXXIIIb), 3-0-acetyl erythrodiol (CXXXIVb) and 3,23-0,0-diacetyl erythrodiol (CXXXVb), respectively, on the basis of their PMR data (compound D (Fig. 16) \( δ_{\text{ppm}} \): 5.1, 1H, ə (olefinic proton), 3.75, 2H, ABq, J 10Hz (acetoxymethyl), 3.15, 1H, m (hydroxymethine), 1.98, 3H, s (one acetylmethyl) and 0.87-1.26 (7 C-methyls); compound E (Fig. 17) \( δ_{\text{ppm}} \): 5.1, 1H, ə (olefinic proton), 4.5, 1H, m (acetoxymethine), 3.35, 2H, ABq, J 10Hz (hydroxymethyl), 2.0, 3H, s (one acetylmethyl), 0.85-1.2 (7 C-methyls); compound F (Fig. 18) \( δ_{\text{ppm}} \): 5.1, 1H, ə (olefinic proton), 4.42, 1H, m (acetoxymethine), 3.38, 2H, ABq, J 10Hz (acetoxymethyl), 1.95, 6H, s (two acetate methyls) and 0.8-1.2 (7 C-methyls)]. The structure of compound D (CXXXIIIb) was further supported by its IR (Fig. 19) \( \nu_{\text{max}} \): 3480 (OH), 1710 and 1260 (OAc) cm⁻¹ and characteristic mass spectrum (Fig. 20) similar to A \( \text{Scheme 73} \). D, E and F were correlated to erythrodiol in the same manner as that with compounds A, B and C.

It is interesting to note that in the above reactions with either uvaol or erythrodiol not a trace of any oxidation product could be detected and it turned out that the reaction ended in mere acetylation of uvaol or erythrodiol to different extents. In fact, the

FIG-14 MASS SPECTRUM OF 28-O-ACETYL UVAOL (A)
WAVELENGTH IN MICRONS
WAVENUMBER CM$^{-1}$

FIG. 15 IR SPECTRUM (IN KBr) OF: I 3,28-0,0 DIACETYL UVAOL (C)
II ACETYLATION PRODUCT OF B
III ACETYLATION PRODUCT OF A
FIG. 16 PMR SPECTRUM OF 28-O-ACETYL ERYTHRODIOL (D)
FIG 18 PMR SPECTRUM OF 3,28-O-DIACETYL ERYTHRODIOL (F)
FIG. 19 IR SPECTRUM OF 28-O-ACETYL ERYTHROLID (D) IN KBr
FIG. 20 MASS SPECTRUM OF 28-O-ACETYL ERYTHRODIOL (D)
Scheme 73

Mass fragmentations of compounds A and D

\[ m/e 484 (M^+) \]

A (OGLXXXIIIa) : \( R_1 = R_3 = \text{Me}, R_2 = H \)
D (OGLXXXIIIb) : \( R_1 = H, R_2 = R_3 = \text{Me} \)

- \( -\text{H}_2\text{O}, -\text{CH}_2=\text{O} \)
- \( m/e 276 \)
- \( m/e 208 \)
- \( m/e 203 \)
- \( m/e 133 \)
- \( m/e 484 \)
- \( m/e 207 \)
- \( m/e 189 \)
same results were obtained on identical treatment of uvaol or erythrodiol with 80% acetic acid in absence of hydrogen peroxide. The products of the above reactions are depicted in Scheme 74.

The total absence of any oxidation product in the attempted oxidative transformations of uvaol and erythrodiol with hydrogen peroxide in acetic acid established the significant role played by the 17-carboxyl group in initiating oxidative reactions of ursolic and oleanolic acid acetates under identical reaction conditions and necessitated reconsideration of certain assumptions made in the original mechanistic interpretation of the formation of various oxidation products of (CXXII) and (CCLXXVI)
with H$_2$O$_2$/HOAc. The role of the 17-carboxyl group was further indicated by the results of similar oxidation of the following triterpenoids of the $\alpha$- and $\beta$-amyrin skeleta bearing at 2-17 functional groups other than a carboxyl group. Thus when $\alpha$-amyrin acetate (CCLXXXVI) and acetylmethyl ursolate (CCLXXXVIIa) was subjected to the above reaction, the former was only partially hydrolysed to form trace of its deacetyl derivative (CCLXXXVIII), while the latter was oxidised only in trace to a compound C$_{33}$H$_{52}$O$_5$, m.p. 272$^o$, which from its spectral data $\gamma_{\text{max}}$ 1735 and 1235 (OAc and O$_2$Me), 1700 ($\geq$90) cm$^{-1}$ (Fig.21) was shown to be the 12-ketodihydro derivative (CCLXXXIXa). Similar oxidation of acetyl methyl oleanolate (CCLXXXVIIb) gave also a very small amount of an oxidation product, C$_{33}$H$_{52}$O$_5$, m.p. 177$^o$ $\gamma_{\text{max}}$ 1725 and 1240 (OAc and O$_2$Me), 1700 ($\geq$90) cm$^{-1}$ (Fig. 22) characterised as the corresponding 12-ketodihydro derivative (CCLXXXIXb) (Scheme 75).
FIG. 21 IR SPECTRUM OF 3-O-ACETYL 12-KETO DIHYDRO METHYL URSOLATE IN KBr
FIG. 22  IR SPECTRUM OF 3-O-ACETYL 12-KETODIHYDRO METHYL OLEANOLATE IN KBr
The latter was, however, obtained in a slightly better yield than its ursane analogue (CCLXXXI).

The foregoing observations thus clearly demonstrate that for any appreciable oxidation with \( \text{H}_2\text{O}_2 \) to be initiated by the 12,13-double bond of the triterpenoids of both ursane and oleanane skeleta, the presence of the 17-carboxyl group is an essential requirement. These observations further advocate the possibility that for processes in the oxidation of (CXXII) and (CCLXXVI) requiring the intermediacy of the corresponding \( \text{12}\beta,13\beta \)-epoxide, the 17-carboxylic group in their molecules is first converted to a percarboxylic acid function (CCXC) which is sterically well-poised to epoxidise the 12,13-double bond intramolecularly (path 'g') as shown in the Scheme 76.

**Scheme 76**

Due to excessive steric crowding the alternative intermolecular epoxidation of the 12,13-double bond by peracetic acid formed in situ, as postulated earlier (path 'a', Scheme 69), is possibly less facile, though not excluded completely. This would possibly account for
the absence of any appreciable oxidation product with triterpenoids bearing functional
groups at C-17 other than a carboxylic group. With a view to providing supportive evi-
dence for the above assumption attempt was made to prepare the percarboxy acid (CCXC)
corresponding to (CILXXa) and to carry out the transformation directly with (CCXC). For
this purpose (CXXII) was treated with oxalyl chloride to give the corresponding acid
chloride (CCXCI), m.p. 293°, \( \nu_{\text{max}} \) 1800 cm\(^{-1}\) (CDCl) (Fig. 23), which was treated with
alkaline \( \text{H}_2\text{O}_2 \) or with \( \text{Na}_2\text{O}_2 \) in toluene in the usual manner (Scheme 77). Neutralisation
of the product in either case, however, failed to produce any percarboxy acid (CCXC),
and, instead, afforded the unreacted acid chloride (CCXCI). This has been attributed to
the remarkable stability of (CCXCI) towards \( \text{S}_2 \text{H}^2 \) reaction on steric ground. Incidentally,
(CCXCI) has been found to be one of the most stable acid chlorides, hitherto known,
which remains unchanged under ordinary hydrolytic conditions and can be crystallised and
chromatographed.

**Scheme 77**

![Scheme 77](image)

Although the attempted preparation of the percarboxy acid (CCXC) as described
above has failed, the participation of (CCXC) in the oxidation of (CXXII) and (CCLXXVI)
has, however, gained credence from the results of oxidation of (CXXII) and its methyl
ester (CCLXXVIIa) with \( \text{H}_2\text{O}_2 \) in absence of \( \text{HOAc} \), thereby excluding the possibility of the
formation of peracetic acid. Thus treatment of (CXXII) with \( \text{H}_2\text{O}_2 \) in benzene gave the
12-ketodihydroacid (CXXV) \( \text{characterised as its methyl ester (CCLXXXIa)}, \) albeit in
poor yield \( \text{Scheme 78}, \). The thin-layer chromatogram of the total reaction product,
FIG. 23 IR SPECTRUM OF 3-O-ACETYL URSOLIC ACID CHLORIDE IN KBr
however, indicated the formation, in traces, of two more compounds which were different from (CXXIII) and (CXXIV). Under identical reaction condition, (CCLXXXVIIa), on the other hand, remained unchanged. This, therefore, demands the generation of (CCXC) for the formation of the 13β,13β-epoxide (CCLXXIA) acting as the obligatory intermediate for the formation of (CXXV) as shown in Scheme 78. The nonreactivity of (CCLXXXVIIa) towards oxidation with H₂O₂ is due to its failure to produce any percarboxy acid intermediate.

Scheme 78

![Scheme 78](image)

It may be recalled here that regarding the formation of (CCLXXIIIa) or (CCLXXIIIb) two possible mechanisms, path 'e' and 'd', Scheme 69 have been envisaged. One of these (path 'e') involving the intermediacy of the 11-hydroperoxy derivative
(CCLXXIV) has already been discouraged in view of the low availability of the triplet oxygen under the boiling reaction condition for any appreciable formation of (CCLXXIV). The alternative mechanism (path 'd') involving the intermediate 11,12-olefinic γ-lactone (CCLXXIVa) appears to be more attractive.

It was, therefore, felt necessary to prepare an appropriate Δ11,12-ursane derivative and to examine its behaviour towards H2O2 in boiling HOAc. The report by Kitagawa et al54 of the formation of (CCLXI) which was assumed to be a precursor of a number of physiologically active saikogenins, prompted the author to prepare its ursane counterpart (CCLXIIa), as it would also serve to establish the validity of the mechanistic path 'd' for the formation of (CCLXIIIa) and (CCLXIIIb).

For this purpose uvaol (CCLXXIIa) was treated99 with NBS in aqueous dioxan and the reaction mixture was exposed to light from a 500 Watt electric lamp. This has yielded two crystalline compounds G, C30H47O2Br (M+ 519), m.p. 204°, and H, C30H49O2Br (M+ 521), m.p. 189°. The IR spectrum of compound G (Fig. 24) shows absorption for >C=O in a 6-membered ring (ν max 1698 cm\(^{-1}\)), which is replaced by hydroxyl absorption (ν max 3400 cm\(^{-1}\)) in the spectrum of compound H (Fig. 25). The PMR spectrum of compound G (Fig. 26) showing signals at 6 4.17 (1H, m, Wh/2 3Hz; -CH2-CH2(Gb)-), 3.45 (2H, ABq, J 7Hz; -O-C-CH2-), 2.55 (2H, -O-(CH2)-) and 0.84-1.26 (7 G-methyls) are essentially similar to that of compound H (Fig. 27) 6 4.20 (1H, m, Wh/2 3Hz -CH2-CH2(Gb)-).

Fig. 24 IR Spectrum of Compound 6 in KBr
Fig. 25  IR Spectrum of Compound H in KBr
3.45, 2H, ABq, J 7 Hz (C-C-C-C-C), 3.16, 1H, m (>CH-OH) and 0.30-1.26 (7 G-methyls) except that the signal for a keto-methylene group in the former is replaced by that of a hydroxymethine in the latter. The spectra of both the compounds show that the primary hydroxyl group of uvaol is no longer free, but has cyclised to form a cyclic ether in each compound, and that the olefinic proton of uvaol is replaced by a signal attributable to a bromo-methylene proton. The low Wh/2 value of this signal speaks of its equatorial nature. The mass spectrum of compound G (Fig. 28) showing significant peaks at m/e 519 (M+), 437, 431, 301, 299, 245, 234, 233, 231, 219, 215, 207, 205, 203, 201, 191 and 163 coupled with the above spectral data establish structure (CCXCIII) and (CCXCIV) for compounds G and H respectively.

Scheme 79
Mass fragmentation of Compound G

\[
\text{Compound G (CCXCIII)}
\]

\[
\text{m/e 519(M+), m/e 431, m/e 301, m/e 299, m/e 245, m/e 234, m/e 233, m/e 231, m/e 219, m/e 215, m/e 207, m/e 205, m/e 203, m/e 201, m/e 191 and m/e 163.}
\]
FIG. 28  MASS SPECTRUM OF COMPOUND G
Reduction of compound G with NaBH₄ afforded compound H and superimposable IR spectra (Fig. 29) thereby confirming their interrelationship.

**Scheme 80**

Mechanistically, the formation of compounds G and H may be assumed to involve bromination of uvaol at C-12 from the β-side with concomitant cyclisation of its primary hydroxyl at C-13 (Scheme 81), the 3-keto function of G being generated by a separate process of oxidation of a secondary alcohol to the corresponding ketone with NBS.

**Scheme 81**
IR SPECTRUM (KBr) OF: I. NaBH₄ REDUCTION PRODUCT OF 6, II. COMPOUND - H
Having achieved the introduction of 13,28-oxide moiety in the ursane skeleton, the next step in the proposed transformation is the generation of a 11,12-double bond in the said system. This was thought to be achieved by dehydrobromination of (CCXCIV). Accordingly, (CCXCIV) was treated with collidine\(^{100}\) at 140° for 2 hr under nitrogen atmosphere. Contrary to expectation, this has resulted in the regeneration of uvaol (Scheme 82). This may be explained by the fact that collidine being a bulky base fails to abstract an axial hydrogen at C-11 of (CCXCIV) due to severe 1,3-diaxial interaction in the transition state, and, instead, eliminates bromine at C-12 as a bromonium ion as shown in Scheme 82.

![Scheme 82](image)

It is interesting to note that treatment of (CCXCIV) with LiF\(^{101}\) in DMF providing a base like F\(^-\) of considerably smaller volume also failed to bring about the desired transformation.

---

dehydrobromination. This has, however, produced in very poor yield an uncharacterised compound, m.p. $>300^\circ$, which is devoid of any olefinic proton as evident from its PMR spectrum (Fig. 30).

When all attempts to dehydrobrominate (CXXIV) failed, an alternative route for the preparation of the desired $\Delta_{11,12}$-ursane derivative (CXXVIIa) was tried. In this method, acetyl methyl ursolate (CCLXXXVIIa) was treated with NBS to give a compound I, $C_{33}H_{50}O_5$ ($M^+$ 526), m.p. 235$^\circ$, which shows UV absorption $\lambda_{max}$ 250 nm $(\log \epsilon 4.06)$ characteristic of an $\alpha,\beta$-unsaturated ketone of the type $\gamma C = CH - C = O$. This was also supported by its IR spectrum (Fig. 32) showing bands at 1620 and 1658 cm$^{-1}$ besides those for CO$_2$Me (1732 cm$^{-1}$) and acetoxy (1720 and 1235 cm$^{-1}$) functions. The mass spectrum of compound I (Fig. 33) shows significant peaks at m/e 526 ($M^+$), 511, 467, 466, 317, 276, 261, 257, 249, 248, 217, 189 and 175, together with its UV and IR spectral data are consistent with the structure (CXXVIIa) for the compound. Compound I is analogous to that of its oleanane counterpart (CXXVIIb) obtained from acetylmethyl oleanolate (CCLXXXVIIb) with $t$-butyl chromate in $CCl_4$ (Scheme 85). Reduction of (CXXVIIa) with LiAlH$_4$ afforded the compound J, $C_{30}H_{50}O_3$ ($M^+$ 458), m.p. 213$^\circ$ which from its IR $\gamma_{max}$ 3340-3380 cm$^{-1}$ (OH) (Fig. 34) and mass (Fig. 35) with significant peaks at m/e 458 ($M^+$), 441, 440, 271, 234, 216, 207, 203 and 189 (Scheme 84) spectral data was shown to have the structure (CXXVIIa). It would be interesting to note that compound J was found to be fairly stable compared to its oleanane analogue (CXXVIIb) which was reported to be highly unstable (Scheme 85). This is another example of the divergence in the chemical behaviour of two isomeric members of oleanane and ursane skeletons, and this was further borne out from a comparison of the results of chemical transformation of the two compounds (CXXVIIa) and (CXXVIIb) as described in the sequel.

Treatment of compound J with TSOH gave the compound K, $C_{30}H_{48}O_2$ ($M^+$ 440), m.p. 210$^\circ$. It shows the IR band at 3340 cm$^{-1}$ (Fig. 36) for hydroxyl group and gave a monoacetyl derivative, $C_{32}H_{50}O_3$ ($M^+$ 482), m.p. 220$^\circ$ with $Ag_2O/Py$. The PMR spectrum
FIG. 30 PMR SPECTRUM OF LiF REACTION PRODUCT OF COMPOUND H

CHCl₃
FIG. 31 UV SPECTRUM OF COMPOUND I IN ETIOH

$\lambda_{\text{max}} \text{ nm (log } \varepsilon) = 206 (3.61) & 250 (4.06)$
FIG. 32 IR SPECTRUM OF COMPOUND I IN KBr

WAVELENGTH IN MICRONS
3 3.5 4 4.5 5 5.5 6 6.5 7 7.5 8 9 10 11 12
WAVENUMBER CM⁻¹
3000 3500 4000 4500 5000 5500 6000

3000 2000 1800 1400 1200

FiguRe 32: IR Spectrum of Compound I in KBr.
FIG. 33 MASS SPECTRUM OF COMPOUND I
FIG. 34  IR SPECTRUM OF COMPOUND J IN KBr
FIG. 36  IR SPECTRUM OF COMPOUND K IN KBr

WAVENUMBER (cm⁻¹)

TRANSMITTANCE (%)
Scheme 83
Mass fragmentation of Compound I

**Chemical Structures and Reactions**

- **m/e 467**: 
  - \(-\text{CO}_2\text{Me}\) 
  - \(\text{CC}^\text{Me}\)

- **m/e 526 (M\(^+\))**: 
  - \(\text{Compound I (CCXCVa)}\)

- **m/e 511**: 
  - \(-\text{CH}_3^*\)

- **m/e 243**: 
  - \(18\text{H} \rightarrow 14\)

- **m/e 249**: 
  - \(\text{AcO}\)
  - \(-\text{HOAc}\)
  - \(\text{m/e 189}\)

- **m/e 189**: 
  - \(\text{AcO}\)

- **m/e 175**: 
  - \(\text{m/e 217}\)
  - \(\text{m/e 257}\)
  - \(\text{m/e 261}\)
Scheme 84

Mass fragmentation of Compound J

m/e 440

m/e 271

m/e 441

m/e 216

m/e 458 (m⁺)

Compound J (CXXVIIa)

m/e 207

m/e 203

m/e 234

m/e 189
of Compound K (Fig. 37) shows signals (Table 1) for two olefinic protons at δ 5.37 and 5.67, a one-proton multiplet at δ 3.20 for a hydroxymethine proton and a two-proton AB quartet at δ 3.34 for the system $\equiv C - O - CH_2 - C \equiv$, besides the usual signals for seven C-methyls. In the PMR spectrum of its acetyl derivative (Fig. 38) the two-proton AB quartet remains unaltered and only the hydroxymethine proton ($\equiv CH - OH$) of compound K is shifted downfield to δ 4.45 ($\equiv CH$-OAc), the methyl protons of the acetyl group appearing at δ 1.95 (Table 1). This is indicative of the fact that in both compound K and its acetate $\int_{\text{max}}^{} 1730$ and 1250 (OAc) cm$^{-1}$ (Fig. 39), the 17-hydroxymethyl group of compound J (CCXVla) is no longer free but has cyclised to form the 13,23-oxide ring with concomitant acid-catalysed elimination of the 11-hydroxyl group and migration of the
Figure 39: IR Spectrum of Acetyl Derivative of Compound K in KBr
<table>
<thead>
<tr>
<th>Chemical shifts (δ ppm)</th>
<th>PMR signals of Compound K</th>
<th>Probable assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.72-1.02</td>
<td>2H</td>
<td>7 C-methyls</td>
</tr>
<tr>
<td>3.20</td>
<td>1H, m</td>
<td>-CO-CH₂-CH-</td>
</tr>
<tr>
<td>3.34</td>
<td>2H, ABq, J 6Hz</td>
<td>-CO-CH₂-CH-</td>
</tr>
<tr>
<td>5.37</td>
<td>1H, dd, J₁ 10Hz, J₂ 3Hz</td>
<td>-CH = CH-</td>
</tr>
<tr>
<td>5.67</td>
<td>1H, d, J 10Hz</td>
<td>-CH = CH-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical shifts (δ ppm)</th>
<th>PMR signals of acetyl derivative of compound K</th>
<th>Probable assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8-1.0</td>
<td>2H</td>
<td>7 C-methyls</td>
</tr>
<tr>
<td>1.95</td>
<td>3H, s</td>
<td>-CO-CH₃</td>
</tr>
<tr>
<td>3.32</td>
<td>2H, ABq, J 6Hz</td>
<td>-CO-CH₂-CH-</td>
</tr>
<tr>
<td>4.45</td>
<td>1H, m</td>
<td>-CH₂-CH₃</td>
</tr>
<tr>
<td>5.35</td>
<td>1H, dd, J₁ 10Hz, J₂ 3Hz</td>
<td>-CH = CH-</td>
</tr>
<tr>
<td>5.67</td>
<td>1H, d, J 10Hz</td>
<td>-CH = CH-</td>
</tr>
</tbody>
</table>
12,13-double bond to 11,12-position as shown in scheme 86. Compound K was thus assigned the structure (CCXCV Ia) which is consistent with its mass spectral fragmentation producing significant peaks at m/e 440 (M+), 409, 290, 257, 206, 203, 189 and 175 (Fig. 40). Incidentally, this is the compound having a 13,23-oxide moiety and a 11,12-double bond in the ursane skeleton, which was needed to verify the proposed mechanism of formation of (CCLXXIIIa) from ursolic acid acetate (CCLXXa). This would also serve to act as a precursor of possible ursane analogues of saikogenins yet to be isolated from nature.

More interesting results have emerged from the action of H2O2/TsOH on compound J. Thus treatment of compound J (CCXCVIa) with a mixture of H2O2 and TsOH in tBuOH - CH2Cl2 at ambient temperature for 42 hr gave, besides (CCXCVIIa), a second compound L, C30H43O3 (M+ 540), m.p. 235°, the latter being the major compound. The IR spectrum of compound L (Fig. 41) shows bands for hydroxyl (νmax 3400-3520 cm⁻¹) and an oxirane (νmax 880 cm⁻¹) group. It gave a diacetyl derivative, C34H52O5 (M+ 564), m.p. 185° (OAc) and 880 (epoxide) (Fig. 42). The PMR spectrum of compound L (Fig. 43) shows the presence of an olefinic proton (δ 4.47, 1H, d), an oxirane system of the type -CH = CH - O - CH (δ 3.65, 1H, t, J 5 Hz), a
FIG. 40  MASS SPECTRUM OF COMPOUND K
FIG. 41 IR SPECTRUM OF COMPOUND L IN KBr
FIG. 43  PMR SPECTRUM OF COMPOUND L
secondary (δ 3.25, 1H, m) and a primary (δ 3.12, 2H, s) hydroxyl group and seven C-methyls (δ 0.75-1.1) \( ^{38} \)Table 2\( ^{38} \). In the PMR spectrum of its diacetyl derivative (Fig. 44) the signals for hydroxymethine and hydroxymethyl protons of compound L show usual downfield shifts \( ^{38} \)Table 2\( ^{38} \) leaving those for the epoxide protons unchanged. This suggests that the 17-hydroxymethyl group of compound J has not cyclised in compound L as in compound (OCXCVIIa).

The mass spectral fragmentations of compound L \( ^{38} \)significant peaks at m/e 456 (M\(^+\)), 425, 407, 391, 317, 287, 271, 253, 241, 237, 217 and 205 (Fig. 45) \( ^{38} \)Scheme 88\( ^{38} \) and its diacetyl derivative \( ^{38} \)significant peaks at m/e 540 (M\(^{2+}\)), 522, 391, 359, 343, 329, 317, 271, 253, 241, 217, 189, 175 and 135 (Fig. 46) \( ^{38} \)Scheme 88\( ^{38} \) are typical of a taraxerene skeletal system \(^{98}\) bearing a 11,12-epoxide moiety.

Based on the foregoing spectral data compound L \( ^{38} \)significant peaks at m/e 456 (M\(^+\)), 425, 407, 391, 317, 287, 271, 253, 241, 237, 217 and 205 (Fig. 45) \( ^{38} \)Scheme 88\( ^{38} \) and its diacetyl derivative \( ^{38} \)significant peaks at m/e 540 (M\(^{2+}\)), 522, 391, 359, 343, 329, 317, 271, 253, 241, 217, 189, 175 and 135 (Fig. 46) \( ^{38} \)Scheme 88\( ^{38} \) are typical of a taraxerene skeletal system \(^{98}\) bearing a 11,12-epoxide moiety.

The formation of compound L from (OCXCVIIa) by the action of H\(_2\)O\(_2\)/TosOH may be assumed to be initiated by the generation of a 11-hydroperoxy function, followed by acid-catalysed rearrangement involving migration of 14-methyl to C-13 \( ^{38} \)Scheme 89\( ^{38} \).

The alternative route involving nucleophilic participation of the 17-hydroxymethyl group to give the 11,12-epoxide (CCCa) does not work at all with (OCXCVIIa), whereas under identical reaction condition, the oleanane analogue (OCXCVIIb) is reported \(^{54}\) to give both (OCXCVIIb) and (CCCa) the latter being the major product \( ^{38} \)Scheme 89\( ^{38} \).

Such difference in the chemical behaviour of the isomeric ursane and oleanane isomers (OCXCVIIa) and (OCXCVIIb) may again be assumed to be due to steric effect of the 19-methyl group in the former. The severe non-bonded interaction between 14- and 19-methyl groups in the 11-hydroperoxy intermediate (CCCI) derived from ursane derivative (OCXCVIIa) forces the reaction exclusively towards the thermodynamically \(^{53}\) less stable product (OCXCVIIa), totally suppressing the alternative course to give the 11,12-epoxy compound (CCCa). In the absence of any such steric interaction the
FIG. 44 PMR SPECTRUM OF DIACETYL DERIVATIVE OF COMPOUND L
FIG-45 MASS SPECTRUM OF COMPOUND L (From m/e 71-287) [Contd]
FIG. 45a MASS SPECTRUM OF COMPOUND L (From m/e 301-456)
FIG. 46 MASS SPECTRUM OF ACETYL DERIVATIVE OF COMPOUND L (From m/e 135-331) [Contd]

Relativie Abundance (%)
FIG 46a MASS SPECTRUM OF ACETYL DERIVATIVE OF COMPOUND L (From m/e 332-540)
PMR spectral data of L and its acetyl derivative

<table>
<thead>
<tr>
<th>Chemical shifts (ppm)</th>
<th>No. of protons, multiplicity</th>
<th>Assignments</th>
<th>PMR signals of acetyl derivative of compound L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Chemical shifts (ppm)</td>
</tr>
<tr>
<td>0.75-1.1</td>
<td>21H</td>
<td>7 C-methyls</td>
<td>0.88-1.24</td>
</tr>
<tr>
<td>2.87</td>
<td>1H, d, J 5 Hz</td>
<td>CH=CH - C=O</td>
<td>2.04</td>
</tr>
<tr>
<td>3.05</td>
<td>1H, t, J 5 Hz</td>
<td>CH=CH - C=O</td>
<td>2.87</td>
</tr>
<tr>
<td>3.12</td>
<td>2H, s</td>
<td>CH₂OH</td>
<td>2.05</td>
</tr>
<tr>
<td>3.25</td>
<td>1H, m</td>
<td>CH₂OH</td>
<td>3.05</td>
</tr>
<tr>
<td>5.47</td>
<td>1H, m</td>
<td>CH₂OH</td>
<td>3.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.48</td>
</tr>
</tbody>
</table>
It would be interesting to note that compound (CCXCVIIa) obtained by the above sequence of reactions is a compound very close to the one conceived as an intermediate (path 'd', scheme 69) for the formation of (CCLXXIIIa). The behaviour of the acetyl derivative (CCXCVIII) of (CCXCVIIa) towards epoxidation by peracids would serve to verify the mechanism of formation of (CCLXXIIIa) as envisaged above. Compound (CCXCVIII) was first treated with m-chloroperbenzoic acid at ambient temperature for 22 hr to give a compound M, C_{32}H_{48}O_4 (M^+ 496), m.p. 244°C. Its IR spectrum (Fig. 47) shows bands for γ-lactone (1755 cm\(^{-1}\)), and acetoxy group (1725 and 1235 cm\(^{-1}\)) but does not indicate any absorption for an epoxide function. This was also evident from its PMR spectrum (Fig. 48) which still contains the signals for the two olefinic protons of (CCXCVIII), and shows the absence of any signal to be attributed for an epoxide (-O\_CH\_ = CH\_) or oxymethylene (-\_O - CH\_ = CH\_) protons [Table 3].

### Table 3

<table>
<thead>
<tr>
<th>Chemical shifts (ppm)</th>
<th>No. of protons and multiplicity</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.86-1.16</td>
<td>2H</td>
<td>7 C-methyla</td>
</tr>
<tr>
<td>2.04</td>
<td>3H, s</td>
<td>-O-OCMe_3</td>
</tr>
<tr>
<td>4.52</td>
<td>1H, m</td>
<td>-COAc</td>
</tr>
<tr>
<td>5.56</td>
<td>1H, dd, J_1 10Hz, J_2 3Hz</td>
<td>-_C - CH = CH -</td>
</tr>
<tr>
<td>5.98</td>
<td>1H, d, J 10 Hz</td>
<td>-_C - CH = CH -</td>
</tr>
</tbody>
</table>

Based on these spectral data and its characteristic mass fragmentation [Scheme 90] Significant peaks at m/e 496(M^+), 480, 350, 257, 255, 233, 202, 199, 189, 175, 159, 133, 119, 107 and 94 (Fig. 49) [structure (CCCII) was assigned to compound M.

The above transformation of an oxymethylene bridge in (CCXCVIII) to a lactone moiety in (CCCII) may be assumed to take place by the autooxidation of the
FIG. 47 IR SPECTRUM OF COMPOUND M IN KBr

WAVELENGTH IN MICRONS

WAVENUMBER CM⁻¹
FIG. 48 PMR SPECTRUM OF COMPOUND M
FIG-49 MASS SPECTRUM OF COMPOUND M
Scheme 90

Mass fragmentation of compound M

m/e 257 → -2H⁺ → m/e 255

m/e 496 (m⁺⁺⁺)

Compound M (C21C21)

- H2Ac⁺, - 3OCl2, - 7H⁺, - O2H⁺

m/e 233, m/e 159

m/e 450 - H2Ac⁺

m/e 390

m/e 175 → m/e 133

m/e 189

m/e 202

m/e 257

m/e 255
28-methylene group of the former by the triplet oxygen generated from m-chloroperbenzoic acid. The failure of the 11,12-double bond to undergo epoxidation may be attributed to the steric hindrance to the approach of the fairly bulky m-chloroperbenzoic acid to the 11,12-double bond. This view was substantiated by the following observation.

Treatment of the compound (CCXII) which is the exact intermediate assumed for the conversion of ursolic acid acetate to the epoxy-γ-lactone (CCXXIIIa) with H₂O₂ in boiling HOAc under the condition employed by Jeger et al. gave (CCXXIIIa) identified by comparison with an authentic sample: m.p. and superimposable IR spectra (Fig. 50). Treatment of compound (CCXVIII) with H₂O₂ in boiling HOAc, on the other hand, gave, besides two minor uncharacterised products, compound N, C₃₂H₅₀O₄ (M⁺ 498), m.p. 170⁰, which shows in its IR spectrum (Fig. 51) bands for epoxide (870 cm⁻¹), an acetoxy group (1742 and 1242 cm⁻¹), but no absorption for a γ-lactone function. The PMR spectrum of compound N (Fig. 52) still contains the signals (δ 3.49) for the oxymethylene protons of (CCXVIII) while the signals for the two olefinic protons of the latter are replaced by two oxirane protons in the former (Table 4).

Table 4
PMR signals of Compound N

<table>
<thead>
<tr>
<th>Chemical shifts b (ppm)</th>
<th>No. of protons and multiplicity</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8-1.22</td>
<td>2H,s</td>
<td>7 C-methyls</td>
</tr>
<tr>
<td>2.02</td>
<td>3H, s</td>
<td>- O - O - O₃</td>
</tr>
<tr>
<td>2.22</td>
<td>1H, d, J 4Hz</td>
<td>- CH₂ - CH -</td>
</tr>
<tr>
<td>3.02</td>
<td>1H, Br signal, Wh/2 4Hz</td>
<td>- C - H₂ - CH -</td>
</tr>
<tr>
<td>3.49</td>
<td>2H, ABq, J 7Hz</td>
<td>- C - CH₂ - O -</td>
</tr>
<tr>
<td>4.54</td>
<td>1H, m</td>
<td>- OAc</td>
</tr>
</tbody>
</table>

These spectral data coupled with its typical mass spectral fragmentation (Scheme 91) establish the structure of compound N to be (CCXIII). It may be noted that in the above
**Figure 50** IR Spectrum (in KBr) of

I. H₂O₂−HOAc Reaction Product of Compound M
II. O−I⁻
III. m-CPBA Oxidation Product of Compound N
FIG. 53 MASS SPECTRUM OF COMPOUND N (From m/e 39-250) [Contd.]
FIG. 53a MASS SPECTRUM OF COMPOUND N (From m/z 253 - 498)
Scheme 91
Mass fragmentation of compound N

![Chemical structure diagram showing mass fragmentation of compound N](attachment:image.png)
transformation, while the 11,12-double bond of (CCXCVIII) has undergone epoxidation, the oxymethylene bridge remains unaffected. This may be due to the fact that while peracetic acid (formed in situ) can approach the 11,12-double bond of (CCXCVIII) due to its relatively smaller volume compared to that of m-chloroperbenzoic acid, the autooxidation of the oxymethylene group fails to take place due to nonavailability of triplet oxygen under the boiling reaction condition. Treatment of compound (CCCIII) with m-chloroperbenzoic acid at ambient temperature, however, afforded the expected epoxy-γ-lactone (CCLXXIIIa) [Scheme 92]. The above transformation reactions of compound (CCXCVIII) [Scheme 92] thus not only provide a method of partial synthesis of (CCLXXIIIa), but also speak strongly in favour of the mechanistic path 'd' for the formation of (CCLXXIIIa) and probably also (CCLXXIIIb). The alternative path 'e' involving the intermediacy of the 11-hydroperoxy derivative (CCLXXIV) seems to be an unfavourable process in view of the boiling reaction condition which does not ensure the presence of molecular oxygen necessary for such reaction to occur to any appreciable extent.
EXPERIMENTAL

General:

M.p.s were determined in a Kofler block and were uncorrected. IR spectra were run in KBr disc in Beckman Infrared Spectrophotometer (Model 20). NMR spectra were recorded in 80 MHz Varian FT-20 and 100 MHz Jeol instruments in CDCl\textsubscript{3} using TMS as the internal standard. Mass spectra were run in an AEI MS9 instrument equipped with a direct inlet system and operating at 70 eV. Metastable peaks are indicated by m* and the figures in first brackets attached to m/e values indicate relative abundance.

Silica gel (60-100 mesh) was used for column chromatography and silica gel G was used for tlc performed at room temperature. All analytical samples were routinely dried over P\textsubscript{2}O\textsubscript{5} at 55-138\degree depending on the m.ps of the compounds for 24 hr in vacuo. Anhydrous Na\textsubscript{2}SO\textsubscript{4} was used for drying organic solvents and petrol used had b.p. 60-80\degree.

Formation of O-I and O-II. Pure oleanolic acid acetate (0.45g), m.p. 263\degree, was dissolved in glacial HOAc (5.5 ml). A mixture of 30\% H\textsubscript{2}O\textsubscript{2} (2.8 ml) and glacial HOAc (2.8 ml) was prepared from which 3.9 ml were added uniformly to the oleanolic acid acetate solution during 15 min and the reaction was allowed to proceed for 15 min. After 2 hr the remaining solution was added during 10 min and the reaction was allowed to proceed for another hr. The entire reaction was carried out at a temperature of 100-105\degree with continuous stirring. The mixture was largely diluted (75 ml). The solid separated was extracted with ether, washed with NaHCO\textsubscript{3}, dried and the solvent evaporated. The residue was methylated with diazomethane in the usual manner and the methylated product was chromatographed. The petrol-EtOAc (50:1) eluate on evaporation gave the methyl ester of unreacted oleanolic acid acetate (0.4g), m.p. 210\degree. The early fractions of the petrol-EtOAc (10:1) gave O-I (0.025g), crystallised from CHCl\textsubscript{3}-MeOH (1:9), m.p. 295\degree, \(m^+\) 512, \(m^+\) 497 (20), 494 (7), 486 (7), 468 (7), 452 (9), 437 (9), 277 (57), 263 (57), 249 (17),
The latter fractions of petrol-\text{EtOAc} (5:1) eluate gave C-II (0.01 g), crystallised in fine needles from petrol-EtOAc mixture, m.p. 277\degree \pm 6.8^\circ (\text{CHCl}_3); R_f 0.5 in petrol-EtOAc (2:1) as the developer; $\gamma_{\text{max}}$ 3540 (OH), 1770 ($\gamma$-lactone), 1730 and 1240 (OAc)$\text{cm}^{-1}$; $\delta_{\text{ppm}}$ 4.4, 1H, m (\text{\gamma-DOAc}), 3.60, 1H, m, WH/2 7 Hz (\text{\gamma-DOH}), 1.97, 3H, s (-\text{OCDOAc}) and 0.79-1.23 (7 \text{C-methylene}); m/e 514 (M$^+$ 21), 499 (42), 496 (12), 454 (23), 453 (40), 300 (16), 264 (30), 250 (28), 249 (28), 246 (23), 234 (16), 223 (16), 222 (14), 218 (44), 207 (16), 206 (19), 205 (65), 204 (42), 203 (30), 201 (21), 191 (16), 190 (30), 189 (100), 188 (14), 187 (16), 177 (53), 176 (21), 175 (39), 173 (14), 163 (14), 161 (23), 147 (23), 136 (19), 135 (28), 134 (16), 133 (21), 123 (19), 121 (35), 120 (14) and 119 (28). m$^*$ m/e 485, 453, 411.5, 401, 383, 217, 216.5, 215.5, 189, 180, 175, 152.5, 143.5 and 140.5.

Acid-catalysed hydrolysis of C-I, formation of (CCLXXX) and (CCLXXXI)

A solution of C-I (0.015 g) in 6N H$_2$SO$_4$ (2.5 ml) and abs EtOH (3 ml) was refluxed for 40 min according to the method of Kitagawa et al.$^{54}$ The reaction product was chromatographed and the petrol-EtOAc (5:1) eluate gave, on evaporation, CCLXXX (0.012 g). It was acetylated with Ac$_2$O/Py to give CCLXXXI (0.01 g), crystallised from petrol-EtOAc mixture m.p. 272\degree. It was identical in all respects with the compound obtained by chromic acid oxidation of C-II following the method of Kitagawa et al.$^{54}$

Treatment of uvaol with H$_2$O$_2$/HOAc

Uvaol (0.5 g) m.p. 21\degree in glacial acetic acid (6 ml) was treated with a mixture of 30\% H$_2$O$_2$ (3 ml) and glacial HOAc (3 ml) in the same manner as in case of oleanolic acid acetate. The product after work up as in the previous case was chromatographed. The petrol-EtOAc (50:1) eluate afforded C (0.043 g), crystallised from CHCl$_3$-MeOH (1:9), m.p. 151\degree; $\gamma_{\text{max}}$ 1735 and 1245 cm$^{-1}$ (OAc); $\delta_{\text{ppm}}$ 5.16, 1H, m (-C = CH$_2$ -), 4.53, 1H,
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m ( - C = OAc ), 3.33, 2H, ABq, J 10 Hz ( - C = OAc ), 2.03, 6H, s ( -OOCCH3 ) and 0.86-1.23 (7 G-methyls). It was identified with an authentic sample of uvaol diacetate by co-tlc and m.m.p. The early fractions of the petrol-EtOAc (20l) yielded B (0.015 g), crystal-

lised from CHCl3-MeOH (11:9), m.p. 242°. (Found : C, 79.5; H, 10.7. C32H52O3 requires : C, 79.3; H, 10.8%).  max 3560 (OH), 1720 and 1265 (OAc) cm\(^{-1}\);   ppm 5.1, 1H, m ( -C=CH2 - ), 4.4, 1H, m ( -C=OAc ), 3.35, 2H, ABq, J 10 Hz ( - C = OAc ), 2.05, 3H, s ( -OOCCH3 ) and 0.86-1.24 (7 G-methyls). The later fractions of the petrol-EtOAc (20l) eluate afforded A (0.345 g), crystallised from CHCl3-MeOH, m.p. 159°. (Found : C, 79.2; H, 10.9. C32H52O3 requires : C, 79.3; H, 10.8%).  max 3620 (OH), 1725 and 1230 (OAc) cm\(^{-1}\);   ppm 5.19, 1H, m ( -C=CH2 - ), 3.77, 2H, ABq, J 10 Hz ( - C = OAc ), 3.28, 1H, m ( -C=OAc ), 1.99, 3H, s ( -OOCCH3 ) and 0.76-1.20 (7 G-methyls); m/e 484 (M\(^+\), 7), 466 (5), 424 (5), 276 (11), 220 (5), 217 (20), 216 (100), 208 (10), 207 (46), 204 (17), 203 (86), 202 (6), 201 (10), 191 (7), 190 (20), 189 (18), 188 (6), 187 (15), 177 (5), 175 (11), 173 (6), 161 (8), 158 (11), 149 (7), 147 (15), 146 (9), 145 (12), 135 (14), 134 (10), 133 (36), 132 (8), 131 (14), 127 (17), 122 (9), 121 (19), 119 (15) and 118 (28).

Treatment of erythrodiol with H2O2/HOAc

Erythrodiol (0.25 g) was treated with 30% H2O2 in HOAc exactly in the same manner as in the case of uvaol. The product after usual work up was chromatographed. The petrol-

-EtOAc (50l) eluate afforded F (0.023g), crystallised from CHCl3-MeOH (11:9), m.p. 182°.   ppm 5.1, 1H, m ( -C=CH2 - ); 4.42, 1H, m ( -C=OAc ), 3.38, 2H, ABq, J 10 Hz ( - C = OAc ), 1.95, 6H, s ( -OOCCH3 ) and 0.8-1.2 (7 G-methyls). It was identified with an authentic sample of erythrodiol diacetate by co-tlc and m.m.p.

Further elution of the column with petrol-EtOAc (20l) afforded E (0.008g), m.p. 155° and D (0.10g), m.p. 181°, both crystallised from CHCl3-MeOH (11:9). (For E found : C, 79.4; H, 10.7. C32H52O3 requires : C, 79.3; H, 10.8%). For D found : C, 79.2; H, 10.9. C32H52O3 requires : C, 79.3; H, 10.8%). D  max 3480 (OH), 1710 and 1260 (OAc) cm\(^{-1}\);   ppm 5.1, 1H, m ( -C=CH2 - ), 3.75, 2H, ABq, J 10 Hz ( - C = OAc ), 3.15, 1H, m ( -C=OAc ),
1.98, 3H, s (-OOCCH$_3$) and 0.87-1.26 (7 C-methyls); m/e 484 (M$^+$ 24), 424 (24), 411 (9),
276 (34), 221 (7), 217 (47), 216 (100), 215 (14), 208 (20), 207 (76), 204 (62), 203 (96),
202 (29), 201 (40), 191 (22), 190 (36), 189 (36), 188 (24), 187 (40), 177 (14), 176 (11),
175 (31), 173 (22), 147 (38), 133 (45), 122 (14) and 119 (74); E: $^2$ppm 5.1, 1H, m
(-C = CH - CH$_2$ - ), 4.5, 1H, m (>C=OAc), 3.35, 2H, ABq, J 10 Hz (-C = OCH$_2$), 2.0, 3H,
s (-OOCCH$_3$), and 0.85-1.2 (7 C-methyls).

Both A and B gave C and both D and E gave F on acetylation with Ac$_2$O/Py in the
usual manner.

Treatment of uvaol and erythrodiol with 30% HOAc

Uvaol (0.05 g) and erythrodiol (0.05 g) were separately treated with 30% HOAc in
absence of H$_2$O$_2$ under the above condition. The products from uvaol were A, B and C and
those from erythrodiol were D, E and F formed in the same proportion as above.

Treatment of C and F with $^2$H$_2$/HOAc

C (0.03 g) and F (0.03 g) were separately treated with 30% $^2$H$_2$ in HOAc in the same
manner as in the case of oleanolic acid acetate. The products in each case were worked up
in the usual manner and chromatographed. C gave A (0.01 g) and B (0.003 g), while F gave D
(0.012 g) and E (0.003 g).

Treatment of $\alpha$-amyrin acetate, 3-O-acetyl methyl ursolate and 3-O-acetyl methyl oleanolate
with $^2$H$_2$/HOAc

$\alpha$-Amyrin acetate (0.02 g), 3-O-acetylmethyl ursolate (0.05 g) and 3-O-acetyl
methyl oleanolate (0.05 g) were separately treated with 30% $^2$H$_2$ in HOAc in the same manner
as in the previous cases. The products in each case were worked up and subjected to column
chromatography. $\alpha$-Amyrin acetate afforded 0.002g of $\alpha$-amyrin, 3-O-acetyl methyl ursolate gave
CCLXXXIXa (0.002 g), crystallised from CHCl$_3$-MeOH (1:9), m.p. 272$^\circ$, $\nu$$_{max}$ 1735 and 1235 (OAc
and O$_2$Me) and 1700 (>C=O) cm$^{-1}$, while 3-O-acetyl methyl oleanolate gave CCLXXXIXb (0.003 g),
crystallised from petrol-EtOAc, m.p. 177$^\circ$, $\nu$$_{max}$ 1725 and 1240 (OAc and O$_2$Me) and 1700
(>C = 0) cm$^{-1}$.
Atteropted formation of perursolic acid acetate

Ursolic acid acetate (0.3 g) was dissolved in benzene (10 ml). To it was added oxalyl chloride (1 ml) in the cold and the mixture was kept overnight under anhyd. condition. Benzene was removed under reduced pressure. The residue was taken in toluene (15 ml) and a mixture of 30% H₂O₂ (0.5 ml) and 1N NaOH (0.3 ml) was added to it. The mixture was stirred at room temperature for 3 hr, neutralised, extracted with toluene, dried and the solvent removed under reduced pressure. The residue did not liberate iodine from an acidified solution of KI. The product was chromatographed. The petrol-EtOAc (50:1) eluate furnished the acid chloride (0.08 g), crystallised from CHCl₃-MeOH, m.p. 295°C, vₘₐₓ 1800 (-COCl), 1730 and 1240 (OAc) cm⁻¹. Stirring the acid chloride with Na₂O₂ in a mixture of toluene and DMSO for 3 hr also did not bring about a change.

Treatment of ursolic acid acetate and 3-O-acetyl methyl ursolate with H₂O₂ in benzene

A solution of ursolic acid acetate (0.1 g) in benzene was refluxed with 30% H₂O₂ (7 ml) for 10 hr. The product was extracted with benzene and the solvent removed. The residue was treated with Cl₂N₂ and the methylated product was chromatographed. The petrol-EtOAc (50:1) eluate gave 3-O-acetyl methyl ursolate (0.09 g). Further elution of the column with petrol-EtOAc (20:1) gave a solid (0.005 g). Tlc of this solid indicated the presence of three compounds. The major spot was identified with 12-keto dihydro 3-O-acetyl methyl ursolate using multiple run tlc technique.

A solution of 3-O-acetyl methyl ursolate (0.10 g) was treated in a similar manner. The tlc of the reaction product did not show any spot other than the starting material.

Reaction of uvaol with NBS

A solution of uvaol (0.5 g) in dioxan (15 ml) was stirred for 1 hr at room temperature with finely powdered GaCl₃ (0.11 g) following the method of Thomson et al. 99 The reaction mixture was kept exposed to light from a 500 Watt electric lamp. The reaction mixture was filtered and the filtrate was diluted with water, extracted with ether, dried and the solvent removed. The residue was
The petrol-EtOAc (80:1) eluate gave G (0.04 g), crystallised from CHCl₃-MeOH (1:9), m.p. 204°. (Found: C, 69.1; H, 8.9. C₃₀H₄₇O₂Br requires: C, 69.4; H, 9.0%.)  δ max 1698 ( >C=O) cm⁻¹, δ ppm 4.17, 1H, m, Wh/2 3Hz ( >C-C-Br), 3.45, 2H, ABq, J 7Hz ( - C - O - Cl₂ - C - ), 2.55, 2H, m ( -O-Cl₂- ) and 0.84-1.26 (7 C-methyl); m/e 519 (M⁺, 2), 439 (40), 431 (17), 301 (13), 299 (15), 245 (11), 234 (21), 233 (100), 231 (36), 219 (38), 215 (28), 207 (13), 205 (43), 203 (51), 201 (24), 191 (42), 163 (17), 147 (11), 135 (17), 133 (17), 123 (15), 121 (25) and 119 (19), m⁺ m/e 439, 404, 331.5, 198.5, 122.

Further elution of the column with petrol-EtOAc (50:1) furnished H (0.06 g), also crystallised from CHCl₃-MeOH, m.p. 189°. (Found: C, 69.2; H, 9.2. C₃₀H₄₇O₂Br requires: C, 69.09; H, 9.42%). δ max 3400 (OH); δ ppm 4.2, 1H, m, Wh/2 3Hz ( >C-C-Br), 3.45, 2H, ABq, J 7Hz ( - C - O - Cl₂ - C - ), 3.16, 1H, m ( >CHOH) and 0.8-1.26 (7 C-methyls).

NaBH₄ reduction of G

To a solution of G (0.015 g) in MeOH was added NaBH₄ (0.006 g) in portions, and the solution was kept overnight. MeOH was removed under reduced pressure and the residue was treated with water. Extracted with ether, washed, dried and the solvent removed. The residue was crystallised from MeOH to give H (0.013 g).

Attempted dehydrobromination of H with collidine

A solution of H (0.05 g) in collidine (5 ml), was heated at 140° for 2 hr in an atmosphere of nitrogen. The reaction mixture was then acidified with 6N HCl, extracted with ether, dried and the solvent removed. The residue was chromatographed. The petrol-EtOAc (10:1) eluate, on evaporation, gave uvaol (0.045 g).

Attempted dehydrobromination of H with LiF

A solution of H (0.62 g) in dry DMF (10 ml) was refluxed with LiF (0.155 g) for 2½ hr. The reaction mixture was then diluted with water, acidified with conc. HCl, extracted with ether, dried and the solvent removed. The residue was then chromatographed. The
petrol-EtOAc (50:1) eluate gave 0.005 g of unreacted H. Further elution of the column with petrol-EtOAc (10:1) afforded an uncharacterised compound (0.012 g), crystallised from CHCl₃-MeOH (1:9), m.p. > 300°C. δ ppm 4.85 (1H, s), 3.24 (1H, s), 3.12 (2H, ABq, J 7Hz) and 0.76-0.97 (7 C-methyls).

**NBS oxidation of 3-O-acetyl methyl urso late and formation of I**

A solution of acetyl methyl urso late (1 g) in dioxan (30 ml) was stirred at room temperature with freshly crystallised NBS (0.6 g) in presence of finely divided CaCOpO₃ (0.226 g) in the same manner as in the case of uvaol. The product after work up was chromato­graphed. The petrol-EtOAc (10:1) eluate gave I (0.35 g) crystallised from petrol-EtOAc mixture, m.p. 235°C. λₑTOH 250 nm (log ε 4.06); λmax 1732 (O₂Me), 1720 and 1235 (OAc), 1658 and 1620 (–C = C – C = 0) cm⁻¹; m/e 526 (M⁺ 65), 511 (9), 467 (16), 466 (16), 451 (14), 343 (7), 319 (9), 318 (65), 317 (100), 315 (16), 277 (51), 276 (99), 271 (10), 261 (19), 259 (14), 249 (12), 243 (17), 232 (10), 218 (12), 217 (56), 216 (16), 215 (12), 201 (14), 199 (14), 189 (99), 175 (99), 174 (56), 159 (31), 143 (70), 133 (37), 123 (17), 121 (54), and 119 (99). m* m/e 525, 491, 413, 399, 316, 275, 274, 273, 208, 191, 182.5, 145, 129.5 and 101.

**LAH reduction of I**

A solution of 0.3 g of I in THF (15 ml) was reduced by a slurry of LAH (0.5 g) in THF (10 ml) in the usual manner. The reaction product after usual work up was repeatedly crystallised from petrol-EtOAc mixture to give pure J (0.25 g), m.p. 213°C. (Found: C, 73.9; H, 10.9. C₃₀H₅₀O₃ requires: C, 73.6, H, 11.0%). λmax 3340-3380 (OH) cm⁻¹; m/e 458 (M⁺ 2), 443 (4), 442 (13), 441 (28), 440 (81), 427 (4), 411 (9), 271 (11), 235 (9), 234 (37), 216 (11), 207 (31), 204 (31), 203 (100), 201 (7), 190 (9), 189 (13), 187 (11), 177 (9), 175 (11), 163 (7), 161 (9), 159 (11), 157 (7), 149 (9), 147 (13), 145 (13), 135 (13), 134 (9), 133 (39), 132 (9), 131 (13), 121 (13), and 119 (24). m* m/e 439.5, 405, 380.5, 377, 176.5, and 87.
Formation of K from J

A solution of J (0.12 g) in a mixture of CH₂Cl₂ (10 ml) and tBuOH (2 ml), was stirred with TsOH (0.035 g) at room temperature for 27 hr. Solvent was removed under reduced pressure and the residue was treated with water, extracted with ether, washed with NaHCO₃. The ether extract was dried and the solvent removed. The residue was chromatographed. The petrol-ET₃Ac (10:1) eluate gave K (0.105 g) crystallised from CHCl₃-MeOH (1:9), m.p. 210°. (Found: C, 31.6; H, 11.0. C₃₀H₄₈O₂ requires: C, 81.8, H, 10.9%). \( \gamma_{\text{max}} \) 3340 (OH) cm⁻¹; δ ppm 5.67, 1H, d, J 10 Hz (- C - CH = CH - ), 5.37, 1H, dd, J₁ 10 Hz, J₂ 3 Hz (- C - CH = CH - CH-), 3.34, 2H, ABq, J 6 Hz (- C - O - - C - ), 3.20, 1H, m (OH) and 0.72-1.02 (7 G-methyls); m/e 440 (M⁺, 42), 409 (2), 290 (26), 257 (35), 206 (10), 203 (35), 201 (12), 191 (11), 189 (19), 187 (16), 177 (17), 175 (21), 173 (23), 171 (14), 163 (22), 152 (12), 161 (60), 159 (27), 157 (20), 149 (32), 147 (34), 145 (30), 136 (26), 135 (63), 131 (32), 123 (51), 122 (34), 121 (69), 119 (52), 109 (49), 95 (39), and 81 (100).

Acetyl derivative crystallised from CHCl₃-MeOH (1:9), m.p. 220°. \( \gamma_{\text{max}} \) 1730 and 1250 (OAc) cm⁻¹; δ ppm 5.67, 1H, d, J 10 Hz (H-12), 5.35, 1H, dd, J₁ 10 Hz, J₂ 3 Hz (H-11), 4.45, 1H, m (H-3), 3.32, 2H, ABq, J 6Hz (H₂-28), 1.95, 3H, s (-OCOCH₃), and 0.8-1.0 (7 G-methyls).

Treatment of J with H₂O₂/TsOH and formation of K and L

A solution of J (0.2 g) in a mixture of CH₂Cl₂ (6 ml) and tBuOH (2 ml) was stirred with 30% H₂O₂ (0.5 ml) and TsOH (0.06 g) at room temperature for 42 hr. The residue obtained after removal of solvent under reduced pressure was worked up as before and the product was chromatographed. The petrol-ET₃Ac (10:1) eluate gave K (0.07 g). Further elution of the column with petrol-ET₃Ac (5:1) yielded 0.02 g of unreacted J. The petrol-ET₃Ac (1:1) eluate gave L (0.1 g), crystallised from petrol-ET₃Ac mixture, m.p. 235°. (Found: C, 78.7; H, 10.6. C₁₉H₂₇O₃ requires: C, 78.9, H, 10.5%). \( \gamma_{\text{max}} \) 3400-3520 (OH), 3000 (- CO - - CH - ) cm⁻¹; δ ppm 5.47, 1H, m (H-15), 3.25, 1H, m (H-3), 3.12, 2H, s (H₂-28), 3.05, 1H, t, J 5 Hz and 2.87, 1H, d, J 5 Hz (H-11 and H-12) and 0.75-1.1 (7 G-methyls); m/e 456 (M⁺, 11), 425 (25), 407 (47), 391 (33), 317 (67), 302 (28), 301 (68), 287 (49),...
Diacetate crystallised from CHCl$_3$-MeOH; m.p. 185°; $\gamma_{\text{max}}$ 1740 and 1250 (OAc), 880 (-CH - CH -) cm$^{-1}$; $\delta$ ppm 5.48, 1H, m (H-15), 4.48, 1H, m (H-3), 3.68, 2H, s (H$_2$-28), 3.05, 1H, t, J 9 Hz and 2.37, 1H, d, J 5 Hz (H-11, H-12), 2.04, 6H, s (OOCCH$_3$), 0.88-1.24 (7 C-methyls); m/e 540 (m$^+$, 30), 525 (17), 511 (18), 490 (45), 465 (52), 462 (43), 449 (20), 437 (17), 420 (29), 399 (18), 387 (32), 344 (25), 343 (43), 329 (22), 317 (32), 290 (15), 284 (20), 271 (40), 269 (55), 262 (10), 243 (25), 241 (55), 231 (30), 230 (19), 229 (33), 217 (35), 215 (60), 203 (52), 202 (57), 201 (83), 189 (77), 175 (72), 161 (65) and 139 (100).

Treatment of acetate of K with m-chloroperbenzoic acid

Acetate of K (0.3 g) in CH$_2$Cl$_2$ was stirred with m-chloroperbenzoic acid (0.2 g) at room temperature for 22 hr. The solvent was removed and the product was diluted with water, neutralised and extracted with ether. The ether extract was dried and the solvent was evaporated. The residue obtained was chromatographed. The petrol-EtOAc (20:1) eluate on evaporation afforded M (0.04 g), crystallised from CHCl$_3$-MeOH; m.p. 244°; $\gamma_{\text{max}}$ 1755 (c$'$-lactones), 1725 and 1235 (OAc) cm$^{-1}$; $\delta$ ppm 5.98, 1H, d, J 10 Hz (H-12), 5.56, 1H, dd, J$_1$ 10 Hz, J$_2$ 3Hz (H-11), 4.52, 1H, m (H-3), 2.04, 3H, s (OOCCH$_3$), 0.86-1.16 (7 C-methyls); m/e 496 (m$^+$, 4), 468 (4), 450 (13), 390 (9), 375 (7), 332 (4), 300(5), 285 (5), 279 (5), 269 (5), 267 (25), 256 (18), 255 (18), 253 (15), 241 (18), 240 (11), 239 (31), 234 (5), 233 (11), 202 (22), 201 (35), 189 (54), 187 (41), 175 (35), 167 (18), 159 (39), 149 (35), 145 (55), 133 (54), 129 (31), 121 (48), 119 (39), 107 (62), 105 (74), 95 (78) and 94 (100).

Treatment of acetate of K with H$_2$O$_2$/HOAc

Acetate of K (0.3 g) was refluxed with 30% H$_2$O$_2$ in glacial HOAc in a manner similar to that used for oleanolic acid acetate. Usual work up of the product followed by chromatography gave N (0.03 g), crystallised from petrol-EtOAc, m.p. 170°. (Found : C$_{77}$H$_{77}$O$_{4}$.
H10.1. \( \text{C}_3\text{H}_5\text{O}_4 \) requires: C, 77.1, H, 10.0%. \( \nu_{\text{max}} \) 1742 and 1242 (OAc), 870 (epoxide) cm\(^{-1}\); \( \delta_{\text{ppm}} \) 4.54, 1H, m (H-3), 3.49, 2H, ABq, J 7 Hz (H-29), 3.02, 1H, br signal, Wh/2 4Hz (H-11), 2.82, 1H, d, J 4Hz (H-12), 2.02, 3H, s (-COOCH\(_3\)) and 0.8-1.21 (7 C-methyls); m/e 498 (M\(^+\)*), 483 (6), 466 (6), 451 (6), 423 (5), 409 (5), 407 (6), 391 (6), 313 (5), 299 (5), 291 (5), 283 (6), 279 (6), 277 (8), 273 (8), 257 (11), 255 (11), 253 (6), 249 (6), 243 (8), 239 (8), 231 (8), 229 (8), 227 (6), 219 (8), 217 (11), 215 (9), 205 (9), 204 (8), 203 (21), 202 (11), 201 (14), 199 (9), 193 (12), 191 (13), 189 (27), 187 (19), 185 (11), 177 (16), 175 (22), 163 (17), 161 (20), 147 (19), 133 (22), 119 (29), 107 (25), 95 (25), 79 (16), 69 (24), 57 (29), 55 (52) and 43 (100).

Treatment of M with H\(_2\text{O}_2\)/HOAc

M (0.015 g) was refluxed with 30% H\(_2\text{O}_2\) in glacial acetic acid in a manner used for previous cases. The reaction product after usual work up was chromatographed. Petrol-EtOAc (10:1) eluate gave U-1 (0.005 g), crystallised from petrol-EtOAc, m.p. 280°.

Treatment of N with m-chloroperbenzoic acid

N (0.015 g) in CH\(_2\)Cl\(_2\) was stirred with m-chloroperbenzoic acid (0.01 g) at room temperature for 22 hr. The product was worked up in the manner similar to that used for acetate of K and subjected to column chromatography. The petrol-EtOAc (10:1) eluate gave U-I (0.008 g), crystallised from petrol-EtOAc, m.p. 280°.