CHAPTER IV
AN ATTEMPT TOWARDS THE SYNTHESIS OF FRIEDOOLEAN-25-OL

The functionalised products 3β-acetoxy-7β, 25-oxidofriedooleanane (218b) and 7β, 25-oxidofriedooleanane (218a) may serve as important starting materials for the synthesis of friedoolean-25-ol (192d) which was previously synthesised by Courtney et al. in 1965. This group of workers isolated a number of 25-oxygenated triterpenoids of Δ: A-friedooleanane group and suggested their structures but as stated earlier a direct correlation with a triterpene of known structure and configuration has not been possible yet. Now we have attempted to correlate the naturally occurring Δ: A-friedooleanane derivatives with a triterpene of known structure and configuration. However, we have not yet reached the goal and further work is in progress. Here we shall discuss the extent to which we have progressed and the shortest route by which we can achieve our aim.
It was expected that a Lewis acid like boron trifluoride would attach itself to the oxygen atom of the oxide (218a or b) to form the intermediate (230) with a positive oxygen atom, which is a good leaving group. Further, the conformation of this rigid system is such that the leaving group is in antiperiplanar orientation with the hydrogen atom at C-8. Thus the stereoelectronic requirement for elimination was completely satisfied. Indeed as is shown below these oxido compounds underwent elimination very smoothly to furnish the friedoolan-7-en systems.

Boron trifluoride-Etherate rearrangement of 7β, 25-Oxidofriedooleanane (218a) : 25-Acetoxyfriedoolean-7-ene (231a)

The compound (218a) on mild treatment with BF$_3$-etherate in acetic anhydride followed by chromatography and crystallisation of the product gave only the 25-acetoxyfriedoolean-7-ene (231a) (Scheme-17), m.p. 122-6°, $[\alpha]_D$ - 46.4°. It gave a positive tetranitromethane test which revealed the unsaturated nature of the compound. Analytical data and mass spectrometric study suggested the molecular formula to be C$_{32}$H$_{52}$O$_2$, M$^+$ 468.
Infra-red spectrum of the ene-acetate (231a) (Figure-19) showed bands at 1730 and 1252 cm\(^{-1}\) characteristic of the acetoxy group and 889 cm\(^{-1}\) due to the trisubstituted double bond.

NMR spectrum of the ene-acetate (231a) (Figure-20) at 60 megacycles showed the following characteristic signals.

(i) Signals at \(\delta 0.74\) (3 H, ill defined doublet, \(J = 4\) Hz) for the secondary methyl group and in the region \(\delta 0.80-1.12\) for six tertiary methyl groups.

(ii) The acetoxy methyl protons at C-25 appeared as a singlet at \(\delta 2.02\) (3H).

(iii) The methylene protons of the group \(-\text{CH}_2-0.0.\text{CO.CH}_3\) at C-25 appeared as doublet of doublets at \(\delta 3.99\) and 4.29 (2H, \(J = 7\) Hz).

(iv) The olefinic proton at C-7 (-C = C-H -) appeared as a pair of doublets (\(J = 2\) Hz) at \(\delta 5.76\) (1 H).

The mass spectrum of the compound will be discussed later on.

Boron trifluoride-Etherate Rearrangement\(^{97}\) of \(3\beta\)-Acet oxy-7\(\beta\), 25-Oxidofriedooleanane (218b): \(3\beta\), 25-Diacetoxyfriedoolean-7-ene (231b).

Similar treatment of the compound (218b) with BF\(_3\) -etherate in acetic anhydride followed by subsequent chromatography and crystallisation afforded only the ene-acetate (231b) (Scheme-17),
m.p. 160-62°, $\alpha_D^0 - 50°$. The compound also exhibited positive tetranitromethane test. C, H-analysis agreed well with the molecular formula C$_{34}$H$_{54}$O$_4$ which was also supported from mass spectral studies, M$^+$ 526.

Infra-red spectrum of the ene-acetate (231b) (Figure-21) showed bands at 1720 and 1252 cm$^{-1}$ characteristic of the acetoxy groups, and 890 cm$^{-1}$ due to the trisubstituted double bond.

NMR spectrum of the ene-acetate (231b) (Figure-22) at 60 megacycles showed the following characteristic signals.

(i) Signals at $\delta$ 0.82 (3H, d, $J = 4$ Hz) for the secondary methyl group and in the region $\delta$ 0.90-1.16 for the six tertiary methyl groups.

(ii) The acetoxy methyl protons at C-3 and C-25 appeared as a singlet at $\delta$ 2.09 (6H).

(iii) The methylene protons at C-25 and the proton at C-3 appeared as an ill defined triplet at $\delta$ 4.23 (3H) due to overlapping.

(iv) The olefinic proton at C-7 (-C=O-H) showed a broad signal at $\delta$ 4.92 (1 H).

Mass spectrometric studies of the ene-acetates (231a and 231b)

The mass spectra (Figures 23 and 24) (Chart-14, 15) of each of 231a and 231b showed a prominent peak at m/e 285 corresponding to the ion (232)$^{98,99}$ formed by RDA cleavage followed by elimination
of \(-\text{CH}_2\text{OAc}\). The appearance of peaks at \text{m/e} 243 and at \text{m/e} 301 corresponding to the respective ions (233a) and (233b) and also at \text{m/e} 344 and at \text{m/e} 402 due to the ions (234a) and (234b) correctly established the structures of the ene-acetates as (231a) and (231b) obtained by the \(\text{BF}_3\)-etherate rearrangement of the oxido compounds (218a) and (218b) respectively.

\[
\begin{align*}
\text{m/e} & \quad 285 \\
(232) & \\
\end{align*}
\]

\[
\begin{align*}
(233) & \\
\alpha & \quad R = H, \quad \text{m/e} \ 243 \\
\beta & \quad R = \text{OAc}, \quad \text{m/e} \ 301 \\
\end{align*}
\]

\[
\begin{align*}
(234) & \\
\alpha & \quad R = H, \quad \text{m/e} \ 344 \\
\beta & \quad R = \text{OAc}, \quad \text{m/e} \ 402 \\
\end{align*}
\]
The final object of our synthesis was to reduce the olefinic linkage in 231a. However, an examination of the model (235) revealed that catalytic hydrogenation would not be easy, since the approach of catalyst from $\beta$-face was prohibited by the three axial groups at C-24, C-25 and C-26 while the approach from $\alpha$-face was hindered by the axial H at C-6 and the C-27 axial $\alpha$-methyl group. Indeed an attempt for catalytic hydrogenation failed and only the starting ene-acetate was recovered.

We now proceeded by a roundabout method i.e. to oxidise (231a) to the $\alpha$, $\beta$-unsaturated ketone (237) and to attempt Birch reduction on the enone (237) to the saturated ketone (238) (Scheme-18). Here we expected to get the thermodynamically stable isomer since metal-ammonia reduction is a thermodynamically.
controlled process and gives the stable isomer.

**Mechanism of En-one Reduction**

Recently House et al.\(^{100}\) have suggested a reaction sequence, the essence of which is shown below.

\[ \text{Reaction 1:} \quad \text{C} = \text{C} - \text{O} + e' \rightleftharpoons \text{C} - \text{C} = \text{C} - \text{O} \]

\[ \text{Reaction 2:} \quad \text{C} - \text{C} = \text{C} - \text{O} - \text{NH}_2 \rightleftharpoons \text{C} - \text{C} = \text{C} - \text{O} - \text{H} - \text{NH}_2 \]

\[ \text{Reaction 3:} \quad \text{C} - \text{C} = \text{C} - \text{O} - \text{H} + e' \rightarrow \text{C} - \text{C} = \text{C} - \text{O} - \text{H} \]

\[ \text{Reaction 4:} \quad \text{C} - \text{C} = \text{C} - \text{O} - \text{H} + \text{NH}_3 \rightarrow \text{C} - \text{C} = \text{C} - \text{O} - \text{H} + \text{NH}_2 \]

\[ \text{Reaction 5:} \quad \text{C} - \text{C} = \text{C} - \text{O} - \text{H} + \text{NH}_2 \rightleftharpoons \text{C} - \text{C} = \text{C} - \text{O} - \text{H} + \text{NH}_2 \]
Reversible electron addition to the enone forms the radical anion (eq. 1). Rate determining protonation of the radical anion occurs on oxygen to afford an allylic free radical (eq. 2) which undergoes rapid reduction to an allylic carbanion (eq. 3). Rapid protonation of this ion is followed by proton removal from the oxygen of the neutral enol to afford the enolate ion (eq. 5).
Sodium dichromate Oxidation of 25-Acetoxyfriedoolean-7-ene (231a)

The aforesaid 25-acetoxyfriedoolean-7-ene (231a) on oxidation with sodium dichromate dihydrate in acetic acid and benzene furnished a gummy mixture which could be resolved into three components: Solid J, m.p. 120-23°, Solid K and Solid L, m.p. 257-62° on chromatography over silica gel.

Examination of Solid J: 25-Acetoxyfriedoolean-7-ene (231a)

The least polar compound on crystallisation from a mixture of acetone and methanol was found to be the unchanged starting material 25-acetoxyfriedoolean-7-ene (231a) by non-depression of the melting point with an authentic specimen and by mixed TLC.

Examination of Solid K: 25-Acetoxyfriedoolean-7-en-6-one (237)

Solid K on several crystallisations from a mixture of chloroform and methanol afforded pure Solid K, m.p. 186-88°, \[ [\alpha]_D = 127^\circ \]. Analytical data fitted well with the molecular formula \( \text{C}_{27}\text{H}_{40}\text{O}_5 \), which was in good agreement with the molecular
weight 482 (M+) determined from mass spectrometry.

Ultraviolet spectrum of Solid K (237) (Figure-25) \( \lambda_{\text{max}} \) nm

\((\log \varepsilon)\): 251 (3.99), 330 (2.50) were characteristic of an \( \alpha,\beta \)-unsaturated enone system.

Infra-red spectrum of Solid K (237) (Figure-26), showed bands at 1680 cm\(^{-1}\) characteristic of the \( \alpha,\beta \)-unsaturated six membered ring ketone and bands at 1740, 1242 cm\(^{-1}\) characteristic of the acetoxy group and at 855 cm\(^{-1}\) due to the trisubstituted double bond.

NMR spectrum of Solid K (237) (Figure-27) at 60 megacycles showed the following characteristics.

(i) Signals for one secondary and six tertiary methyl groups in the region \( \delta \) 0.82-1.16.

(ii) Signals at \( \delta \) 2.08 (3 H, s) for the acetoxy methyl protons.

(iii) The methylene protons at C-25 appeared at \( \delta \) 4.05 and 4.32 (2H, J = 12 Hz).

(iv) The olefinic proton at C-7 was shifted to \( \delta \) 6.01 due to deshielding by the adjacent 6-keto group.
Fig. 25
Mass spectrum of Solid K (237) (Figure-28) (Chart-16)

Mass spectrum of Solid K (237) showed besides the molecular ion at m/e 482 a prominent peak at m/e 358 due to the ion (240) formed by RDA cleavage followed by expulsion of a methyl group accompanied by addition of a proton. The other principal peaks appeared at m/e 409, 285, 284 and 257.

The above physical evidences are in complete agreement with the structure (237) for Solid K.

Examination of Solid L; 25-Acetoxy-4, 5-secofriedoolean-5, 7-dien-4, 6-dione (236)

The last and the most polar component on several crystallisations from a mixture of chloroform and methanol afforded pure solid L, m.p. 259-63°, [α]_D + 57°. Analytical data and molecular
Fig - 28
C_{32}H_{50}O_{3}  
M^+ 482  
(7%)  

RDA cleavage followed by elimination of an \(-\text{CH}_3\) group:

CH_{3}COOH  
m/e 285  
(2%)

\[ \text{m/e 285} \xrightarrow{-\text{CH}_2\text{O}\text{COCH}_3} \text{m/e 257} \quad (15\%) \]

- CO
weight, 496 (M+) were in good agreement with the molecular formula C\textsubscript{32}H\textsubscript{48}O\textsubscript{4}.

**Ultra-violet spectrum** of Solid L (236) (Figure-29)

\[ \text{EtOH} \quad \lambda \quad \text{nm (log} \varepsilon \text{)} : 246 (4.18), 334 (2.38) \]

were characteristic of \( \alpha', \beta' \)-unsaturated dienone system.

**Infra-red spectrum** of Solid L (236) (Figure-30) exhibited bands at 1648 cm\(^{-1}\) characteristic of the \( \alpha', \beta' \)-unsaturated six membered ring ketone, at 1700 cm\(^{-1}\) characteristic of the keto methyl group and at 1735, 1225 cm\(^{-1}\) characteristic of the acetoxy group and at 896 cm\(^{-1}\) due to the two trisubstituted double bonds.

**NMR spectrum** of Solid L (236) (Figure-31), at 60 megacycles showed the following characteristic signals.

(i) Signals for the five tertiary methyl groups in the region \( \delta \) 0.84-1.30.

(ii) An AB quartet centred around \( \delta \) 4.38 (2H, \( J = 6 \text{ Hz} \)) for the methylene protons of the group \(-\text{CH}_2-0.\text{COOH}_2\).

(iii) A triplet at \( \delta \) 3.24 (2H, \( J = 7.5 \text{ and } 8.5 \text{ Hz}; \text{ gem coupling} \)) due to the protons at C-1.

(iv) A singlet at \( \delta \) 1.98 (3H) due to the acetoxy methyl protons.
Fig. 29
(v) A singlet at $\delta 1.88$ (3H) due to the keto methyl protons.
(vi) A singlet at $\delta 1.70$ (3H) due to the olefinic methyl group.

Mass spectrum of Solid L (236) (Figure-32) (Chart-17)

Mass spectral fragmentation pattern of the Solid L was very much similar to that of the enone (237). Here also a prominent peak appeared at m/e 358 due to the ion (240) formed by the same mechanism as stated earlier for the enone (237). It thus established the fact that the rings C, D and E remained unchanged and also that the enone system remained intact. The other prominent peaks appeared at m/e 467, 423, 285 and 257, some of which were common to those obtained from the enone (237).

The above physical evidences conclusively established the structure (236) for Solid L.

Birch Reduction followed by Huang-Minlon Reduction of 25-Acetoxy-friedoolean-7-en-6-one (236) : 25-Hydroxyfriedoolean-6-one (238)

The enone compound (236), $C_{32}H_{50}O_3$ on Birch reduction followed by Huang-Minlon reduction afforded two components on chromatographic separation. The less polar component, Solid N could not be investigated further due to very poor yield. The more polar component, on
CHART - 17

C₃₂H₄₈O₄
M⁺ 496 (7%)

RDA cleavage followed by elimination of a-CH₃ group

m/e 357

m/e 358 (100%)

m/e 257 - CO

m/e 255

(2%) (3%)
crystallisation from a mixture of chloroform and acetone yielded pure Solid 0, m.p. 221-223°, $[\alpha]_D^24 = 24°$, (M$^+$) 442. The molecular ion suggested the molecular formula to be $C_{30}H_{50}O_2$ which also agreed well with C, H-analytical data. Thus it is evident that the hindered carbonyl group has not been reduced by the condition used for W. K. reduction.

**Infra-red spectrum** of Solid 0 (238) (Figure-33) showed bands at 3500 cm$^{-1}$ for the hydroxyl group and 1699 cm$^{-1}$ for the saturated six membered ring ketone.

**Mass spectrum** of Solid 0 (238) (Figure-34) (Chart-18) afforded the principal peaks at m/e 442 (M$^+$), 427, 424, 411, 396, 395, 393, 259, 241 and 205.

**Ultra-violet spectrum** of Solid 0 (238) showed no absorption maxima between 210-300 nm indicating the absence of $\alpha,\beta$-unsaturated enone system.

From the above three physical evidences Solid 0 is found to be 25-hydroxyfriedoolean-6-one (238).

The last step of our programme remains to be worked out i.e. the reduction of the 6-keto group which is in progress. This reduction will conveniently lead to our desired product friedoolean-25-ol (199) synthesised by Courtney et al$^{44}$. 

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**Infra-red spectrum** of Solid 0 (238) (Figure-33) showed bands...
EXPERIMENTAL

Treatment of $7^\beta$, 25-Oxidofriedooleanane (218a) with Acetic Anhydride and Borontrifluoride-Etherate: 25-Acetoxyfriedoolean-7-ene (231a)

$7^\beta$, 25-Oxidofriedooleanane, (218a; 0.214 g) was dissolved in acetic anhydride (13 ml) at 25° and was treated with BF$_3$-ether complex with stirring. After stirring for 30 minutes the reaction product was poured into ice cold water and the mixture was stirred for about an hour. An oily substance separated out which slowly turned into a white gummy solid. The solid was taken up in ether and washed with 5% NaHCO$_3$ and water successively, until it was neutral. Ether was evaporated to yield an oily residue (0.200 g) which was subsequently chromatographed over a column of silica gel (10 g). The column was eluted with different solvent mixtures as shown in Chart-19.

**CHART-19**

Each fraction collected was 10 ml in volume

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-8</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>28-35</td>
<td>Pet ether : benzene (4:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>36-39</td>
<td>Pet ether : benzene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>40-45</td>
<td>Pet ether : benzene (1:4)</td>
<td>Nil</td>
</tr>
<tr>
<td>46-50</td>
<td>Benzene</td>
<td>Nil</td>
</tr>
</tbody>
</table>
Examination of gummy solid H: 25-Acetoxyfriedoolean-7-ene (231a)

The gummy solid H (0.20g) of the above chromatogram from fractions 9-27 (Chart-19) was crystallised from a mixture of acetone and methanol, when pure crystals of 25-acetoxyfriedoolean-7-ene (231a, 0.071 g) m.p. 122-126°, $[\alpha]_D^{25} = -45.4° (c, 0.948)$ were obtained.

Found: C, 82.26; H, 11.09 (M+ 468).

Calculated for C$_{32}$H$_{52}$O$_2$: C, 81.99; H, 11.18%

It gave positive test with tetranitromethane IR, NMR and Mass spectral evidences have been discussed in theoretical.

Treatment of $3\beta$-Acetoxy-7$\beta$, 25-Oxidofriedooleanane (218b) with Acetic Anhydride and Borontrifluoride-Etherate: $3\beta$, 25-Diacetoxyfriedoolean-7-ene (231b)

The oxido compound (218b, 0.192 g) in acetic anhydride (10 ml) at 25° was treated with BF$_3$- ether complex (2 drops) with stirring. After 5 min. the mixture was poured into ice cold water and stirred for about an hour. At first an oil separated out which gradually turned into a white solid, which was filtered and washed with water. The residue (0.19 g) was chromatographed over a column of silica gel (4 g). The column was eluted with different solvent mixtures as shown in (CHART-20).
Each fraction collected was 5 ml in volume

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
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<tr>
<td>1-4</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>5-10</td>
<td>Pet ether : benzene (4:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>11-19</td>
<td>Pet ether : benzene (3:2)</td>
<td>Solid I, m.p. 155-60°</td>
</tr>
<tr>
<td>20-23</td>
<td>Pet ether : benzene (1:4)</td>
<td>Nil</td>
</tr>
<tr>
<td>24-30</td>
<td>Benzene</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Examination of Solid I: $3\beta$, 25-Diacetoxyfriedoolean-7-ene (231b)

The above crystalline Solid I, m.p. 155-60° from fractions (11-19) of the above chromatogram (Chart-20) on crystallisation from a mixture of acetone and methanol afforded pure $3\beta$, 25-diacetoxyfriedoolean-7-ene (231b), m.p. 160-62° $[\alpha]_D -50°$. It gave yellow colour with tetranitromethane.
Attempted Catalytic Hydrogenation of 25-Acetoxyfriedoolean-7-ene (231a)

A solution of 25-acetoxyfriedoolean-7-ene (231a; 0.108 g) in ethyl acetate was stirred magnetically in hydrogen atmosphere for 24 hours in presence of 10% Pd-charcoal catalyst. The mixture was filtered and evaporated to yield a colourless oily solid (0.09 g), which on subsequent chromatography over silver nitrate impregnated silica gel (3 g) gave the unchanged 25-acetoxyfriedoolean-7-ene (231a) m.p. 122–26°. It showed positive tetranitromethane test and the melting point was undepressed with the starting material. Hydrogenation was also attempted by increasing the time period upto 70 hours and by using Platinum dioxide as catalyst when still no hydrogen uptake was observed.

Sodium Dichromate Oxidation of 25-Acetoxyfriedoolean-7-ene (231a): 25-Acetoxyfriedoolean-7-en-6-one (237) and 25-Acetoxy-4, 5-secofriedoolean-5, 7-dien-4, 6-dione (236)

A mixture of 25-acetoxyfriedoolean-7-ene (231a, 0.155 g), sodium dichromate dihydrate (0.16 g) in benzene (15 ml) and
Glacial acetic acid (15 ml) was refluxed for 4 hrs. The reaction mixture was cooled, diluted with cold water and extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulphate and finally evaporated. The residue (0.155 g), left after removal of solvent was chromatographed over a column of silica gel (12 g). The column was then eluted with different solvent mixtures as shown in Chart-21.

**Chart-21**

Each fraction collected was 5 ml in volume

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-5</td>
<td>Pet ether</td>
<td>Trace wax</td>
</tr>
<tr>
<td>6-12</td>
<td>Pet ether : benzene (9:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>13-22</td>
<td>Pet ether : benzene (4:1)</td>
<td>Solid J, m.p. 120-23°</td>
</tr>
<tr>
<td>23-28</td>
<td>Pet ether : benzene (7:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>29-34</td>
<td>Pet ether : benzene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>35-40</td>
<td>Pet ether : benzene (1:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>41-48</td>
<td>Pet ether : benzene (2:3)</td>
<td>Oily Solid K</td>
</tr>
</tbody>
</table>
Examination of Solid J : 25-Acet oxyfriedoolean-7-ene (231e)

Solid J (0.06 g), from fractions 13-22 (Chart-21) was crystallised from a mixture of acetone and methanol when a pure solid, m.p. 124-26° identical with starting 25-acet oxyfriedoolean-7-ene (231a) (mixed m.p. and mixed TIC) was obtained.

Examination of Oily Solid K : 25-Acet oxyfriedoolean-7-en-6-one (237)

The oily Solid K (0.02 g) from fractions 41-48 (Chart-21) was crystallised from a mixture of chloroform and methanol when pure 25-acet oxyfriedoolean-7-en-6-one (237), m.p. 186-88°, [α]D
-127°, was obtained.

Found : C, 79.51; H, 10.33 (M+ 482).

Calculated for C32H50O3 : C, 79.62; H, 10.44%.

IR, NMR, uv and mass spectral studies have been discussed in theoretical.

Examination of Solid L : 25-Acet oxy-4, 5-secofriedoolean-5, 7-dien-4, 6-dione (236)

The crystalline Solid L (0.03 g) from fractions 49-55 of the above chromatogram (Chart-21) was crystallised from a mixture of chloroform and methanol when pure 25-acet oxy-4, 5-secofriedoolean-5, 7-dien-4, 6-dione (236), m.p. 259-63°,
\([\varepsilon^2]_D + 57^\circ \) (c, 0.99), was obtained.

Found : C, 77.40; H, 9.52 (M^+ 496).

Calculated for C₃₂H₄₈O₄ : C, 77.37; H, 9.74%.

IR, uv, NMR and Mass spectral studies have been discussed in theoretical.

**Lithium-Ammonia Reduction of 25-Acetoxyfriedoolean-7-en-6-one (237)**

A solution of 0.09g of 25-acetoxyfriedoolean-7-en-6-one (237) in 5 ml dry ether and 3 ml tetrahydrofuran was added to about 80 ml of anhydrous liquid ammonia. The mixture was well stirred, 0.05 g of lithium, cut into small pieces was added and the solution turned deep blue. After the addition of lithium was complete, the deep blue solution was stirred for 30 min. At the end of the reaction the blue colour was discharged by the addition of Solid NH₄Cl (0.50 g) and the ammonia was allowed to evaporate at room temperature. The residue was dissolved in water and the mixture acidified with 6N hydrochloric acid. The product was then extracted with ether, washed with brine and dried over anhydrous sodium sulphate. The ether solution was evaporated to afford a gum M (0.08 g).
Attempted Huang-Minlon Reduction\textsuperscript{92} of the Crude Gum M

The aforementioned crude gum M (0.077 g) in diethylene glycol (8 ml) was refluxed with 85\% hydrazine hydrate (0.8 ml) for 1 hr. Then after the addition of potassium hydroxide (0.08 g) the mixture was further refluxed for 1 hr. Then the condenser was removed and the mixture was heated until the inner temperature was raised to 190°. Subsequently, the condenser was replaced and the mixture was refluxed for additional 2\frac{1}{2} hr. The reaction mixture was cooled, diluted with water and the precipitated solid was extracted with ether. The ether solution was washed with water, dried (Na\textsubscript{2}SO\textsubscript{4}) and evaporated to yield an oily residue (0.073 g). Next, it was dissolved in a minimum amount of benzene and placed on a column of silica gel (7 g). The column was eluted with different solvent mixtures as shown in Chart-22.
Each fraction collected was 5 ml in volume

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Residue after removal of solvent</th>
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<td>1-6</td>
<td>Pet ether (40-60)</td>
<td>Trace wax</td>
</tr>
<tr>
<td>7-14</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>15-18</td>
<td>Pet ether : benzene (9:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>19-23</td>
<td>Pet ether : benzene (4:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>24-39</td>
<td>Pet ether : benzene (7:3)</td>
<td>Trace Solid N</td>
</tr>
<tr>
<td>40-48</td>
<td>Pet ether : benzene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>49-53</td>
<td>Pet ether : benzene (1:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>54-65</td>
<td>Pet ether : benzene (2:3)</td>
<td>Trace oil</td>
</tr>
<tr>
<td>66-69</td>
<td>Pet ether : benzene (3:7)</td>
<td>Nil</td>
</tr>
<tr>
<td>70-74</td>
<td>Pet ether : benzene (1:4)</td>
<td>Nil</td>
</tr>
<tr>
<td>75-97</td>
<td>Benzene</td>
<td>Solid 0, m.p. 210-18°</td>
</tr>
<tr>
<td>98-107</td>
<td>Benzene : chloroform (1:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>108-115</td>
<td>Chloroform</td>
<td>Nil</td>
</tr>
<tr>
<td>116-123</td>
<td>Ethyl acetate</td>
<td>Nil</td>
</tr>
</tbody>
</table>
Investigation of the Solid N (fractions 24-39):

Could not be investigated further due to very poor yield.

Examination of Solid 0: 25-Hydroxyfriedoolean-6-one (238)

Solid 0 (0.032 g) from fractions 75-97 (Chart-22) was crystallised from a mixture of chloroform and acetone when a pure solid (238), m.p. 221-23°, $[\alpha]_D^0 + 24°$ was obtained. It gave negative test with tetranitromethane. IR, uv and Mass spectral datas have been discussed in theoretical.