SECTION - C
Synthesis of Steroidal 2,3-Diols:

Several excellent methods were developed for the synthesis of steroidal 2,3-diols. Of them two were general and found wide applications.

a) The first method (Chart-XXIV) consists in hydroxylation of the 2,3-double bond, by the use of stereoselective reagents.
Thus treatment of the 2,3-ene (114) with osmium tetroxide results in the formation of the 2α, 3α-cis dihydroxy compound (115) while peracids generally give the 2α, 3α-epoxide (116) which open with acids to give the 2β, 3α-trans diaxial diol (117). 2β, 3β-cis diols (118) are prepared by the Woodward sequence by treatment with iodine, silver acetate, acetic acid and water. The stablest 2α, 3β-trans diols (119) are formed when any of the above three diols are equilibrated with base (Chart-XXIV).

b) The second method (Chart-XXV) starts from the 3-ketones (120), which are converted into epimeric 2α-acetoxy-3-ketones (121) and 2β-acetoxy-3-ketones (122) by reaction with lead tetra-acetate. Lithium aluminium hydride reduces the 3-keto group mainly to the 3α-(axial) alcohols (115 and 117), but sodium and alcohol reduces it to the stabler 3β-(equatorial) alcohols (118 and 119).
Synthesis of Triterpene-2,3-diols:

By application of the above two general methods, many triterpenic 2,3-diols have been synthesised. The syntheses of the methyl esters of the 2,3-dihydroxyolean-12-en-28-oic acids by Djerassi et al.\(^{112}\) and Tschesche et al.\(^{69b,c}\) have already been discussed in Section A. The syntheses of lupane-2,3-diols (102, A-D)\(^{125}\) and friedelane-2,3-diols (103, A-C)\(^{126}\) are discussed below.

**Synthesis of Lupane-2,3-diols (102)\(^{125}\)** (Chart-XXVI): Lup-2-ene (123) was converted to lupane-2\(\alpha\), 3\(\alpha\)-diol (102A), lupane-2\(\beta\), 3\(\beta\)-diol (102B) and lupane-2\(\alpha\), 3\(\alpha\)-epoxide (124) by the action of osmium tetroxide, iodine-silver acetate-acetic acid and perbenzoic acid respectively. The epoxide (124) was opened...
with acetic acid to give $2\beta$-acetoxy-lupan-3$\alpha$-ol (125) which on mild alkaline hydrolysis yielded the diaxial trans diol, lupane-$2\beta$, $3\alpha$-diol (102D). In order to increase the poor yield of the $2\beta$, $3\beta$-diol (102B) obtained by the above procedure and also to prepare the remaining isomer: lupane-$2\alpha$, $3\beta$-diol (102C), lupan-3-one (126) was treated with lead tetra-acetate to give $2\beta$-acetoxy-lupan-3-one (127) and $2\alpha$-acetoxy-lupan-3-one (128) as the major and the minor products respectively. The $2\beta$-acetoxy isomer (127) could also be prepared by the chromic acid oxidation of $2\beta$-acetoxy-lupan-3$\alpha$-ol (125) mentioned earlier. This acetoxy-ketone (127) upon equilibration with base furnished the $2\alpha$-acetoxy-3-ketone (128) which was then reduced with lithium aluminium hydride mainly to lupane-$2\alpha$, $3\alpha$-diol (102A) and with sodium and isopropanol to lupane-$2\alpha$, $3\beta$-diol (102C). The $2\beta$-acetoxy-3-ketone (127) was similarly reduced with lithium aluminium hydride to give the $2\beta$, $3\alpha$-diol (102D) as the main product and with sodium and isopropanol to the $2\beta$, $3\beta$-diol (102B) (Chart-XXVI).
Synthesis of Friedelane-2α, 3α-(103A), 2β, 3β-(103B) and 2α, 3β-(103C) diols^{126} (Chart-XXVII):

Friedel-2-ene (129), obtained by the pyrolysis of friedelanol benzoate (130) was converted to friedelane-2α, 3α-diol (103A) by the action of osmium tetroxide and to the 2,3-epoxide (131) by the action of m-chloroperbenzoic acid. The 2, 3-epoxide (131) was opened with perchloric acid to yield friedelane-2α, 3β-diol (103C), identical with naturally
occurring pachysandiol A (101). During the work of structure elucidation of pachysandiol A (101), Kikuchi and Toyoda had suggested that cerin acetate was $2\alpha$-acetoxy-friedelan-3-one (132), contrary to its previous formulation as $2\beta$-acetoxy-friedelan-3-one (133) on the following grounds: Pachysandiol A-2-monoacetate (134), obtained by acetylation of pachysandiol A (101) at $0^\circ$, could be oxidised to cerin acetate (132) with chromic acid. The cerin acetate so obtained, on prolonged absorption on alumina, was isomerised to another 2-acetoxy-3-ketone (133), which must hence be the more stable $2\beta$-(equatorial)-acetoxy isomer. Consequently, the original cerin acetate must be the less stable $2\alpha$-(axial)-acetoxy isomer (132). Samson et al. isomerised cerin acetate (132) with potassium acetate in acetic acid and reduced the resulting $2\beta$-acetoxy-friedelan-3-one (133) with lithium aluminium hydride and thus synthesised friedelane-2 $\beta$, 3$\beta$-diol (103B) (Chart-XXVII).
Chart-XXVII
Oleana-2,12-diene (135) as an Intermediate in the Probable Synthesis of Olean-12-ene-2,3-diols (104, A-D) (Chart-XXVIII):

From the foregoing discussions, it seems plausible that oleana-2,12-diene (135) may well serve as a good intermediate for the synthesis of the four epimeric olean-12-ene-2,3-diols (104, A-D) as shown schematically in Chart-XXVIII.
Synthesis of Oleana-2,12-diene (135):

Oleana-2,12-diene (135) could be obtained by the classical method viz. pyrolysis of \( \beta \)-amyrin benzoate (135A). However, methyl oleanolate (89) and methyl crategolate (78) being available in plenty from the flowers of *E. jambolana* (vide Section A), attempts were made to utilise them for the preparation of oleana-2,12-diene (135), the proposed intermediate in the scheme for the synthesis of olean-12-ene-2,3-diols (108) (Chart-XXVIII). The steps through which oleana-2,12-diene (135) was synthesised mainly from methyl oleanolate (89) and on an experimental basis from methyl crategolate (78) are shown schematically in Chart-XXIX.

\[ \text{POCl}_3 / \text{pyridine} \downarrow \]

\[ \text{PdCl}_2 \text{/pyridine} \]

\[ \text{MeOH, d inversion?} \downarrow \]

\[ \beta\text{-TseI} / \text{pyridine} \]

\[ \text{Na, Acetonitrile, Sealed tube} \]

\[ \text{MeOH, d inversion?} \]

\[ \text{(138)} \rightarrow \ast \]
Preparation of Methyl Oleana-2,12-dien-28-oate (90):

a) From Methyl Oleanolate (89): Methyl oleanolate (89) was converted to the above mentioned diene ester (90) by dehydration with phosphorus oxychloride and pyridine according to the procedure of Tschesche et al.\(^6\). The crude product on chromatography over silica gel and crystallisation gave methyl oleana-2,12-dien-28-oate (90), m.p. 180-182\(^\circ\).

b) From Methyl Crategolate (78): The formation of \(\Delta^2\)-compounds from 2\(\alpha\), 3\(\alpha\)- and 2\(\alpha\), 3\(\beta\)-disulphonyl esters has
been reported\textsuperscript{86,144}. Apparently, methyl crategolate could thus serve as a fruitful source of oleana-2,12-dien-28-oate (135) through its ditosyl ester (136). Methyl crategolate (78) was accordingly tosylated and the crude glassy product upon crystallisation from methanol furnished a crystalline solid, m.p. 116-120\degree, (\Delta\,)_D + 56.8\degree which however analysed for C\textsubscript{33}H\textsubscript{54}O\textsubscript{4}. The most rational explanation (Chart-XXIX) is that the crude ditosyl derivative (136) had undergone solvolysis by methanol to give methyl bredemolate dimethyl ether (137), the reaction being accompanied by inversion. Work on this by-product is still incomplete.

In view of the aforementioned rearrangement the crude ditosylate (136) was not crystallised. The thoroughly washed and air-dried crude ditosylate (136) was heated in a sealed tube with sodium iodide in acetone\textsuperscript{86}. However, the crude reaction product was a viscous mixture (T.L.C.) and could not be satisfactorily separated into its constituents by chromatography and crystallisation, presumably because the mixture consisted of double-bond isomers. Only a small yield of the desired diene ester (90) could be obtained pure. This route was clearly unsuitable for large-scale preparation of the diene ester (90) and was abandoned.
Synthesis of oleana-2,12-dien-28-ol (138):

The aforesaid diene ester (90) was reduced with lithium aluminium hydride to yield a crude glassy solid which was chromatographed over alumina. The solid eluted with benzene was the desired oleana-2,12-dien-28-ol (138), m.p. 150-152°, $(\alpha)_D + 118^\circ$. Although attempted acetylation and tosylation did not yield any crystalline derivative, the I.R. and N.M.R. spectra of the compound fully corroborated the assignment of oleana-2,12-dien-28-ol structure (138) to it.

I.R. Spectrum (Figure XVIII) of the diene alcohol (138) showed the absence of absorption in the carbonyl region, but showed peaks at 3400 (OH), 820 (trisubstituted ethylene) and 722 cm$^{-1}$ (cis-disubstituted ethylene)$^{139b}$.  

N.M.R. Spectrum (Figure XIX) of the diene alcohol (138) showed signals of the seven tertiary methyl groups at $\delta$ 0.88 (two), 0.90, 0.97 (two), 0.99 and 1.18 ppm; an AB pattern for the CH$_2$ at C-28 centered around $\delta$ 3.23 and 3.57 ppm ($J = 11$ cps); a vinyl triplet centered around $\delta$ 5.24 ppm for the vinyl hydrogen at C-12 and a pair of lines centered around $\delta$ 5.40 ppm and overlapping with the $\delta$ 5.24 ppm signal due to the olefinic protons at C-2 and C-3.

The above dien-ol (138) on tosylation furnished a glassy solid (139?) which resisted all attempts at crystallisation and hence a potential route to oleana-2,12-diene (135) through lithium aluminium hydride reduction of the tosyl
ester (139) was not pursued further.

Synthesis of Oleana-2,12-dien-28-al (140):

a) By Sarett Oxidation of Oleana-2,12-diene-28-ol (138): Oleana-2,12-diene-28-ol (138) described above was oxidised with chromic acid in pyridine according to the method of Sarett et al. The crude product on chromatography over alumina and crystallisation gave pure oleana-2,12-dien-28-al (140), m.p. 164-170°, (α)D + 127.7°, however in poor yield.

b) By Jones Oxidation of the Dien-ol (138): Oxidation of the dien-ol (138) with Jones chromic acid reagent gave the desired oleana-2,12-dien-28-al (140) in satisfactory yield in contrast with the Sarett oxidation result. The two dien-aldehydes obtained by Sarett and Jones oxidations were identical (mixed m.p. and I.R.). In this connection, it may be mentioned that failure of Sarett oxidation to give good yields of aldehydes is not uncommon. I.R. Spectrum of the dien-aldehyde (140) showed the absence of absorption in the hydroxyl region, but showed a peak at 1720 cm⁻¹ (aldehyde carbonyl)

N.M.R. Spectrum (Figure XX) of the dien-aldehyde (140) showed signals of the seven tertiary methyls at $\delta$ 0.78, 0.89, 0.91-0.95 (four) and 1.14 ppm; signals of the three olefinic protons (C-2, C-3 and C-12) all centered around
Figure XX

Figure XXI
5.40 ppm and the signal of the aldehydic proton at C-28 at $\delta$ 9.40 ppm.

Preparation of Oleana-2,12-diene ($\beta$-Amyrilene-II, 135$^{143}$): The above mentioned oleana-2,12-dien-28-al (140) was reduced by the Huang-Minlon procedure$^{140}$ to yield oleana-2,12-diene (135), m.p. 148-150°, ($\chi$)$_D$ + 133.6°.

I.R. Spectrum (Figure XXI) of the diene (135) showed the absence of absorption in the carbonyl and hydroxyl regions, but showed peaks at 820 (trisubstituted ethylene) and 725 cm$^{-1}$ (cis-disubstituted ethylene)$^{139b}$. 
Experimental

Section-A

All m.p.s are uncorrected. Pet ether used had b.p. 60-80\(^\circ\) throughout. Rotations were measured in chloroform. Neutral or deactivated alumina refers to Brockmann I alumina (E. Merck) treated with 10\% AcOH (3 ml) per 100 g. T.L.C. was carried on silica gel G (E. Merck).

Ethanol Extract of the Flowers of E. Jambolana: The dried flowers of E. jambolana (500 g) were extracted with 95\% ethanol (3 x 1 lito) in a percolator in the cold for 38 days. The dark brown alcoholic extract was concentrated under reduced pressure to a viscous gummy matter which was filtered with great difficulty to yield a brown residue (56 g). The latter was triturated with ether (3 x 1 lit) and the ether soluble fraction (Fraction S, Chart-XI) filtered from the ether insoluble substance (26 g).

Investigation of the Ether Soluble Ethanol Extract (Fraction S): The dark brown ether solution obtained as above was washed with cold 5\% aq. KOH (3 x 200 ml) and then with water until neutral, dried (Na\(_2\)SO\(_4\)) and the ether distilled off to yield the ether soluble neutral product (Fraction N, Chart-XII) as a viscous brown gum (12 g). The aq. alkaline layer was
acidified with cold conc. HCl and the precipitated solid was taken up in ether. The ether layer was washed with water, dried (Na₂SO₄) and evaporated to furnish the crude ether soluble acid mixture (Fraction A, Chart-XII = 1.1 g).

Examination of the Neutral Ether Soluble Matter (Fraction N, Chart-XII): The above neutral ether soluble gum (12 g) was placed on a column of deactivated alumina (300 g) and chromatographed (Chart-XXX). Each fraction collected was about 50 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Pet ether</td>
<td>Oil</td>
</tr>
<tr>
<td>5-8</td>
<td>Pet ether : benzene (4:1)</td>
<td>Oil</td>
</tr>
<tr>
<td>9-12</td>
<td>Pet ether : benzene (3:2)</td>
<td>Wax</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether : benzene (2:3)</td>
<td>Wax</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether : benzene (1:4)</td>
<td>Trace waxy solid from methanol</td>
</tr>
<tr>
<td>21-28</td>
<td>Benzene</td>
<td>Wax, solid from methanol</td>
</tr>
<tr>
<td>29-32</td>
<td>Benzene : ether (4:1)</td>
<td>Trace gum</td>
</tr>
<tr>
<td>33-36</td>
<td>Benzene : ether (3:2)</td>
<td>Trace gum</td>
</tr>
<tr>
<td>37-48</td>
<td>Benzene : ether (2:3)</td>
<td>Solid 1 from methanol, m.p. 122 - 125°C</td>
</tr>
<tr>
<td>49-52</td>
<td>Benzene : ether (1:4)</td>
<td>Trace Solid 1</td>
</tr>
<tr>
<td>53-56</td>
<td>Ether</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Chart-XXX
**β-Sitosterol (95A)**: Fractions 37-52 were combined to give the crude solid 1 (1.5 g) which was crystallised from a mixture of acetone and methanol to furnish a crystalline solid (0.41 g), m.p. 134-136°, identical (mixed m.p.) with an authentic sample of β-sitosterol (95A).

**β-Sitosterol Acetate (95B)**: The above β-sitosterol (0.5 g) was acetylated with acetic anhydride (5 ml) and pyridine (5 ml) on the steam bath and gave on usual work up followed by crystallisation from a mixture of acetone and methanol, pure β-sitosterol acetate (0.12 g), m.p. 124-126°, identical (mixed m.p.) with an authentic sample of β-sitosterol acetate (95B).

**Esterification of the Ether Soluble Acidic Part (Fraction A, Chart-XII)**: The crude ether soluble acid mixture (Fraction A, 14.1 g) was esterified with an ethereal solution of diazomethane (prepared from 14.1 g of nitrosomethylurea). Excess of diazomethane was decomposed with glacial acetic acid (10 ml). The ether solution was washed with cold 5% aq. KOH and water, dried (Na$_2$SO$_4$) and the ether distilled off to furnish the crude ester mixture (14.1 g).
Chromatography of the Ester Mixture from Fraction A: The aforementioned ester mixture (14.1 g) was placed on a column of neutral alumina (400 g) and chromatographed (Chart-XXXI). Each fraction collected was about 50 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-8</td>
<td>Pet ether</td>
<td>Oil</td>
</tr>
<tr>
<td>9-12</td>
<td>Pet ether : benzene (4:1)</td>
<td>Oil</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether : benzene (3:2)</td>
<td>Oil and gum</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether : benzene (2:3)</td>
<td>Gum</td>
</tr>
<tr>
<td>21-24</td>
<td>Pet ether : benzene (1:4)</td>
<td>Trace Solid A\textsubscript{1} from methanol</td>
</tr>
<tr>
<td>25-40</td>
<td>Benzene</td>
<td>Solid A\textsubscript{1} from methanol, m.p.110-126°</td>
</tr>
<tr>
<td>41-44</td>
<td>Benzene : ether (4:1)</td>
<td>Trace Solid A\textsubscript{1}</td>
</tr>
<tr>
<td>45-48</td>
<td>Benzene : ether (3:2)</td>
<td>Trace Solid A\textsubscript{1}</td>
</tr>
<tr>
<td>49-52</td>
<td>Benzene : ether (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>53-56</td>
<td>Benzene : ether (1:4)</td>
<td>Trace gummy solid</td>
</tr>
<tr>
<td>57-72</td>
<td>Ether</td>
<td>Solid A\textsubscript{2}, m.p.214-218°</td>
</tr>
<tr>
<td>73-76</td>
<td>Ether : chloroform (4:1)</td>
<td>Trace Solid A\textsubscript{2}</td>
</tr>
<tr>
<td>77-80</td>
<td>Ether : chloroform (1:1)</td>
<td>Coloured gum</td>
</tr>
<tr>
<td>81-84</td>
<td>Chloroform</td>
<td>Trace gummy solid</td>
</tr>
</tbody>
</table>

Chart-XXXI
Examination of Solid A₁: The crude Solid A₁ (9.1 g) from fractions 21-48 (Chart-XXXI) did not show a sharp m.p. even on crystallisation from methanol or pet ether and gave two spots in T.L.C. and was rechromatographed.

Rechromatography of Solid A₁: Solid A₁ (8.2 g) was placed on a column of neutral alumina (250 g) and chromatographed (Chart-XXXII). Each fraction collected was 50 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-8</td>
<td>Pet ether</td>
<td>Oil and gum</td>
</tr>
<tr>
<td>9-12</td>
<td>Pet ether : benzene (4:1)</td>
<td>Trace gum</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether : benzene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether : benzene (2:3)</td>
<td>Trace Solid A₁ from methanol</td>
</tr>
<tr>
<td>21-24</td>
<td>Pet ether : benzene (1:4)</td>
<td>Solid A₁ from methanol, m.p. 110 - 162°</td>
</tr>
<tr>
<td>25-36</td>
<td>Benzene</td>
<td>Solid A₁ from methanol, m.p. 110 - 168°</td>
</tr>
<tr>
<td>37-40</td>
<td>Benzene : ether (4:1)</td>
<td>Trace Solid A₁</td>
</tr>
<tr>
<td>41-44</td>
<td>Ether</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Chart-XXXII
Acetylation of Solid A₁: The crude Solid A₁ (5.8 g) from fractions 17-40 (Chart-XXXII) was digested with pet ether and the resulting colourless solid (4.6 g) was acetylated with acetic anhydride (46 ml) and pyridine (46 ml) on the steam bath for 2 hrs. Usual work up furnished the crude Solid A₁ acetate (4.6 g), m.p. 210-212°, which showed two spots in T.L.C. and was fractionally crystallised.

Fractional Crystallisation of A₁ acetate: Isolation of Methyl Oleanolate Acetate (96): The above crude A₁-acetate (4.6 g) was crystallised from a mixture of chloroform and acetone to furnish a crystalline solid (1.8 g), m.p. 214-218°, which on recrystallisation from the same solvent mixture yielded pure methyl oleanolate acetate (1.1 g), m.p. 217-220°, (α)D + 65°, identified (mixed m.p. and I.R.) as methyl oleanolate acetate (96). (Found: C, 77.50; H, 10.30. Mol. wt. (Rast): 468. Calc. for C₃₃H₅₂O₄: C, 77.29; H, 10.22%. Mol. wt. 512). I.R. Spectrum (KBr disc): Figure-1.

Isolation of Methyl Ursolate Acetate (97): The mother liquor from the above crystallisation of A₁-acetate was evaporated to dryness and the residue (2.8 g) was recrystallised from acetone to yield a crystalline solid (1.2 g), m.p. 238-242°, (α)D + 65°, identified (mixed m.p.) as methyl ursolate acetate (97). (Found: C, 77.49; H, 10.23. Calc. for C₃₃H₅₂O₄: C, 77.29; H, 10.22%).
Rechromatography of Solid A<sub>2</sub>: The crude Solid A<sub>2</sub> (3.8 g) from fractions 57-76 (Chart-XXXI) was rechromatographed (Chart-XXXIII) over neutral alumina (200 g). Each fraction collected was about 50 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Pet ether</td>
<td>Trace oil</td>
</tr>
<tr>
<td>5-8</td>
<td>Pet ether : benzene (4:1)</td>
<td>Trace gum</td>
</tr>
<tr>
<td>9-12</td>
<td>Pet ether : benzene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether : benzene (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether : benzene (1:4)</td>
<td>Nil</td>
</tr>
<tr>
<td>21-28</td>
<td>Benzene</td>
<td>Trace Solid A&lt;sub&gt;1&lt;/sub&gt; from methanol</td>
</tr>
<tr>
<td>29-32</td>
<td>Benzene : ether (4:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>33-36</td>
<td>Benzene : ether (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>37-40</td>
<td>Benzene : ether (2:3)</td>
<td>Trace coloured gum</td>
</tr>
<tr>
<td>41-44</td>
<td>Benzene : ether (1:4)</td>
<td>Trace Solid A&lt;sub&gt;2&lt;/sub&gt;, m.p. 210-214°</td>
</tr>
<tr>
<td>45-60</td>
<td>Ether</td>
<td>Solid A&lt;sub&gt;2&lt;/sub&gt;, m.p. 214-218°</td>
</tr>
<tr>
<td>61-64</td>
<td>Ether : chloroform (4:1)</td>
<td>Trace Solid A&lt;sub&gt;2&lt;/sub&gt;, m.p. 216-220°</td>
</tr>
<tr>
<td>65-68</td>
<td>Ether : chloroform (1:1)</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Chart-XXXIII
**Isolation of Methyl Crategolate (78):** Solid A$_2$ (3.2 g) from fractions 45-64 (Chart-XXXIII) was crystallised from a mixture of benzene and pet ether. The pure Solid A$_2$ (1.2 g), m.p. 220-222°, (α)$_D^0$ + 36° thus obtained was identical (I.R.) with an authentic sample of methyl crategolate (78) of Tschesche$^{69}$. (Found : C, 76.24; H, 10.23. Mol. wt. (Rast): 473. Calc. for C$_{31}$H$_{50}$O$_4$: C, 76.54; H, 10.28%. Mol. wt. 486). I.R. Spectrum (chloroform): Fig. II.

**Methyl Crategolate Diacetate (80):** Methyl crategolate (0.52 g) in pyridine (5 ml) and acetic anhydride (5 ml) was allowed to stand at room temp. for 4 days. The crude glassy mass obtained after working up as usual, was chromatographed over neutral alumina (50 g). Elution with benzene provided the crude acetate (0.46 g), m.p. 138-158° which on crystallisation from dil. methanol furnished pure methyl crategolate diacetate (0.11 g), m.p. 166-168°, (α)$_D^0$ + 24°, identical (I.R.) with an authentic sample of methyl crategolate diacetate of Tschesche$^{69}$. (Found : C, 73.68; H, 9.29. Calc. for C$_{35}$H$_{54}$O$_6$: C, 73.64; H, 9.54%). I.R. Spectrum (chloroform) = (Fig. III). N.M.R. Spectrum (Fig. IV) has been discussed in Section A, theoretical.

**Investigation of the Ether Insoluble Fraction (Chart-XI):** The ether insoluble residue (26 g) from the ethanol extract of the flowers of *E. jambolana* (Chart-XI) was digested with acetone and filtered from the acetone insoluble residue (14 g).
Evaporation of the solvent afforded a solid (11.4 g) = (Fraction B, Chart-XI), which on esterification with ethereal diazomethane (prepared from 11.4 g of nitrosomethyl-urea) gave a crude ester mixture (10.8 g). It was non-homogeneous (T.L.C.) and was chromatographed (Chart-XXXIV) over neutral alumina (300 g). Each fraction collected was about 50 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Pet ether</td>
<td>Oil</td>
</tr>
<tr>
<td>5-8</td>
<td>Pet ether : benzene (4:1)</td>
<td>Oil</td>
</tr>
<tr>
<td>9-12</td>
<td>Pet ether : benzene (3:2)</td>
<td>Gum</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether : benzene (2:3)</td>
<td>Trace gum</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether : benzene (1:4)</td>
<td>Trace solid B₁ from methanol</td>
</tr>
<tr>
<td>21-32</td>
<td>Benzene</td>
<td>Solid B₁ from methanol, m.p.110-190°</td>
</tr>
<tr>
<td>33-35</td>
<td>Benzene : ether (4:1)</td>
<td>Trace Solid B₁ from methanol</td>
</tr>
<tr>
<td>37-40</td>
<td>Benzene : ether (3:2)</td>
<td>Coloured gum</td>
</tr>
<tr>
<td>41-44</td>
<td>Benzene : ether (2:3)</td>
<td>Coloured gum</td>
</tr>
<tr>
<td>45-60</td>
<td>Benzene : ether (1:4)</td>
<td>Solid B₂, m.p.210-214°</td>
</tr>
<tr>
<td>61-64</td>
<td>Ether</td>
<td>Trace Solid B₂</td>
</tr>
<tr>
<td>65-76</td>
<td>Ether</td>
<td>Solid B₃, m.p.118-126°</td>
</tr>
<tr>
<td>77-80</td>
<td>Ether : chloroform (4:1)</td>
<td>Trace Solid B₃</td>
</tr>
<tr>
<td>81-84</td>
<td>Ether : chloroform (1:1)</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Chart-XXXIV
Examination of Solid B₁ : Solid B₁ (5.2 g) from fractions 17-36 (Chart-XXXIV) was rechromatographed on neutral alumina and crystallised from pet ether and then from methanol to yield a solid having the same long range of m.p. and showing two spots in T.L.C. The crude Solid B₁ (4.6 g) was hence acetylated at 100° with acetic anhydride (46 ml) and pyridine (46 ml). Usual work up furnished the crude B₁-acetate (4.6 g).

Fractional Crystallisation of B₁-Acetate : Isolation of Methyl Oleanolate Acetate (96) and Methyl Ursolate Acetate (97) : The above crude B₁-acetate (4.6 g) on crystallisation from a mixture of chloroform and acetone furnished a first crop of crystals (1.4 g), which on recrystallisation from a mixture of the same solvent mixture gave pure methyl oleanolate acetate (96; 0.6 g), m.p. 214-218°, identical (mixed m.p. and I.R.) with an authentic specimen.

The first mother liquor from the above crystallisation on concentration gave a second crop of crystals (1.8 g); m.p. 204-238° which on recrystallisation from acetone furnished pure methyl ursolate acetate (97, 0.62 g), m.p. 238-243°, identical (mixed m.p.) with an authentic sample.

Examination of Solid B₂ : Isolation of Methyl Crategolate (78) : Solid B₂ (1.9 g) from fractions 45-60 (Chart-XXXIV) was rechromatographed over neutral alumina (100 g). Elution with
ether furnished a solid (1.5 g), m.p. 216-220°, which was crystallised from a mixture of acetone and pet ether to yield pure methyl crategolate (78, 0.85 g), m.p. 225-227°, $(\alpha)_D + 36°$, identical (mixed m.p. and I.R.) with an authentic specimen. (Found : C, 76.14; H, 10.47. Mol. wt. (Rast) : 486. Calc. for $C_{31}H_{50}O_4$ : C, 76.54; H, 10.28%. Mol. wt. 486). I.R. Spectrum (KBr disc) : Fig. V.

Examination of Solid $B_3$ : Isolation of $\beta$-Sitosterol Acetate (95B) : Solid $B_3$ (0.9 g) from fractions 65-80 (Chart-XXXIV) was rechromatographed over neutral alumina (30 g). Elution with ether and with a mixture of ether and chloroform (4:1) gave a solid (0.52 g), m.p. 130-135° which was directly acetylated with acetic anhydride (5.2 ml) and pyridine (5.2 ml) at 100°. Working in the usual manner, a solid acetate was obtained which upon crystallisation from acetone furnished pure $\beta$-sitosterol acetate (95B, 0.25 g), m.p. 126-128°, identical (mixed m.p.) with an authentic specimen.

Investigation of the Acetone Insoluble, Methanol Soluble Fraction (Fraction C, Chart-XI) : The residue (14 g) left after digestion with acetone (Chart-XI) was taken up in methanol, filtered from some slimy material and the methanol evaporated to give a colourless solid (11.2 g), which was esterified with ethereal diazomethane (prepared from 11 g of
nitrosomethylurea\textsuperscript{148}). The crude ester mixture (10.4 g) obtained after usual work up was chromatographed (Chart-XXXV) over neutral alumina (300 g). Each fraction collected was about 50 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Pet ether</td>
<td>Trace oil</td>
</tr>
<tr>
<td>5-8</td>
<td>Pet ether : benzene (4:1)</td>
<td>Trace gum</td>
</tr>
<tr>
<td>9-12</td>
<td>Pet ether : benzene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether : benzene (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether : benzene (1:4)</td>
<td>Trace Solid C\textsubscript{1}, m.p. 122-172\degree C from methanol</td>
</tr>
<tr>
<td>21-40</td>
<td>Benzene</td>
<td>Solid C\textsubscript{1} from methanol, m.p. 122-172\degree C</td>
</tr>
<tr>
<td>41-44</td>
<td>Benzene : ether (4:1)</td>
<td>Trace Solid C\textsubscript{1}</td>
</tr>
<tr>
<td>45-48</td>
<td>Benzene : ether (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>49-52</td>
<td>Benzene : ether (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>53-56</td>
<td>Benzene : ether (1:4)</td>
<td>Trace gum</td>
</tr>
<tr>
<td>57-64</td>
<td>Benzene : ether (1:4)</td>
<td>Solid C\textsubscript{2}, m.p. 210-216\degree C</td>
</tr>
<tr>
<td>65-68</td>
<td>Ether</td>
<td>Trace Solid C\textsubscript{2}, m.p. 220-222\degree C</td>
</tr>
<tr>
<td>69-72</td>
<td>Ether : chloroform (4:1)</td>
<td>Trace Solid C\textsubscript{3}, m.p. 128-132\degree C</td>
</tr>
<tr>
<td>73-76</td>
<td>Ether : chloroform (1:1)</td>
<td>Nil</td>
</tr>
</tbody>
</table>
Examination of Solid C₁ : Solid C₁ (6.2 g), from fractions 17-44 (Chart-XXXV) was rechromatographed over a column of neutral alumina (200 g). Elution with benzene afforded a solid (5.8 g) which had a long range of m.p. (112-130°), not improved by crystallisation from a mixture of acetone and pet ether or from methanol. It showed 2 spots in T.L.C.

Acetylation of Solid C₁: Isolation of Methyl Oleanolate Acetate (96) and Methyl Ursolate Acetate (97) : The above Solid C₁ (5.5 g) was acetylated with acetic anhydride (55 ml) and pyridine (55 ml) on the water bath. Usual work up gave the crude C₁-acetate (5.5 g). The above C₁-acetate was crystallised from a mixture of chloroform and acetone to yield a crystalline solid (1.9 g), m.p. 204-218°, which upon recrystallisation from the same solvent mixture gave pure methyl oleanolate acetate (96, 1.1 g), m.p. 214-218°, identical (mixed m.p.) with an authentic sample.

The first mother liquor of the above crystallisation furnished a second crop of crystals (2.1 g), m.p. 190-238° which on recrystallisation from acetone yielded pure methyl ursolate acetate (97, 0.9 g), m.p. 237-240°, identical (mixed m.p.) with an authentic specimen.
authentic methyl oleanolate acetate (96) as the first crop. The mother liquor, known to contain methyl ursolate acetate (97) was not investigated.

**Isolation of Methyl Crategolate (78) from Solid A₂ (Chart-XXXVI):**

Solid A₂ (3.2 g), m.p. 212-220°, from fractions 61-76 (Chart-XXXVI) was rechromatographed on a column of neutral alumina (150 g) and the solid (2.5 g), m.p. 220-222°, eluted with ether was crystallised from a mixture of benzene and pet ether to yield pure methyl crategolate (78; 1.25 g), m.p. 227-228°, identical (mixed m.p.) with authentic methyl crategolate (78).

**Methyl Oleanolate (89) from Methyl Oleanolate Acetate (96):**

Methyl oleanolate acetate (96; 2.2 g) in benzene (20 ml) was refluxed with 10% methanolic KOH (50 ml) for 8 hrs and worked up as usual to furnish the crude deacetylated product (2 g), which was chromatographed over neutral alumina (100 g) and the crystalline solid (1.85 g) eluted with benzene, m.p. 190-194°, was crystallised from a mixture of acetone and methanol to yield pure methyl oleanolate (89; 1.1 g), m.p. 198-200°, (α)D + 70°, identical (mixed m.p. and L.R.) with an authentic specimen. (Found: C, 79.59; H, 10.68. Calc. for C₃₁H₅₀O₃: C, 79.10; H, 10.71%).
Crategolic Acid (76A) from Methyl Crategolate (78) : Methyl crategolate (78; 3 g) was refluxed with KOH (100 g) in diethylene glycol (360 ml) for 30 hrs. The reaction mixture was cooled, diluted with water and washed with ether. The aq. solution was acidified with cold conc. HCl and extracted with chloroform. The chloroform solution was washed with water, dried (Na₂SO₄) and evaporated to furnish the crude slightly coloured acid (2.8 g), m.p. 264-268°, which was dissolved in methanol, treated with active charcoal and filtered to a colourless solution. On concentration and dilution with water, the solution yielded crystalline crategolic acid (76A; 1.7 g), m.p. 265-269°. (Lit.68,69 m.p. 267-269°).

Isolation of Crategolic Acid (76A) from the Benzene Extract of the Flowers of E.Jambolana (Procedure III) : The acidic material (10 g) from the benzene extract of the flowers of E.jambolana (loc. cit.) was dissolved in a large volume of benzene and chromatographed (Chart-XXXVII) on a column of silica gel (300 g) set up in benzene. Each fraction collected was about 50 ml in volume.
<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-12</td>
<td>Benzene</td>
<td>Trace gum</td>
</tr>
<tr>
<td>13-20</td>
<td>Benzene : ether (4:1)</td>
<td>Trace gum</td>
</tr>
<tr>
<td>21-32</td>
<td>Benzene : ether (3:2)</td>
<td>Solid A, m.p. 235-289°</td>
</tr>
<tr>
<td>33-40</td>
<td>Benzene : ether (1:1)</td>
<td>Solid B, m.p. 215-240°</td>
</tr>
<tr>
<td>41-44</td>
<td>Benzene : ether (2:3)</td>
<td>Trace Solid, m.p. 190-210°</td>
</tr>
<tr>
<td>45-48</td>
<td>Benzene : ether (1:4)</td>
<td>Trace Solid C, m.p. 258-255°</td>
</tr>
<tr>
<td>49-60</td>
<td>Ether</td>
<td>Solid C, m.p. 260-268°</td>
</tr>
<tr>
<td>61-64</td>
<td>Ether : chloroform (4:1)</td>
<td>Trace Solid C, m.p. 255-255°</td>
</tr>
<tr>
<td>65-68</td>
<td>Ether : chloroform (1:1)</td>
<td>Trace Solid, m.p. 235-255°</td>
</tr>
<tr>
<td>69-72</td>
<td>Ether : chloroform (1:4)</td>
<td>Nil</td>
</tr>
<tr>
<td>73-76</td>
<td>Chloroform</td>
<td>Nil</td>
</tr>
<tr>
<td>77-80</td>
<td>Methanol</td>
<td>Gummy coloured Solid D from methanol, m.p. 225 - 235°</td>
</tr>
</tbody>
</table>

**Chart-XXXVII**

Solid C (2.6 g) from fractions 45-60 (Chart-XXXVII) was rechromatographed over a column of silica gel (100 g). The crystalline material (2.1 g) eluted with ether was crystallised
from dil. methanol to furnish pure crategolic acid (1.5 g), m.p. 265-269°, identical (mixed m.p.) with the authentic sample of crategolic acid (76A) obtained earlier (loc. cit.) by the hydrolysis of methyl crategolate (78).

Crategolic Acid Diacetate (79) : The above crategolic acid (76A; 1.5 g) was refluxed with acetic anhydride (30 ml) and pyridine (15 ml) for 1 hr. The reaction mixture was cooled, poured into water and the precipitated crude acetate (1.5 g), m.p. 190-215° was filtered off. It showed 2 spots in T.L.C. and was refluxed with methanol (100 ml) for 1 hr to decompose any mixed anhydride that might have been formed. The residue left after the removal of methanol (1.5 g) was chromatographed over a column of silica gel (50 g). Elution with benzene : ether (9:1) furnished the crystalline diacetate (1.2 g), m.p. 225-230°, which upon crystallisation from a mixture of ether and pet ether yielded pure (single spot in T.L.C.) crategolic acid diacetate (79; 0.75 g), m.p. 232-236°. (Lit.68,69 m.p. 235-239°).
Attemped Preparation of the Acetonide of Methyl Crategolate (106A): (a) Methyl crategolate (78; 1.04 g), m.p. 218-220° was dissolved in purified acetone (80 ml) and the solution was treated with a drop of perchloric acid. After allowing to stand for 7 days at room temp., the reaction mixture was poured into 20% aq. Na₂CO₃ solution (80 ml) and the precipitated solid (1 g), m.p. 204-208° was filtered. On crystallisation from a mixture of acetone and pet ether, unchanged methyl crategolate (78; 0.62 g), m.p. 216-220° was recovered.

(b) Methyl crategolate (78; 0.5 g), m.p. 216-220° was refluxed in pure acetone (40 ml) with a few crystals of p-toluenesulphonic acid for 5 hrs. Work up as in procedure (a) furnished original methyl crategolate (78; 0.48 g), m.p. 214-218°.

(c) Methyl crategolate (0.48 g), m.p. 214-218° in pure acetone (40 ml) was treated with a drop of conc. H₂SO₄ and the mixture allowed to stand at room temp. for 24 hrs. After working up as in method (a), a crude crystalline solid (0.48 g), m.p. 140-150° was obtained, which showed 2 spots in T.L.C. But the crude acetonide (106A ?) on attempted crystallisation from a mixture of acetone and methanol regenerated the original methyl crategolate (0.28 g), m.p. and mixed m.p. 216-218°.
Attempted Preparation\textsuperscript{127} of Bis-dihydropyranyl Ether of Methyl Crategolate (106B) : To a solution of methyl crategolate (78; 0.75 g) in anhydrous ether (100 ml) was added dihydropyran (4 ml, freshly distilled over KOH) and the mixture allowed to stand at room temp. for 7 days under anhydrous condition\textsuperscript{127}. To the resulting coloured solution a few beads of KOH were added and the ether solution was filtered. The solvents were removed in vacuum to yield an oily substance (1 g) which was chromatographed over activated alumina (20 g). Elution with pet ether : benzene (1:1) and benzene furnished a solid (0.7 g), m.p. 200-205° which on crystallisation from a mixture of acetone and methanol yielded original methyl crategolate (78; 0.43 g).

Preparation of Olean-12-ene-2\(\alpha, 3\beta, 28\)-triol (109A) : Methyl crategolate (1.06 g) in purified\textsuperscript{150} tetrahydrofuran (40 ml) was refluxed with a suspension of lithium aluminium hydride (2.5 g) in tetrahydrofuran (90 ml) for 8 hrs. The reaction mixture was allowed to cool, the excess of lithium aluminium hydride was decomposed by the cautious addition of cold water and the organic contents extracted with chloroform. The chloroform layer was washed with water, dried (Na\textsubscript{2}SO\textsubscript{4}) and evaporated to furnish a glassy solid (1.05 g). The latter upon crystallisation from dil. methanol gave olean-12-ene-2\(\alpha, 3\beta, 28\)-triol (109A), m.p. 158-165°, (\(\alpha\))\textsubscript{D} + 45° in good yield (0.9 g). (Lit.\textsuperscript{68}* (for anhydrous triol) :
m.p. 275-279°, ($\alpha$)$_D$ + 63°). (Found: C, 75.49; H, 10.36.
C$_{30}$$H_{50}$$O_3$, CH$_3$OH requires: C, 75.92; H, 11.02%). I.R.
Spectrum (Nujol) = (Fig. VI) has been discussed in
Section B (Theoretical).

2 $\alpha$, 3 $\beta$, 28-Triacetoxyolean-12-ene (109B): The above triol
(3.2 g) was dissolved in acetic anhydride (6.4 ml) and
pyridine (3.2 ml) and the solution allowed to stand at room
temp. for 7 days. Usual work up furnished a crude acetate
(2.9 g) as a glassy solid. It was crystallised from aq.
methanol to yield the desired 2 $\alpha$, 3 $\beta$, 28-triacetoxy
olean-12-ene (109B; 2.1 g), m.p. 184-188°, ($\alpha$)$_D$ + 8°.
(Lit.$^{68}$ m.p. 187-188°, ($\alpha$)$_D$ + 17.8°). (Found: C, 74.25;
H, 9.52. C$_{36}$$H_{56}$$O_6$ requires: C, 73.97; H, 9.57%). I.R.
Spectrum (Nujol) = (Fig. VII) and N.M.R. Spectrum (Fig. VIII)
have been discussed in Section B (Theoretical).

Attempted Preparation of 2 $\alpha$, 3 $\beta$-Diacetoxyolean-12-en-28-ol
(109C): (a) The above triacetate (109B; 0.76 g) in
methanol (100 ml) was allowed to stand at room temp. for
24 hrs after treatment with a solution of anhydrous Na$_2$CO$_3$
(0.64 g) in minimum quantity of water. The solution was
neutralised with a drop of dil. HCl and poured into cold
water. The resulting precipitate was taken in ether and the
ether solution was washed with water, dried (Na$_2$SO$_4$) and
evaporated to furnish the crude reaction product (0.75 g), m.p. 116-160°. The product was chromatographed over a column of neutral alumina (50 g). Elution with methanol and crystallisation of the eluted solid (0.73 g) gave the completely hydrolysed triol (109A; 0.65 g), m.p. 158-162°, identified by mixed m.p. determination with the original triol (109A).

(b) The triacetate (109B; 1.3 g) dissolved in benzene (5 ml) was treated in small portions with an ethanolic solution of KOH (1 M, 2.3 ml) and allowed to stand at room temp. for 18 hrs. Working up as in procedure (a) an amorphous solid (1.3 g) was obtained which resisted crystallisation from all attempted solvents. Chromatography of the amorphous solid over neutral alumina furnished mainly 2 solids: the unhydrolysed triacetate (109B; 0.6 g) and the completely hydrolysed triol (109A; 0.48 g), the former (109B) eluted with pet ether and pet ether : benzene (1:1) and the latter (109A) eluted with chloroform : methanol (3:2) respectively. The intermediate fractions could not be crystallised.

(c) The triacetate (2 g) was first chromatographed over silica gel (60 g). The fraction eluted with pet ether : benzene (4:1) was crystallised to give very pure and homogeneous (T.L.C.) triacetate (1 g), m.p. 184-187°. The latter dissolved in anhydrous benzene (30 ml) was magnetically
Solid A and Solid C were identical (mixed m.p.) with the unhydrolysed triacetate (109B) and the completely hydrolysed product, the triol (109A) respectively. Fractions 17-32 (Chart-XXXVIII) were combined to furnish the crude Solid B (0.7 g) as a gum that crystallised with great difficulty from dil. methanol to yield a crystalline solid (0.17 g), m.p. 190-192°, (α)D + 63°. I.R. Spectrum (Nujol) = (Fig. IX) and N.M.R. Spectrum (Fig. X) : have been discussed in Section B (Theoretical).

(d) Preferential monodeacetylation of the primary acetoxy group at C-28 of the triacetate (109B) was attempted under various other conditions. The amount of alkali, the time of reaction, temp. of the reaction, reaction medium etc. were varied, but all without success.

Preparation of the Acid Chloride of Grategolic Acid Diacetate (111) : (a) With Oxalyl Chloride : Grategolic acid diacetate (79; 0.5 g), m.p. 232-235° was refluxed with oxalyl chloride132 (5 ml) in dry benzene (10 ml) for 3 hrs. The volatile components were eliminated in vacuo and the resulting gum was directly used in the subsequent Rosenmund reduction.
(b) *With Thionyl Chloride*: Crategolic acid diacetate (79; 0.41 g), m.p. 232-235° was refluxed in dry benzene (10 ml) with purified and freshly distilled thionyl chloride (2 ml) for 1 hr. The solvent and the excess of reagent were removed under reduced pressure, fresh dry benzene (10 ml) was added and the benzene removed again under suction to ensure complete removal of thionyl chloride. The resulting gum when kept in a vacuum desiccator over KOH overnight set to a solid, m.p. 195-205°.

**Attempted Rosenmund Reduction according to Hahn et al**: The acid chloride (111) prepared from crategolic acid diacetate (79; 0.5 g) and oxalyl chloride (5 ml) was dissolved in anhydrous toluene (40 ml) and refluxed with 5% Pd-BaSO₄ catalyst (0.6 g) in a strong stream of dry H₂ until the evolution of HCl as determined by titration, ceased (2 hrs). The passage of H₂ was stopped and the reaction mixture was cooled and filtered. Toluene was removed by steam distillation and the gummy residue (0.5 g) was taken in ether. The ether solution was washed with cold 3% aq. KOH and water, dried (Na₂SO₄) and evaporated to furnish the crude neutral product as a gum (0.35 g), which was chromatographed (Chart-XXXIX) over neutral alumina (15 g). Each fraction collected was about 12 ml in volume.
<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Pet ether</td>
<td>Trace oil and gum</td>
</tr>
<tr>
<td>5-12</td>
<td>Pet ether</td>
<td>Solid A from methanol, m.p. 85-115°</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether</td>
<td>Trace Solid A from methanol</td>
</tr>
<tr>
<td>17-24</td>
<td>Pet ether : benzene (4:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>25-32</td>
<td>Pet ether : benzene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>33-40</td>
<td>Pet ether : benzene (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>41-48</td>
<td>Benzene</td>
<td>Trace gum</td>
</tr>
<tr>
<td>49-56</td>
<td>Benzene : ether (1:1)</td>
<td>Gum B</td>
</tr>
<tr>
<td>57-64</td>
<td>Ether</td>
<td>Trace Gum B</td>
</tr>
<tr>
<td>65-72</td>
<td>Chloroform</td>
<td>Nil</td>
</tr>
</tbody>
</table>

**Chart-XXXIX**

**Treatment of Solid A (Chart-XXXIX) with Girard Reagent T:**

Solid A (0.12 g) from fractions 5-12 (Chart-XXXIX) was non-crystallisable from all solvents attempted. A part (0.08 g) of Solid A was refluxed with Girard Reagent T (0.04 g), glacial acetic acid (0.08 ml), methanol (1.25 ml) and water (1 drop) for 1 hr. The reaction mixture was cooled and thoroughly shaken after the addition of water (5 ml), ether (5 ml) and saturated NaCl solution (2.5 ml). The resulting aq. layer was washed with ether (3 x 5 ml) and heated with
The precipitated solid was filtered and crystallised from pet ether to yield the desired 2α, 3β-diacetoxyolean-12-en-28-al (110; 0.03 g), m.p. 195-205°, identical (mixed m.p.) with the authentic diacetoxy-aldehyde (110) obtained subsequently by Rosenmund reduction of the acid chloride (111) in xylene (loc. cit.). The ether solution from the above separation of carbonylic fraction on evaporation furnished a non-carbonylic gum, which was not investigated.

**Examination of Gum B:** Gum B (0.21 g) from fractions 49-56 (Chart-XXXIX) could not be crystallised and no carbonylic fraction could be obtained from it by treatment with Girard Reagent T. It was not investigated further.

**Rosenmund Reduction according to Ruzicka et al:** Crategolic acid diacetate (79; 0.8 g), described in Section A was converted to the acid chloride (111), m.p. 195-205°, with purified thionyl chloride (5 ml). Anhydrous xylene (10 ml) was refluxed with 5% Pd-BaSO₄ catalyst (0.6 g) in a three-necked round-bottom flask equipped with a mercury-sealed mechanical stirrer, a condenser, a gas inlet and outlet system and a liquid addition device with pressure equaliser.
Examination of Solid C₂: Isolation of Methyl Crategolate (78): Solid C₂ (1.3 g) from fractions 57-68 (Chart-XXXV) was rechromatographed over a column of neutral alumina (100 g). Elution with ether afforded a crystalline substance (1.1 g), m.p. 218-220°, which on crystallisation from a mixture of chloroform and acetone furnished pure methyl crategolate (78; 0.48 g), m.p. 220-224°, identical (mixed m.p. and I.R.) with an authentic sample. (Found: C, 76.30; H, 10.47. Mol. wt. (Rast): 465. C₃₁H₅₀O₄ requires: C, 76.54; H, 10.28%. Mol. wt. 486). I.R. Spectrum (KBr disc): Fig. V.

β-Sitosterol Acetate from Solid C₃: Solid C₃ (0.1 g) from fractions 69-72 (Chart-XXXV) was directly acetylated with acetic anhydride (1 ml) and pyridine (1 ml) on the steam bath. The crude acetate (0.1 g) obtained after usual work up, on crystallisation from a mixture of acetone and methanol furnished β-sitosterol acetate (95B, 0.04 g)¹²⁰, m.p. 124-127°, identical (mixed m.p.) with an authentic sample.

Isolation of the Acidic Matter from the Benzene Extract of the Flowers of E. Jambolana (Procedure II, Chart-XVIII): Dried flowers (1 kg) of E. jambolana were extracted with benzene in a Soxhlet apparatus for 8 hrs. The crude
semi-crystalline solid (60 g) left after the removal of benzene was digested with a large volume of ether and the ether solution was separated by filtration from ether insoluble material (8 g). The ether solution was extracted with cold aq. 5% KOH solution and the aq. alkaline layer acidified with cold conc. HCl. The precipitated crystalline acidic material (Fraction A, Chart-XVIII) = (22 g) was filtered, washed with water and air-dried. The neutral ether solution (Fraction B), known to contain β-sitosterol (95%), as the only crystalline component was not investigated.

<table>
<thead>
<tr>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pet ether</td>
<td>Oil</td>
</tr>
<tr>
<td>Pet ether : benzene (4:1)</td>
<td>Oil and gum</td>
</tr>
<tr>
<td>Pet ether : benzene (2:3)</td>
<td>Gum</td>
</tr>
<tr>
<td>Pet ether : benzene (1:4)</td>
<td>Trace gum</td>
</tr>
</tbody>
</table>

The above crude acidic matter (Fraction A, 22 g) was esterified with an ethereal solution of diazomethane (prepared from 22 g of nitrosomethylurea (148)). Usual work up furnished the crude ester mixture (450 g) and chromatographed (Chart-XXXVIV). Each fraction collected was about 50 ml in volume.
<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>21-24</td>
<td>Pe: ether : benzene (1:4)</td>
<td>Trace Solid A₁ from methanol</td>
</tr>
<tr>
<td>25-44</td>
<td>Benzene</td>
<td>Solid A₁ from methanol, m.p. 110 - 120°</td>
</tr>
<tr>
<td>45-48</td>
<td>Benzene : ether (4:1)</td>
<td>Trace Solid A₁ from methanol</td>
</tr>
<tr>
<td>49-52</td>
<td>Benzene : ether (3:2)</td>
<td>Coloured gum</td>
</tr>
<tr>
<td>53-56</td>
<td>Benzene : ether (2:3)</td>
<td>Trace coloured gum</td>
</tr>
<tr>
<td>57-60</td>
<td>Benzene : ether (1:4)</td>
<td>Trace Solid A₂, m.p. 210-213°</td>
</tr>
<tr>
<td>61-76</td>
<td>Ether</td>
<td>Solid A₂, m.p. 212-220°</td>
</tr>
<tr>
<td>77-80</td>
<td>Ether : chloroform (4:1)</td>
<td>Trace Solid A₂</td>
</tr>
<tr>
<td>81-84</td>
<td>Ether : chloroform (1:1)</td>
<td>Coloured gum</td>
</tr>
</tbody>
</table>

**Chart-XXXVI**

**Isolation of Methyl Oleanolate Acetate:** Solid A₁ (8.5 g) from fractions 21-48 (Chart-XXXVI) on acetylation with acetic anhydride (85 ml) and pyridine (85 ml) at 100° afforded the crude A₁-acetate (8.5 g) after usual working up. The crude acetate on fractional crystallisation from a mixture of chloroform and acetone gave crystals of methyl oleanolate acetate (96; 3.6 g), m.p. 218-220°, identical (mixed m.p.) with
Anhydrous benzene (5 ml) was added to the refluxing suspension of the catalyst, a stream of dry $H_2$ was passed through the mixture and about 8 ml of the mixed solvent was distilled off under reduced pressure to ensure the complete exclusion of moisture in the system. The above-mentioned acid chloride (I11) in anhydrous xylene (10 ml) was added through the liquid addition device and the passage of dry $H_2$ through the rapidly agitated refluxing mixture was continued until the evolution of HCl gas as determined by titration with N/10 KOH (7 ml) ceased (5 hrs). The reaction mixture was cooled, the passage of $H_2$ was stopped, the catalyst was filtered off and washed with benzene. The combined xylene solution and benzene washings were evaporated at 100° under suction and the crude Rosenmund reduction product was taken up in ether (250 ml). The ether solution was washed with cold aq. 3% KOH (3 x 50 ml), followed by water, dried ($Na_2SO_4$) and evaporated to yield a neutral gummy solid (0.58 g), which was placed on a column of deactivated alumina (15 g) and chromatographed (Chart-XL). Each fraction collected was 25 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>Pet ether</td>
<td>Trace oil</td>
</tr>
<tr>
<td>3-4</td>
<td>Pet ether</td>
<td>Trace solid from methanol, m.p. 195 - 205°</td>
</tr>
<tr>
<td>5-8</td>
<td>Pet ether</td>
<td>Solid from methanol, m.p. 195-205°</td>
</tr>
<tr>
<td>9-16</td>
<td>Pet ether</td>
<td>Solid from methanol, m.p. 200-205°</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Chart-XL
acetone-12-en-28-al (110; 0.26 g), m.p. 200-205°. (Found: C, 75.36; H, 9.44. Requires: C, 75.51; H, 9.69%). I.R. Spectrum \( \delta (\text{pig. XI}) \) and N.M.R. Spectrum (Fig. XII) have been discussed in Section B (Theoretical).

Preparation of Benzylthiol: In a 2 liter three-necked round-bottom flask fitted with a mechanical stirrer, a reflux condenser and a liquid addition device were placed benzyl alcohol (54 g, 0.5 mole), thiourea (38 g, 0.5 mole) and constant-boiling 48% \( \text{HBr} \) (170 ml = 121.5 g, 1.5 mole) and the mixture refluxed for 9 hrs with stirring. A solution of \( \text{NaOH} \) (60 g, 1.5 mole) in water (600 ml) was then added, a stream of nitrogen was passed over the surface of the liquid and the mixture refluxed without stirring 2 hrs, when an oily foul-smelling layer of the thiol separated above. The layers were separated after cooling, and the aqueous layer was extracted with ether (3 x 100 ml). The extracts and the original organic layer were dried, dried (\( \text{Na}_2\text{SO}_4 \)) and fractionally distilled. The fraction distilling at 190-194° was redistilled under reduced pressure.
Attempted Preparation of Benzylthiocrategolate Diacetate (112) following the Method of Levin et al\textsuperscript{137} : The crude acid chloride (111), prepared from crategolic acid diacetate (79; 0.18 g), m.p. 230-235\textdegree was dissolved in pure and dry benzene (2 ml) and treated with dry pyridine (0.05 ml) and benzylthiol\textsuperscript{138} (0.4 ml, freshly distilled over phosphorus pentoxide). The reaction mixture was allowed to stand at room temp. for 24 hrs under anhydrous condition and then poured into water. Working up as usual\textsuperscript{137}, the original crategolic acid diacetate (79; 0.15 g), m.p. and mixed m.p. 228-232\textdegree was recovered.

Preparation of Benzylthiocrategolate Diacetate (112) : The acid chloride (111) prepared from crategolic acid diacetate (79; 0.35 g), m.p. 230-235\textdegree in dry benzene (10 ml) and dry pyridine (10 ml) was heated in a sealed tube with benzylthiol\textsuperscript{138} (2 ml, freshly distilled over phosphorus pentoxide) for 96 hrs. The contents of the tube were then cooled, poured into ice-cold water and extracted with ether. The ether solution was washed successively with cold 1\% HCl, water, 1\% NaOH solution and water, dried (Na\textsubscript{2}SO\textsubscript{4}) and evaporated to furnish a gummy solid (0.33 g), which was crystallised twice from a mixture of acetone and methanol to yield the pure benzylthiocrategolate diacetate (112, 0.12 g), m.p. 198-205\textdegree,
(\alpha)_D + 45.25^\circ. \quad (\text{Found: } \text{C}, 74.49; \text{H}, 8.59; \text{S}, 4.99. \quad \text{C}_{41}\text{H}_{58.05}\text{S requires: } \text{C}, 74.28; \text{H}, 8.32; \text{S}, 4.83\%). \quad \text{I.R. Spectrum (Nujol) = (Fig. XIII)} \quad \text{has been discussed in Section B (Theoretical).}

\textbf{Preparation of \textit{Raney Nickel Catalyst}^{136} :} \quad \text{A solution of NaOH (19 g) in water (75 ml) was taken in a 500 ml beaker and stirred mechanically, the temp. being kept at 10^\circ by external cooling. Nickel-aluminium alloy (15 g) was added to it in portions at such a rate that the temp. did not rise above 25^\circ (2 hrs). Stirring was stopped and the reaction mixture was allowed to come to room temp. When the evolution of hydrogen became slow at room temp., the reaction mixture was heated gradually on a water bath until the vigorous evolution of hydrogen slowed down again (8 hrs). Water was added to restore the original volume, the mixture was stirred for a while, then allowed to settle and the supernatant clear solution decanted off. The residual nickel was transferred to a graduated stoppered cylinder with water and the water decanted off. A solution of NaOH (2.5 g) in water (25 ml) was then added, the mixture was shaken to disperse the catalyst thoroughly, allowed to settle and the alkali solution was decanted off. The nickel was washed by suspension with water (24 washings) and decantation, until the washing were
neutral and 10 times more to ensure complete removal of alkali. The process was repeated with rectified spirit (10 x 20 ml) and finally with absolute alcohol (3 x 20 ml) to dry the catalyst. The resulting highly pyrophoric Raney Nickel catalyst was kept in a bottle completely filled with absolute ethanol and tightly stoppered.

Reductive Desulphurisation of Benzylthiocrotategolate Diacetate (112)\textsuperscript{137} : Raney Nickel (1.8 g), prepared\textsuperscript{136} as above was refluxed with purified\textsuperscript{149} acetone (3.6 ml) for 1 hr. A solution of benzylthiocrotategolate diacetate (112; 0.18 g) in acetone\textsuperscript{149} (5.4 ml) was added to the refluxing mixture followed by water (5.4 ml) and the mixture refluxed for a further period of 1 hr. The contents were thereafter cooled, the catalyst was filtered off and the solvent evaporated. The resulting gum (0.18 g) was taken up in ether and the ether layer was washed with 3\% aq. Na\textsubscript{2}CO\textsubscript{3} and then with water, dried (Na\textsubscript{2}SO\textsubscript{4}) and evaporated to furnish an oily substance (0.16 g), which was chromatographed (Chart-XLI) over a column of neutral alumina (5 g). Each fraction collected was 12 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3</td>
<td>Pet ether</td>
<td>Oil</td>
</tr>
<tr>
<td>4</td>
<td>Pet ether</td>
<td>Trace gum</td>
</tr>
</tbody>
</table>
The solid (0.12 g), m.p. 190-195°, from fractions 5-12 (Chart-XLI) after crystallisation from a mixture of acetone and methanol gave the desired diacetoxy aldehyde (110; 0.1 g), m.p. 198-205°, identical (mixed m.p. and I.R.) with the diacetoxy aldehyde (110) obtained by Rosenmund reduction (loc. cit.). I.R. Spectrum (Chloroform) = (Fig. XLV).

Huang-Minlon Reduction\textsuperscript{140} of the Diacetoxy Aldehyde (110):

\textbf{Synthesis of Olean-12-ene-2\(\alpha\), 3\(\beta\)-diol (104C)}: The above 2\(\alpha\), 3\(\beta\)-diacetoxyolean-12-en-28-al (110; 0.38 g) in ethanol (5 ml) and diethylene glycol (40 ml) was refluxed with 80% hydrazine hydrate (4.5 ml) for 2 hrs. Then solid KOH (0.38 g) was added and the mixture was further refluxed for one hr. The condenser was removed and the solvents distilled off until the inner temp. was raised to 210°. A dry condenser
was attached and the reaction mixture was refluxed for an additional period of 3 hrs. The contents were cooled, poured into water and extracted with ether. The ether solution was washed with water, dried (Na₂SO₄) and evaporated to give the crude diol (0.38 g), which was chromatographed (Chart-XLII) over activated alumina (10 g). Each fraction collected was 12 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Pet ether : benzene (1:1)</td>
<td>Trace oil</td>
</tr>
<tr>
<td>5-8</td>
<td>Pet ether : benzene (1:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>9-16</td>
<td>Pet ether : benzene (1:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>17-24</td>
<td>Benzene</td>
<td>Nil</td>
</tr>
<tr>
<td>25-32</td>
<td>Benzene : ether (9:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>33-40</td>
<td>Benzene : ether (4:1)</td>
<td>Trace solid from methanol, m.p. 185-190°</td>
</tr>
<tr>
<td>41-44</td>
<td>Benzene : ether (7:3)</td>
<td>Solid from methanol, m.p. 185-192°</td>
</tr>
<tr>
<td>45-56</td>
<td>Benzene : ether (7:3)</td>
<td>Solid, m.p. 195-201°</td>
</tr>
<tr>
<td>57-64</td>
<td>Benzene : ether (7:3)</td>
<td>Trace solid, m.p. 183-192°</td>
</tr>
<tr>
<td>65-72</td>
<td>Benzene : ether (1:1)</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Chart-XLII
The solid (0.21 g), m.p. 195-201°, from fractions 45-56 (Chart-XLI) was crystallised twice from a mixture of chloroform and methanol to furnish the pure crystalline olean-12-ene-2\(\alpha\), 3\(\beta\)-diol (104C; 0.11 g), m.p. 193-203°, \((\alpha)_D + 79.91°\). (Found: C, 81.39; H, 11.18. \(C_{30}H_{50}O_2\) requires: C, 81.39; H, 11.38%). I.R. Spectrum (Chloroform) = (Fig. XV) has been discussed in Section B (Theoretical).

**Acetylation of the Diol (104C):** Olean-12-ene-2\(\alpha\), 3\(\beta\)-diol Diacetate (113): The above diol (0.15 g) was heated on the steam bath with acetic anhydride (3 ml) and pyridine (1.5 ml) for 2 hrs and allowed to stand at room temp. overnight. The resulting crude acetate (0.15 g), obtained after usual work up, on two crystallisations from a mixture of acetone and methanol furnished the pure olean-12-ene-2\(\alpha\), 3\(\beta\)-diol diacetate (113; 0.09 g), m.p. 179-181°, \((\alpha)_D + 35.46°\).

(Found: C, 77.41; H, 10.09. \(C_{34}H_{54}O_4\) requires: C, 77.52; H, 10.33%). I.R. Spectrum (Chloroform) = (Fig. XVI) and N.M.R. Spectrum (Fig. XVII) have been discussed in Section C (Theoretical).
EXPERIMENTAL

SECTION-C

Methyl Oleana-2,12-dien-28-oate (90) from Methyl Oleanolate (89)69c: Methyl oleanolate (89; 2.8 g), described in Section A, was heated on the steam bath with freshly distilled phosphorus oxychloride (4.4 ml) and pyridine (28 ml) for 2 hrs and then refluxed for 5 mins. The reaction mixture was well cooled and poured into crushed ice. The precipitated solid (2.8 g) was filtered, washed with water, air-dried and chromatographed (Chart-XLIII) over a column of neutral alumina (100 g). Each fraction collected was 50 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>3-4</td>
<td>Pet ether</td>
<td>Solid from methanol, m.p. 140-164°</td>
</tr>
<tr>
<td>5-12</td>
<td>Pet ether</td>
<td>Solid from methanol, m.p. 170-176°</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether</td>
<td>Trace solid from methanol</td>
</tr>
<tr>
<td>17-20</td>
<td>Benzene</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Chart-XLIII
The solid (2.2 g), m.p. 170-176°, from fractions 5-12 (Chart-XLI) on two crystallisations from acetone gave pure methyl oleana-2,12-dien-28-oate (90; 1.2 g), m.p. 180-182°. (Lit.69c m.p. 180-186°).

**Tosylation of Methyl Crategolate (78)**: To a cooled solution of methyl crategolate (78; 1.05 g) in dry pyridine (50 ml) was added p-toluenesulphonyl chloride (3 g) and the mixture allowed to stand at room temp. for 3 days under anhydrous condition. The reaction mixture was then poured into crushed ice and the precipitated solid taken up in ether. The ether solution was washed successively with cold aq. 2N HCl, 20% aq. NaHCO₃ and water, dried (Na₂SO₄) and evaporated to yield the crude ditosylate of methyl crategolate (136) as a glassy solid (1.25 g).

**Attempted Crystallisation of Methyl Crategolate Ditosylate (136) from Methanol**: The above crude ditosylate (1.25 g) was crystallised twice from methanol to furnish a crystalline substance (0.7 g), m.p. 116-120°, (α)D + 56.8°. The product gave negative test for sulphur and analysed for a methyl olean-12-ene-28-oate dimethyl ether (Methyl bredemolate dimethyl ether (137) ?). (Found: C, 77.31; H, 10.56. C₃₃H₅₄O₄ requires: C, 76.99; H, 10.57%).
Methyl oleana-2,12-dien-28-oate (90) from Methyl Crategolate Ditosylate (136) : The crude ditosylate of methyl crategolate (136; 0.3 g) without further purification (in view of the above rearrangement) in pure acetone (30 ml) was heated at 100° in a sealed tube with sodium iodide (0.75 g) for 1 hr. The contents were cooled and poured into water. The precipitated matter was filtered with great difficulty, washed with cold aq. 5% Na₂CO₃ solution and water and air-dried to yield a gummy solid (0.24 g), which was chromatographed (Chart-XLIV) over a column of neutral alumina (10 g). Each fraction collected was 25 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Pet ether</td>
<td>Oil</td>
</tr>
<tr>
<td>5-8</td>
<td>Pet ether : benzene (9:1)</td>
<td>Solid from methanol, m.p. 140-144°</td>
</tr>
<tr>
<td>9-12</td>
<td>Pet ether : benzene (9:1)</td>
<td>Solid from methanol, m.p. 148-162°</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether : benzene (9:1)</td>
<td>Solid from methanol, m.p. 130-142°</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether : benzene (4:1)</td>
<td>Trace solid from methanol</td>
</tr>
<tr>
<td>21-24</td>
<td>Pet ether : benzene (1:1)</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Chart-XLIV
The solid (0.12 g), m.p. 148-162° from fractions 9-12 (Chart-XLV) was rechromatographed over a column of neutral alumina (5 g). Elution with pet ether : benzene (9:1) gave a crystalline substance (0.09 g), m.p. 160-172°, which showed several spots in T.L.C. This solid (0.09 g) on repeated crystallisation from acetone, furnished a small yield (0.03 g) of the pure (single spot in T.L.C.) diene ester (90), m.p. 178-184°, identical (mixed m.p.) with authentic methyl oleana-2,12-dien-28-oate (90) prepared from methyl oleanolate (89).

Synthesis of Oleana-2,12-dien-28-ol (138)\textsuperscript{143b} : A solution of methyl oleana-2,12-dien-28-oate (90; 0.55 g) in purified tetrahydrofuran (40 ml) was added to a well cooled suspension of lithium aluminium hydride (1 g) in tetrahydrofuran (40 ml), and the mixture allowed to attain room temp. Thereafter the mixture was refluxed for 10 hrs. The contents were cooled, and the excess of the reagent was destroyed by the cautious addition of cold water. The resulting slurry was filtered and the residue extracted with chloroform (3 x 100 ml). The filtrate and washings were combined, washed with water, dried (Na\textsubscript{2}SO\textsubscript{4}) and evaporated to yield a glassy solid (0.55 g), which was placed on a column of activated alumina (40 g) and chromatographed (Chart-XLV). Each fraction collected was 25 ml in volume.
Fraction | Eluent | Substance eluted
--- | --- | ---
1-4 | Pet ether | Oil
5-8 | Pet ether : benzene (4:1) | Trace solid from methanol
9-12 | Pet ether : benzene (3:2) | Nil
13-16 | Pet ether : benzene (2:3) | Nil
17-20 | Pet ether : benzene (1:4) | Trace gum
21-24 | Benzene | Trace solid from methanol
25-40 | Benzene : ether (4:1) | Solid from methanol, m.p. 146-152°
41-44 | Benzene : ether (1:1) | Trace solid from methanol
45-48 | Ether | Nil

Chart-XLV

The solid (0.45 g), m.p. 146-152°, from fractions 25-40 (Chart-XLV) was crystallised from aq. methanol to furnish pure oleana-2,12-dien-28-ol (138; 0.38 g), m.p. 150-152°, (α)D + 113°. (Found : C, 85.05; H, 11.51. C30H48O requires : C, 84.84; H, 11.39%). I.R. Spectrum (Nujol) = (Fig. XVIII) and N.M.R. Spectrum (Fig. XIX) have been discussed in Section C (Theoretical).
Attempted Acetylation of Oleana-2,12-dien-28-ol (138) : The above diene alcohol (138; 0.1 g) was heated on the water bath with acetic anhydride (1 ml) and pyridine (1 ml) for 2 hrs and allowed to stand at room temp. overnight. Usual work up furnished a glassy solid (0.1 g) which resisted all attempts at crystallisation.

Attempted Tosylation of Oleana-2,12-dien-28-ol (138) : The diene alcohol (138; 0.1 g) in pyridine (1 ml) was treated in the cold with p-toluenesulphonyl chloride (0.3 g) and the mixture was allowed to stand at room temp. for 90 hrs under anhydrous condition. After working up as usual, a tosyl derivative (139?) was obtained as a glassy solid (0.12 g), which could not be crystallised.

Synthesis of Oleana-2,12-dien-28-al (140)$^{143b}$ : (a) A solution of oleana-2,12-dien-28-ol (138; 0.34 g) in pyridine (3.4 ml) was added to a complex prepared$^{145}$ at 15° from chromic acid (0.34 g) and pyridine (3.4 ml) and the mixture allowed to stand at room temp. for 18 hrs. Excess of the reagent was destroyed by the addition of methanol (2 ml) and the reaction mixture was diluted with ethyl acetate (100 ml). The precipitated chromium salts were filtered and washed with ethyl acetate (5 x 50 ml). The combined ethyl acetate extract
and washings were washed successively with cold aq. 5% HCl (7 x 50 ml), aq. 5% KOH (3 x 50 ml) and water, dried (Na₂SO₄) and evaporated to yield a coloured gum (0.15 g), which was absorbed on a column of neutral alumina (10 g) and chromatographed (Chart-XLVI). Each fraction collected was 12 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>Pet ether</td>
<td>Nil</td>
</tr>
<tr>
<td>3-10</td>
<td>Pet ether</td>
<td>Solid from methanol, m.p. 150-152°</td>
</tr>
<tr>
<td>11-12</td>
<td>Pet ether</td>
<td>Trace solid from methanol</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether : benzene (4:1)</td>
<td>Nil</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether : benzene (3:2)</td>
<td>Nil</td>
</tr>
<tr>
<td>21-24</td>
<td>Pet ether : benzene (2:3)</td>
<td>Nil</td>
</tr>
<tr>
<td>25-28</td>
<td>Pet ether : benzene (1:4)</td>
<td>Trace solid from methanol</td>
</tr>
<tr>
<td>29-32</td>
<td>Benzene</td>
<td>Trace solid from methanol</td>
</tr>
<tr>
<td>33-36</td>
<td>Benzene : ether (1:1)</td>
<td>Trace coloured gum</td>
</tr>
<tr>
<td>37-40</td>
<td>Ether</td>
<td>Coloured gum</td>
</tr>
<tr>
<td>41-44</td>
<td>Methanol</td>
<td>Coloured gum</td>
</tr>
</tbody>
</table>

**Chart-XLVI**
The solid (0.08 g), m.p. 150-152°, from fractions 3-10 (Chart-XLVI) on crystallisation from a mixture of acetone and methanol furnished pure and crystalline oleana-2,12-dien-28-al (140), m.p. 164-170°, (c) D + 127.7° in low yield (0.03 g). (Found: C, 85.24; H, 10.30. C30H46O requires: C, 85.24; H, 10.97%). I.R. Spectrum (KBr disc) and N.M.R. Spectrum (Fig. XX) have been discussed in Section C (Theoretical).

(b) Jone's chromic acid reagent was prepared by dissolving chromic acid (1.75 g) in conc. H2SO4 (1.48 ml) and adding water (5 ml) in portions with cooling. Oleana-2,12-dien-28-ol (138; 2 g) was dissolved in purified acetone (80 ml) and the solution was cooled to 5°. To this cooled and stirred solution was added the above Jone's chromic acid reagent drop by drop till the green precipitate at first formed no longer appeared and the colour of the reagent persisted. The mixture was shaken for a further period of 2 mins., treated with cold water (250 ml) and extracted with chloroform (3 x 50 ml). The chloroform solution was washed with cold aq. 3% KOH (3 x 50 ml) and then with water, dried (Na2SO4) and evaporated to yield a glassy solid (1.38 g), which was placed on a column of silica gel (60 g) and chromatographed (Chart-XLVII). Each fraction collected was 25 ml in volume.
The solid (1.4 g), m.p. 156-160°, from fractions 5-16 (Chart-XLVII) on crystallisation from a mixture of acetone and methanol gave in good yield (0.9 g), the pure and crystalline diacetoxy aldehyde (140), m.p. 164-168°, which was identical (mixed m.p. and I.R.) with the oleana-2,12-dien-23-al (140), obtained earlier by Sarett oxidation of the diene alcohol (138), previously described.
Preparation of Oleana-2,12-diene (\(\beta\)-Amyrilene-II)\(^{143}\) = (135) :

The above oleana-2,12-dien-28-al (140; 0.9 g) in ethanol (5 ml) and diethylene glycol (50 ml) was refluxed\(^{140}\) with 80% hydrazine hydrate (6 ml) for 2 hrs. Powdered KOH (0.9 g) was then added and the mixture further refluxed for 1 hr. The condenser was thereafter removed and the reaction mixture heated until the inner temp. of the reaction mixture was raised to 210°. A dry condenser was re-attached and the contents of the vessel refluxed for an additional period of 3 hrs. The cold reaction mixture was then diluted with water and the precipitated gum extracted with ether (3 x 100 ml). The ether extract was washed with water (7 x 50 ml), dried (\(\text{Na}_2\text{SO}_4\)) and evaporated. The crude gummy residue (0.9 g) was placed on a column of silica gel (50 g) and chromatographed (Chart-XLVIII). Each fraction collected was 25 ml in volume.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Substance eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>Pet ether</td>
<td>Trace solid, m.p. 115-125°</td>
</tr>
<tr>
<td>3-4</td>
<td>Pet ether</td>
<td>Solid, m.p. 126-135°</td>
</tr>
<tr>
<td>5-12</td>
<td>Pet ether</td>
<td>Solid, m.p. 138-146°</td>
</tr>
<tr>
<td>13-16</td>
<td>Pet ether</td>
<td>Trace solid</td>
</tr>
<tr>
<td>17-20</td>
<td>Pet ether : benzene (4:1)</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Chart-XLVIII
The solid (0.7 g), m.p. 138-146° from fractions 5-12 (Chart-XLVIII) on crystallisation from acetone furnished the pure and crystalline oleana-2,12-diene (135; 0.4 g), m.p. 148-150°, \((\alpha)_D + 133.6^\circ\). (Lit.\textsuperscript{143a} m.p. 150-153°, \((\alpha)_D + 139.9^\circ\). (Found : C, 87.96; H, 11.74. Calc. for C\textsubscript{30}H\textsubscript{48} : C, 88.16; H, 11.84\%). \textit{I.R. Spectrum} (Nujol) = (Fig. XXI) has been discussed in Section C (Theoretical).
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