CHAPTER - III

TRITERPENOIDS FROM SALVIA MOORCRAFTIANA.
The term triterpenoids refers to a group of natural products containing thirty carbon atoms based on isoprene units. This definition though generally applicable, is by no means rigid, since several substances which contain more than thirty or less than thirty carbon atoms and also those which do not strictly follow the isoprene rule have been isolated and characterized as triterpenoids during recent years. The invention of highly sophisticated physico-chemical techniques and the contemporary developments in the biogenetic theories have been mainly responsible for the isolation and identification of new unconventional types of triterpenoids. The handbook of naturally occurring compounds contains a comprehensive survey of natural terpenoids classified according to the structural type (Fig. 3.1). Some common classes of triterpenoids are discussed below:

(i) Trimethyl steroids: The members of this group having tetracyclic and pentacyclic ring systems possess the gross carbon skeleton of C_{27}-steroids, with the addition of a gem dimethyl group at C(4) and an angular methyl group at C(14). This class of compounds occupies a position intermediate between the triterpenoids and the steroids. They have helped to establish the biogenetic link between the two families. Most of the trimethyl steroids belong either to lanosterol or euphol series. They differ from each other in the stereochemistry of
FIG. 3.1. TRITERPENE—MAIN SKELETON KEY.
the C/D ring juncture and the side chain.

(ii) Pentacyclic triterpenoids: The majority of members of this class have a perhydropicene nucleus bearing eight methyl groups variously disposed. There are also two series of compounds having a five membered ring E bearing an isopropyl group. The three important series of this group are:

(a) The oleanane (β-amyrin) series: Triterpenes of oleanane series are widely distributed throughout the plant kingdom. Main characteristic features of this class are:

Oxygenation is particularly common along the two edges of the molecule comprising C(16), 28, 22, 21, 30 and C(2), 3, 23, 24 whilst at the other sites it is observed rarely. More detailed patterns are often apparent for the compounds from plants which are botanically closely related. At some positions, e.g., J(2), 16 and 22, the pattern is markedly different for acids and non-acids.

All 13β, 28 ethers are also oxygenated at C(16). The high incidence of C(28) oxygenated compounds suggests that the conversion of β-amyrin into erythrodiol will prove to be a primary step in many biosynthetic pathways.

The occurrence of additional double bonds within the β-amyrin skeleton is rare. Saikogenins E, F and G are formally derivable from 12-ene-11,28-diol system.

(b) Ursane series (α-amyrin): Like oleananes, ursanes are derived from α-amyrin group. Both oleanane and ursane series
are identical in stereochemistry in rings A, B, C and D and at D/E ring juncture but differ in the substitution pattern of ring E and the $\alpha$-configuration of the C(20) methyl group.

(c) **Lupane and hopane series:** These two constitute small but biogenetically important groups. Both have a five membered ring E. Lupeol, the parent member of this group, was first isolated from lupin seeds, and is widely distributed in plants. It is shown to contain an easily reducible double bond and gives formaldehyde and a methyl ketone on ozonolyses, while the dehydrogenation product includes those obtained from the A/B moiety of the amyrin series. Oxidative removal of the isopropenyl group generates a cyclopentanone. The lupeol skeleton arises by the same biosynthetic processes as the ursane and oleanane skeletons.

(iii) **The nortriterpenoids:**

(a) **The C$_{29}$ and C$_{28}$ series:** The members of this group are dimethyl and monomethyl steroids which form part of the biogenetic link between the lanostane and cholestane series. Lophenol$^7$(1), macdougallin$^8$(2) and fusidic acid$^9$(3) are a few examples of this series (Fig. 3.2).

(b) **The C$_{26}$ series:** This series of nortriterpenoids is characterized by compounds where terminal part of the side chain is lost and the remaining part $\overline{\text{C(20) to C(23)}}$ takes the form of a furan ring, e.g., limonin (4). The limonoid bitter principles are a class of C$_{26}$ degraded triterpenes believed to arise as oxidation products of tetracyclic triterpenes. A second group of
FIG. 3.2
related principles, the simarouabalides, occur as further breakdown products in this series. Limonoids constitute stereo-
chemically a homogeneous group and are biogenetically derivable from a triucalolol type of tetracyclic triterpene.

(c) \( \text{C}_{25} \) and \( \text{C}_{20} \) series: The \( \text{C}_{25} \) fungal metabolites ophiobolin\(^{13}\) (5), zizanin A (6a) and zizanin B (6b)\(^{14}\) are the first members of sesterterpenoids and are believed to be derived from geranyl-
geranyl pyrophosphate rather than from the triterpenoids\(^{15}\).

The \( \text{C}_{20} \) groups of lactones related to quassin\(^{16}\) (7), the bitter principles of Quassia, are believed to be true nortri-
terpenoids.

**Structure elucidation of triterpenes:** TLC and GLC permit quick detection and identification of triterpenoids. Developments in the TLC, e.g., impregnation of silica gel G with silver nitrate or fluorescent indicator has enhanced its utility. All triterpenoids respond to Liebermann Burchard test.

IR, UV, NMR and MS spectroscopy are the conventional techniques for structure elucidation. Recent developments in NMR instrumentation, double resonance and deuterium labelling\(^{17}\) have further increased its potentiality as a tool for studying finer details of molecular structure. It is now possible to assign resonance positions to the methyl groups in triterpenoids and their derivatives belonging to all major classes\(^{18-29}\) (viz. euphane, isoepuhae, dammarane, lanostane, oleanane, ursane, lupane and hopane). These assignments have been used for structure
elucidation of unknown substances. Shamma et al. have studied the relationship between the NMR spectra and general structural features of pentacyclic triterpenes. Judicious use of spin-spin coupling has led to the assignment of configuration of substituents in triterpenoid molecules, e.g., C(6)-hydroxyl as \( \alpha \)-equatorial in zeorinin has been deduced on the basis of large \( J \) values for C(6)-methine multiplet. Anisotropy of functional groups also affects the chemical shifts of protons other than methyl groups. In the \( \beta \)-amyrin series a lactone bridge from C(28) to C(21) results in the downfield shift of olefinic proton. A method for the identification of a hydroxyl group through methylation which results in an upfield shift by 0.6 ppm has been reported as an alternative to acetylation. The configuration of the aldehyde group located at C(4) in triterpenoids has also been deduced from the chemical shifts.

Mass spectrometry has some unique advantages over other physico-chemical techniques. It has been found that in general the mode of fragmentation of triterpenoids is controlled by the position of the double bond (retro-Diels-Alder fragmentation). It could either be originally present or generated by elimination of water or acetic acid and therefore characteristic features appear in the MS which frequently allow the assignment to one of the major classes. In addition, functional groups can often be narrowed down by consideration of fragmentation pattern.

The mass spectra of certain \( \Delta^1 \)-3-oxo and \( \Delta^4 \)-3-oxo triterpenes show a very prominent peak corresponding to ring A.
containing C(19) and C(6). The fragmentation of tetracyclic triterpenes of cucurbitacin group has been studied.

The development of 'molecular mass spectrography' is another leap forward in this technique wherein negatively charged M-1 ions are formed by the addition of low energy electrons to the molecule followed by loss of a proton, usually without fragmentation, and this allows an accurate determination of molecular weight up to 2000. It has been reported that the molecular mass spectra of zeorin, methyl ursolate, betulin, \( \gamma \)-onocerin, 3-friedelanol, and friedelin show peaks corresponding to their MW or M-1, while the spectra of allobetula-2-ene, 2-onocerone and primulagenin A give peaks corresponding to values higher than M due to addition of oxygen.

Circular dichroism has been used to determine the conformation of ring A in triterpenoids and the stereochemistry of OH in ring A of cucurbitacin-\( \alpha \)-ketols. The negative Cotton effect of some triterpenoids has been rationalized in terms of octant rule assuming a skewed-boat conformation for ring A. The configuration of C(19)-acetyl group in 3\( \beta \), 28-diacetoxy-30-norlupan-2-one has been shown to be \( \alpha \) by direct comparison with the analogous derivatives of A-nor-5-cholestane. In the unsaturated triterpene acids of oleanane and ursane series, the 28-carboxylic group has been shown to exist in solution in a syn-planar configuration with C(16) - C(17) bond.

X-ray crystallography is being increasingly employed for structural determination of unknown molecules.
The most common triterpenoids isolated so far from the genus *Salvia* are of oleanane and ursane type, although other types have also been isolated, e.g., lupanes from *S. phlomoides* or friedelane from *S. glutinosa*. Recently a dammarane type of triterpenoid has been isolated for the first time from *S. bicolor*. No work regarding isolation of triterpenoids has been reported so far from *Salvia moorcraftiana*, and therefore an attempt has been made to isolate the same and other biogenetically related compounds. The polar triterpenoids are usually obtained from the plant by extraction with methanol or ethanol. The preliminary investigation showed that leaves were rich in triterpenoids, and therefore, ground leaves of *S. moorcraftiana* were repeatedly extracted with methanol in a soxhlet apparatus. The residue obtained after concentration of the extract was chromatographed over a silica gel column. The various pooled fractions on rechromatography and preparative TLC using silica gel yielded six compounds designated as K, L, M, N, O and P. Of these, the first was identified as $\alpha$-sitosterol and the remaining as $\beta$-amyrin, lupeol, anagadiol, oleanolic acid and olean-(13)18-ene-2$\beta$,3$\beta$-diol, respectively.

Compound K, crystallized from methanol as white shining needles, m.p. 134–135°, gave positive Liebermann Burchard test for steroids. The mass spectrum of the compound showed fragmentation peaks at m/z 396 ($M^+ - 18$), 273 ($M^+ - $side chain, $C_{10}H_{21}$) and
m/z 255 (M+ -18-C_{10}H_{21}) besides the molecular ion peak at m/z 414. The identity of the compound as \( \beta \)-sitosterol was established by m.m.p. determination, co-TLC and co-IR with an authentic sample.

Compound L, C_{30}H_{50}, m.p. 157-158° gave violet colouration with Liebermann Burchard reagent and produced intense red colour changing to violet on treatment with TCA. The IR spectrum of the compound contained absorptions at 3450 cm\(^{-1}\) (hydroxyl group), 1595, 885 cm\(^{-1}\) (trisubstituted double bond), 1385, 1450 cm\(^{-1}\) (gem dimethyl). The mass spectral fragmentation of the compound indicated that it underwent typical retro-Diels-Alder-fragmentation of ring 'C' resulting in the base fragment at m/z 218. A prominent peak characteristic of \( \Delta^{12} \)-oleananes was observed at m/z 207. Other fragment ions were also seen at m/z 411 (M+ -15), 393 (M+ -15-18), 208 and 189 (Scheme 3.1). The presence of hydroxyl group was confirmed by the preparation of its monoacetate, m.p. 106-107°. Consequently, the compound was identified as \( \beta \)-amyrin (8).

Compound M crystallized from methanol as white needles, C_{30}H_{50}, m.p. 211°, answered positive Liebermann Burchard test. In its IR spectrum absorptions were seen at 3450 cm\(^{-1}\) (hydroxyl), 1639, 875 (=CH\(_2\)) and 1385 cm\(^{-1}\) (gem dimethyl). The presence of isopropenyl group in IR suggested that compound M could be lupane type of triterpenoid. NMR spectrum of the compound showed signals due to six methyls at \( \delta \) 0.74, 0.78, 0.80, 0.83 and 1.00.
SCHEME: 3.1

Retro-Diels Alder
Carbinol methine proton was observed as a doublet at $\delta$ 3.19. Two doublets were seen at $\delta$ 4.52 and $\delta$ 4.64 due to $-\text{CH}_2$ grouping. Its molecular ion peak in MS was observed at m/z 426. Other fragment ions at m/z 218 (100%), 220, 189 and 207 suggested the structure to be that of lupeol (9). The structure was further confirmed by preparation of its mono-acetate.

Compound N, isolated as diacetate was crystallized from methanol as cream coloured needles, m.p. 250-251°. The IR spectrum exhibited absorptions at 1745 cm$^{-1}$ (acetate carbonyl), 1381 cm$^{-1}$ (gem dimethyl), 1258, 1053 (C-0-C) and 970 cm$^{-1}$. Its NMR spectrum showed the presence of eight angular methyl groups signals between $\delta$ 0.74 - 1.14 and one vinyl hydrogen signal at $\delta$ 4.82. Two three-proton singlets due to C(1)-0Ac and C(3)-0Ac were observed at $\delta$ 2.00 and $\delta$ 1.96 respectively. Two hydrogen atoms on carbons bearing acetoxy groups were seen at $\delta$ 4.69 and $\delta$ 4.56. These two protons giving rise to partially superimposed quartets, part X of two independent ABX systems in NMR, suggested the presence of axial-axial and axial-equatorial couplings between them. These values were found to be compatible only with $1\beta$-OH and $3\beta$-OH configuration. Mass spectrum of the compound N showed molecular ion peak at m/z 526 in addition to other fragment ion peaks at m/z 205, 204 (100%), 177, 189 and 190, fragmentation pattern characteristic of triterpenes of $\Delta^{18}$-oleanane series (36). From these results it was concluded that the corresponding alcohol of compound N must be $1\beta,3\beta$-dihydroxyolean-18-ene (10a). Moreover, all these values were found to be
in agreement with the reported values for anagadiol isolated from *S. broussonetti*.

Compound 0, crystallized from methanol as white crystalline product, C$_{30}$H$_{48}$O$_3$, m.p. 288°, showed in its IR spectrum absorptions at 3450 cm$^{-1}$ (hydroxyl), 1705 (acetate carbonyl), 1645 cm$^{-1}$ (carboxyl carbonyl) and 1385 cm$^{-1}$ (gem dimethyl). In NMR spectrum of the compound 0, three proton singlets were observed at δ 1.20, 1.10, 0.97, 0.95, 0.92, 0.84, and at δ 0.75 for two gem dimethyls and three tertiary methyl groups. A triplet due to C=CH was seen at δ 5.22 (J = 2Hz). A multiplet at δ 3.22 (J = 4Hz), exchangeable with D$_2$O was assigned to secondary hydroxyl. A broad singlet, D$_2$O exchangeable, due to carboxylic hydroxyl proton was centered at δ 2.51. The above values were found to be in agreement with the reported values for oleanolic acid isolated from a wide variety of plants.

Mass spectrum of the compound showed molecular ion peak at m/z 456. Base peak was observed at m/z 248. In addition, other fragment ions were seen at 411 (M$^+\text{-COOH}$), 207 (248-COOH), 202 (248-CHOOH) and 189 (207-H$_2$O).

On methylation, compound 0 yielded a product 0′, m.p. 196.5° which showed IR absorptions at 1695 cm$^{-1}$ (carbonyl), 1392 cm$^{-1}$ (gem dimethyl). In its NMR spectrum seven methyl singlets were seen at δ 1.20, 1.15, 1.00, 0.93, 0.90, 0.84 and 0.77. A triplet at δ 5.21 was assigned to C=CH proton in the vicinity of CH$_2$. A three proton singlet due to -COOCH$_3$ was seen.
at δ 3.6. Broad one proton singlet, exchangeable with D₂O was centered at δ 2.05. Thus on the basis of these observations, compound 0₁ was identified as methyl ether of oleanolic acid and consequently 0 was assigned oleanolic acid structure (11).

Compound P, C₃₀H₅₀O₂, m.p. 226⁰, showed IR absorptions at 3450 cm⁻¹ (hydroxyl group) and 1385 cm⁻¹ (gem dimethyl). NMR spectrum of the compound displayed eight methyl signals at δ 0.78, 0.83, 0.92, 0.99, 1.06, 1.12 and δ 1.18. A broad singlet exchangeable with D₂O and corresponding to two hydroxyls was seen at δ 2.28. The two doublets at δ 3.41 and δ 4.50 were attributed to the presence of C(3)α-H and C(2)α-H respectively. However, no vinylic proton was seen in the spectrum. The study of NMR further revealed the presence of 1, 2 positions of the above hydroxyl groups as evident from a doublet at δ 3.41 (J = 7Hz), and doublet at δ 4.50 (J = 3Hz) confirming an equatorial OH group at C(3) and axial function at C(2) respectively. Its mass spectrum revealed the presence of molecular ion peak at m/z 442. Other fragment ions were seen at m/z 424 (M⁺-18), 218 and 205.

Compound P, on acetylation with Ac₂O/Py afforded a diacetate, P₁, m.p. 114⁰ which showed IR absorptions at 1725 cm⁻¹ (acetate carbonyl) and 1385 cm⁻¹ (gem dimethyl). In NMR spectrum of the compound, two three-proton singlets were at δ 1.98 and δ 2.05 for two acetates. Mass spectrum showed molecular ion peak
at m/z 526. Thus on the basis of above observations, compound P was identified as olean-(13)18-ene-2β,3β-diol (12)⁵⁷.
FIG. 3.3. TRITERPENOIDS FROM LEAVES OF S. MOORCRAFTIANA.
Isolation of triterpenoids from *Salvia moorcraftiana* leaves:

Leaves of the plant *Salvia moorcraftiana* were collected as described earlier. The dried and ground leaves (2 kg) were extracted with methanol in a Soxhlet apparatus. The extract was concentrated *in vacuo* to yield a dark green resinous mass (75 g). The extract (40 g) was subjected to column chromatography on silica gel for preliminary separation. A silica gel column (500 g) was prepared in Pet. ether (60-80°) and the resinous mass pre-adsorbed on silica gel (100-200 mesh, Acme) (100 g) was loaded on the column as described earlier (Chapter II, p. [x]). Elution was carried out with petroleum ether and subsequently with more polar solvent systems using chloroform and methanol. A total of 400 fractions (20 ml each) were collected and monitored by TLC. Like fractions were pooled together and were concentrated by flash evaporation. Eight concentrates were obtained and each was examined separately for the presence of triterpenes by TLC monitoring and spraying with 10% sulphuric acid. Out of eight concentrates five were found to contain triterpenes whereas these were absent in concentrates numbers 2 and 5. The table 3.1 gives details of each fraction.
Table 3.1 Fractions obtained by chromatography of methanol extract of *S. moorcrafliana* (leaves)

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Solvent system</th>
<th>Weight (g)</th>
<th>Number of triterpenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>4.2</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; : CHCl&lt;sub&gt;3&lt;/sub&gt; (95 : 10)</td>
<td>7.3</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; : CHCl&lt;sub&gt;3&lt;/sub&gt; (85 : 15)</td>
<td>3.8</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; : CHCl&lt;sub&gt;3&lt;/sub&gt; (50 : 50)</td>
<td>2.2</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; : CHCl&lt;sub&gt;3&lt;/sub&gt; (20 : 80)</td>
<td>7.7</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.10</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt; : MeOH (95 : 5)</td>
<td>4.3</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt; : MeOH (90 : 10)</td>
<td>2.1</td>
<td>1</td>
</tr>
</tbody>
</table>

Concentrate 1 on repeated crystallization yielded compound K as white shining needles (455 mg, m.p. 134-5°). This compound gave positive test with Liebermann Burchard reagent. Compound K was later on found to be identical with an authentic sample of β-sitosterol (co-TLC, m.p., m.m.p., co-IR and MS). Compound L was obtained by rechromatography of concentrate 3. This was purified by repeated crystallization from methanol as white
needles (110 mg, m.p. 157-158°). It gave violet colouration with Liebermann Burchard reagent and produced intense red colour changing to violet on treatment with TCA. This compound was later on characterized as β-amin. Column chromatography of concentrate 4 (2.2 g) gave a fraction which on TLC was found to be a mixture of two compounds. The major compound M was separated by preparative TLC, followed by crystallization of the white product with methanol (35 mg, m.p. 211°). This compound was characterized as lupeol. Concentrate 6 (3.1 g) was chromatographed over silica gel to afford a mixture of compounds. These could not be separated either by column rechromatography or by preparative TLC. Therefore, the mixture (500 mg) was acetylated with Ac₂O/Py and rechromatographed over silica gel. Elution with C₆H₆:CHCl₃ (90:10) resulted in separation of only one product which on repeated crystallization from methanol afforded compound N as light buff coloured needles (76 mg, m.p. 250-251°). This compound was later on identified as acetate of 1β,3β-dihydroxyolean-18-ene (anagadiol). Column rechromatography of concentrate 7 (4.3 g) yielded compound O as white needles (250 mg, m.p. 288°) and compound P as white crystalline solid (25 mg, m.p. 226°). These two were characterized as oleanolic acid and olean-(13)18-ene-2β,3β-diol, respectively.

β-amin (8), compound L

M.P. 157-158°
IR $\delta_{\text{KBr max}}$ cm$^{-1}$: 3450, 2985, 1595, 1450, 1385, 1020, 995, 885.

NMR $\delta_{\text{TMS CDCl}_3}$ (60 MHz): 0.74 (s, 3H, C(29)-CH$_3$),
0.76 (s, 3H, C(24)-CH$_3$),
0.78 (s, 3H, C(28)-CH$_3$),
0.80 (s, 3H, C(25)-CH$_3$),
0.90 (d, 6H, C(23)-CH$_3$, C(30)-CH$_3$),
1.0 (s, 3H, C(26)-CH$_3$),
1.18 (s, 3H, C(27)-CH$_3$),
4.64 (bm, 1H, C(3)-H),
5.24 (br, s, 1H, Vinylic -H),
3.31 (s, 1H, C(3)-OH, D$_2$O exchangeable).

MS m/z: 426 (M$^+$), 411 (M$^+$-15), 393 (M$^+$-CH$_3$-H$_2$O),
218 (100%), 208, 207, 189 and 177.

**Acetylation of $\beta$-amyrin:**

Compound L (75 mg) was dissolved in pyridine (2 ml) and an equal volume of acetic anhydride was added to it. The mixture was refluxed on oil bath (100$^\circ$) for four hours. After usual work up the acetylated product was purified by column chromatography over silica gel using pet. ether - benzene (70 : 30) to give a white crystalline product (50 mg).

M.P. 106-107$^\circ$

IR $\delta_{\text{KBr max}}$ cm$^{-1}$: 2985, 1730, 1595, 1370, 1380, 880.
NMR δ TMS<sub>CDCl<sub>3</sub></sub> (60 MHz): 0.73 (s, 3H), 0.76 (s, 3H), 0.78 (s, 3H), 0.80 (s, 3H), 0.91 (d, 6H), 1.0 (s, 3H), 1.19 (s, 3H), 2.06 (s, 3H, C(3)-OAc), 4.63 (1H, C(3)-H).

Lupeol (9), (compound M):

M.P. 211°

IR υ<sub>KBr</sub> cm<sup>-1</sup> max: 3450, 2985, 1639, 1385, 875.

NMR δ TMS<sub>CDCl<sub>3</sub></sub> (100 MHz): 0.74, 0.78, 0.80, 0.83, 1.00 (s each, 18H, 6 x CH₃), 1.63 (s, 3H, vinylic methyl), 3.19 (d, 1H, carbinol -H), 4.52, 4.64 (d, 2H, =CH₂).

MS m/z: 426 (M<sup>+</sup>), 218 (100%), 220, 189, 207.

Acetylation of Lupeol:

Lupeol (20 mg) was acetylated with Ac<sub>2</sub>O/Py according to usual procedure. After work up the product obtained was crystallized from methanol as white needles M₁ (15 mg).

M.P. 204°

IR υ<sub>KBr</sub> cm<sup>-1</sup> max: 2985, 1739, 1639, 1385, 1250, 878.

NMR δ TMS<sub>CDCl<sub>3</sub></sub> (100 MHz): 0.75 - 1.00 (s each, 18H, 6 Me's), 1.68 (s, 3H, vinylic methyl), 2.00 (s, 3H, C(3)-OAc), 4.5 (d, 1H, C(3)-H).
Anagadiol (diacetate) (10), (compound N):

M.P. 250-251°

IR v KBr cm⁻¹ : 2985, 1745, 1381, 1258, 1053, 970.

NMR δ TMS CDCl₃ (100 MHz): 0.74–1.14 (s, 24H, 8 Me's),
  1.48 (d, 1H, vinyl-H),
  2.00 & 2.06 (s, 6H, 2 x OAc),
  4.60 (q, 1H, C(1)-H),
  4.56 (q, 1H, C(3)-H).

MS m/z : 526 (M⁺), 205, 204, 190, 189, 177.

Oleanolic acid (11), (compound 0):

M.P. 288°

IR v KBr cm⁻¹ : 3450, 1705, 1645, 1389.

NMR δ TMS CD₃OD (100 MHz): 1.20, 1.10, 0.97, 0.95, 0.92, 0.84,
  0.75 (s, 21H, 7 Me's), 5.22 (t, 1H,
  J = 2 Hz, C=CH),
  3.22 (m, J = 4 Hz, C(3)-OH,
  D₂O exchangeable,
  2.51 (bs, 1H, D₂O exchangeable).

MS m/z : 456 (M⁺), 411 (M⁺-COOH), 248 (base peak),
  207, 203 (248-COOH), 202 (248-HCOOH),
  189 (207-H₂O).
Methylation of oleanolic acid:

Compound Q (25 mg) was methylated with excess of diazomethane. After usual work up, the resultant white product Q was crystallized from MeOH (17 mg).

M.P. 196.5°

IR \(\nu_{\text{KBr}}\) cm\(^{-1}\): 1695, 1656, 1392.

NMR \(\delta\) TMS \(\text{CDCl}_3\) (100 MHz): 1.20, 1.15, 1.00, 0.93, 0.90, 0.84, 0.77 (s, 21H, 7 Me\(^3\)s), 5.21 (t, 1H, \(\gamma\) C=CH), 3.6 (s, 3H, \(-\text{COOCH}_3\)), 3.18 (dd, 1H, \(J = 9\) and \(4\) Hz), 2.05 (bs, 1H, \(D_2O\) exchangeable).

MS m/z: 470 (M\(^+\)), 262 (base peak).

Olean-(13)18-ene-2\(\beta,3\beta\)-diol (12), (compound P):

M.P. 226°

IR \(\nu_{\text{KBr}}\) cm\(^{-1}\): 3450, 2985, 1385.

NMR \(\delta\) TMS \(\text{CD}_{3}OH\) (100 MHz): 0.78, 0.83, 0.92, 0.99, 1.06, 1.12, 1.18 (s, 24H, 8 x Me\(^3\)s), 2.28 (bs, 2H, C(2)-OH, C(3)-OH), \(D_2O\) exchangeable), 3.41 (d, 1H, \(J = 7\) Hz, C(3)\(\alpha\)-H), 4.50 (d, 1H, C(2)\(\alpha\)-H).

MS m/s: 442 (M\(^+\)), 424 (M\(^+\)-18), 218, 205.
Acetylation of olean-(13)18-ene-2\(^{-},3\beta\)-diol:

Compound P (10 mg) was acetylated as per the procedure described earlier to yield a diacetate P\(_1\) (8 mg).

M.P. 114\(^\circ\)

IR \(\nu\) KBr cm\(^{-1}\) : 2985, 1725, 1385, 1255, 1053, 970.

NMR \(\delta\) TMS \(\text{CDCl}_3\) (100 MHz): 0.79, 0.84, 0.96, 1.10, 1.18 (s, 24H, 8 x Me's),
4.50 (d, 1H, \(J = 7\) Hz, C(3)\(\alpha\)-H),
5.25 (d, 1H, \(J = 3\) Hz, C(2)\(\alpha\)-H),
1.98 & 2.05 (s, 6H, 2 x OAc).

MS \(m/z\) : 526 (M\(^+\)).
BIBLIOGRAPHY


