PART – I
INTRODUCTION

Oils and fats are not only the essential part of human and animal diet but also indispensable ingredients in various industries. Thus, the total demand of oils and fats has been increased in ever expanding of oleochemical industries. In comparison, the increase in production has been slower inspite of green revolution and improved seed quality. This has resulted in the gradual widening a gap between production and demand.

The seed oils containing unusual fatty acids are industrially important as, they are used in the protective coatings, plastics, urethane derivatives, surfactants, dispersants, cosmetics, plasticizers, lubricant additives, pharmaceuticals, polymers, soaps, detergents, textiles, and a variety of synthetic intermediates. The ethoxylated derivatives of seed oils containing hydroxy fatty acids are used as stabilizers of hydrophobic substances in industries such as perfumes and cosmetics e.g., castor oil. The polyethoxylated hydroxy fatty acids are non-ionic surfactants and are included in the formulations for cleaning clothes, dishes, hard surfaces, and metals and in textile processing1.
Seed oils containing epoxy fatty acids are of potential interest as stabilizers in plastic formulations and in the preparation of other long-chain compounds e.g., *Vernonia anthelmintica* seed oil. Seed oils containing keto fatty acids are commercially exploited in paints and varnish industries e.g., *Licania rigida* seed oil. Seed oils containing cyclopropenoid fatty acids have attracted much attention owing to their biological effects in animals and co-carcinogenic properties e.g., *Sterculia foetida* seed oil.

The basic objective of the present investigation is to carry out a phytochemical survey and chemical screening of oilseeds of forest origin. The chemical screening of oilseeds will reveal the natural sources of unusual fatty acids along with the other normal fatty acids of their pharmacological and industrial importance. In recent years, the structure and chemical transformation studies of major fatty acids and their related compounds have yielded very useful organic intermediates and compounds of medicinal and industrial importance thus creating avenues for sources of oleochemicals or agrochemicals. This type of study will be extremely useful for developing uses of indigenous oils as the starting materials for organic chemicals much needed in various pharmaceutical and oleochemical industries.

The naturally occurring major fatty acids are versatile group of chemicals that play a vital role in oleochemical industry. There is wide potential of fatty acids derived from minor oilseeds rich in specific kind of fatty acids. Lately, new and
interesting unusual fatty acids present in high concentration of certain oils are being exploited for the commercial use\(^2\).

The extensive compositional studies on oil-bearing seeds have been reported in the literature covering a broad spectrum of plant kingdom. The oil-bearing plants are classified into two groups viz., major-oilseeds and minor-oilseeds. The major-oilseeds are those, which due to their favourable agronomic prospects are widely cultivated for edible oils. The minor-oilseeds, although useful sources for edible oils which belong to less cultivated category of species and serves as non-traditional sources of vegetable oils. The abundance of these wild species rich in oil content demands their agronomic evaluation as prospective oilseed crop.

The naturally occurring fatty acids are chiefly straight chain compounds containing even and odd number of carbon atoms and are conveniently divided into three groups -

1) Saturated fatty acids  

2) Unsaturated fatty acids and

3) Unusual fatty acids.

**Saturated fatty acids**

These saturated fatty acids occurring in oils and fats are listed in Table. Short-chain acids \((C_4-C_{10})\) are present in milk fats, the \(C_{12}-C_{24}\) acids in seed fats and animal fats, and the long-chain acids (upto \(C_{38}\)) in waxes.
<table>
<thead>
<tr>
<th>Chain length</th>
<th>Trivial name</th>
<th>Systematic name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Formic</td>
<td>Methanoic</td>
</tr>
<tr>
<td>2</td>
<td>Acetic</td>
<td>Ethanoic</td>
</tr>
<tr>
<td>3</td>
<td>Propionic</td>
<td>Propanoic</td>
</tr>
<tr>
<td>4</td>
<td>Butyric</td>
<td>Butanoic</td>
</tr>
<tr>
<td>5</td>
<td>Valeric</td>
<td>Pentanoic</td>
</tr>
<tr>
<td>6</td>
<td>Caproic</td>
<td>Hexanoic</td>
</tr>
<tr>
<td>7</td>
<td>Enanthic</td>
<td>Heptanoic</td>
</tr>
<tr>
<td>8</td>
<td>Caprylic</td>
<td>Octanoic</td>
</tr>
<tr>
<td>9</td>
<td>Pelargonic</td>
<td>Nonanoic</td>
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<tr>
<td>10</td>
<td>Capric</td>
<td>Decanoic</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>Hendecanoic</td>
</tr>
<tr>
<td>12</td>
<td>Lauric</td>
<td>Dodecanoic</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
<td>Tridecanoic</td>
</tr>
<tr>
<td>14</td>
<td>Myristic</td>
<td>Tetradecanoic</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>Pentadecanoic</td>
</tr>
<tr>
<td>16</td>
<td>Palmitic</td>
<td>Hexadecanoic</td>
</tr>
<tr>
<td>17</td>
<td>Margaric</td>
<td>Heptadecanoic</td>
</tr>
<tr>
<td>18</td>
<td>Stearic</td>
<td>Octadecanoic</td>
</tr>
<tr>
<td>19</td>
<td>-</td>
<td>Nonadecanoic</td>
</tr>
<tr>
<td>20</td>
<td>Arachidic</td>
<td>Eicosanoic</td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>Heneicosanoic</td>
</tr>
<tr>
<td>22</td>
<td>Behenic</td>
<td>Docosanoic</td>
</tr>
<tr>
<td>23</td>
<td>-</td>
<td>Tricosanoic</td>
</tr>
<tr>
<td>24</td>
<td>Lignoceric</td>
<td>Tetracosanoic</td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>Pentacosanoic</td>
</tr>
<tr>
<td>26</td>
<td>Cerotic</td>
<td>Hexacosanoic</td>
</tr>
<tr>
<td>27</td>
<td>-</td>
<td>Heptacosanoic</td>
</tr>
<tr>
<td>28</td>
<td>Montanic</td>
<td>Octacosanoic</td>
</tr>
<tr>
<td>29</td>
<td>-</td>
<td>Nonacosanoic</td>
</tr>
<tr>
<td>30</td>
<td>Melissic</td>
<td>Triacontanoic</td>
</tr>
</tbody>
</table>
Unsaturated fatty acids

These unsaturated fatty acids occur naturally and are classified as fatty acids with one double bond and fatty acids with more than one double bond and are listed in Table.

<table>
<thead>
<tr>
<th>Chain length</th>
<th>Trivial name</th>
<th>Systematic name</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{10} : 1</td>
<td>Obtusilic</td>
<td>cis-4-Decenoic</td>
</tr>
<tr>
<td>C_{10} : 1</td>
<td>Caproleic</td>
<td>cis-9-Decenoic</td>
</tr>
<tr>
<td>C_{10} : 1</td>
<td>Linderic</td>
<td>cis-4-Dodecenoic</td>
</tr>
<tr>
<td>C_{12} : 1</td>
<td>Lauroleic</td>
<td>cis-9-Dodecenoic</td>
</tr>
<tr>
<td>C_{14} : 1</td>
<td>Tsuzic</td>
<td>cis-4-Tetradecenoic</td>
</tr>
<tr>
<td>C_{14} : 1</td>
<td>Physteric</td>
<td>cis-5-Tetradecenoic</td>
</tr>
<tr>
<td>C_{14} : 1</td>
<td>Myristoleic</td>
<td>cis-9-Tetradecenoic</td>
</tr>
<tr>
<td>C_{16} : 1</td>
<td>Palmitoleic</td>
<td>cis-9-Hexadecenoic</td>
</tr>
<tr>
<td>C_{17} : 1</td>
<td>-</td>
<td>cis-9-Heptadecenoic</td>
</tr>
<tr>
<td>C_{18} : 1</td>
<td>Petroselinic</td>
<td>cis-6-Octadecenoic</td>
</tr>
<tr>
<td>C_{18} : 1</td>
<td>Oleic</td>
<td>cis-9-Octadecenoic</td>
</tr>
<tr>
<td>C_{18} : 1</td>
<td>Elaidic</td>
<td>trans-9-Octadecenoic</td>
</tr>
<tr>
<td>C_{18} : 1</td>
<td>Vaccenic</td>
<td>trans-11-Octadecenoic</td>
</tr>
<tr>
<td>C_{18} : 1</td>
<td>Vaccenic</td>
<td>cis-11-Octadecenoic</td>
</tr>
<tr>
<td>C_{18} : 1</td>
<td>-</td>
<td>cis-5-Eicosenoic</td>
</tr>
<tr>
<td>C_{18} : 1</td>
<td>Gadoleic</td>
<td>cis-9-Eicosenoic</td>
</tr>
<tr>
<td>C_{20} : 1</td>
<td>-</td>
<td>cis-11-Eicosenoic</td>
</tr>
<tr>
<td>C_{22} : 1</td>
<td>Cetoleic</td>
<td>cis-11-Docosenoic</td>
</tr>
<tr>
<td>C_{22} : 1</td>
<td>Erucic</td>
<td>cis-13-Docosenoic</td>
</tr>
<tr>
<td>C_{24} : 1</td>
<td>Selacholeic</td>
<td>cis-15-Tetracosenoic</td>
</tr>
<tr>
<td>C_{26} : 1</td>
<td>Ximenic</td>
<td>cis-17-Hexacosenoic</td>
</tr>
<tr>
<td>C_{30} : 1</td>
<td>Lumequeic</td>
<td>cis-21-Triacontenoic</td>
</tr>
</tbody>
</table>
### Fatty acids with more than one double bond

<table>
<thead>
<tr>
<th>Chain length</th>
<th>Trivial name</th>
<th>Systematic name</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{18})(</em>{2})</td>
<td>Linoleic</td>
<td>(cis,cis-9,12)-Octadecadienoic</td>
</tr>
<tr>
<td>C(<em>{18})(</em>{3})</td>
<td>Linolenic</td>
<td>(cis,cis,cis-9,12,15)-Octadecatrienoic</td>
</tr>
<tr>
<td>C(<em>{18})(</em>{3})</td>
<td>(\gamma) - Linolenic</td>
<td>(cis,cis,cis-6,9,12)-Octadecatrienoic</td>
</tr>
<tr>
<td>C(<em>{18})(</em>{3})</td>
<td>(\alpha) - Eleostearic</td>
<td>(cis,trans,trans-9,11,13)-Octadecatrienoic</td>
</tr>
<tr>
<td>C(<em>{18})(</em>{3})</td>
<td>(\beta) - Eleostearic</td>
<td>(trans,trans,trans-9,11,13)-Octadecatrienoic</td>
</tr>
<tr>
<td>C(<em>{18})(</em>{4})</td>
<td>Parinaric</td>
<td>(cis,trans,trans,cis-9,11,13,15)-Octadecatetraenoic</td>
</tr>
<tr>
<td>C(<em>{20})(</em>{4})</td>
<td>Arachidonic</td>
<td>(cis,cis,cis-5,8,11,14)-Eicosatetraenoic</td>
</tr>
<tr>
<td>C(<em>{22})(</em>{5})</td>
<td>Clupanodonic</td>
<td>(4,8,12,15,19)-Docosa-pentaenoic</td>
</tr>
</tbody>
</table>

### Unusual fatty acids

The new and interesting unusual fatty acids present in high concentration in certain seed oils are being exploited for the industrial utilization and also for medicinal purpose. These fatty acids of unusual structures are highly important to the production of oleochemicals.
Hydroxy fatty acids

Hydroxy fatty acids have a wide spread occurrence in nature\textsuperscript{3,4}. In vegetable oils, they range mostly from \( C_{16} \) to \( C_{24} \) chain length and may be saturated, unsaturated or contain other functional groups. Ricinoleic acid (1) is known to occur in \textit{Ricinus communis} (castor oil) seed oil, which has been the sole commercial source of hydroxy fatty acid. The occurrence of this acid has been reported by several workers\textsuperscript{5,6} in \textit{Hiptage madablota} seed oil. However, the presence of ricinoleic acid in appreciable amounts has also been reported in several other seed oils\textsuperscript{7-19}.

\[
\begin{align*}
\text{OH} \\
\text{CH}_3\text{(CH}_2\text{)}_5\text{-CH-CH}_2\text{-CH=CH-(CH}_2\text{)}_7\text{-COOH} \\
(1) \ 12\text{-Hydroxyoctadec-cis-9-enoic acid}
\end{align*}
\]

Isoricinoleic acid (2) is known to occur in four genera of Apocynaceae plant family viz., \textit{Hollarrheena}\textsuperscript{20}, \textit{Nerium}\textsuperscript{20}, \textit{Strophanhus}\textsuperscript{21} and \textit{Wrightia}\textsuperscript{22}. This isoricinoleic acid has been also reported in the other seed oils\textsuperscript{23-26}. A new isomer (3) has been reported in the seed oil of \textit{Plantago major}\textsuperscript{27}.

\[
\begin{align*}
\text{OH} \\
\text{CH}_3\text{(CH}_2\text{)}_4\text{-CH=CH-(CH}_2\text{)}_5\text{-CH-(CH}_2\text{)}_7\text{-COOH} \\
(2) \ 9\text{-Hydroxyoctadec-cis-12-enoic acid}
\end{align*}
\]

\[
\begin{align*}
\text{OH} \\
\text{CH}_3\text{(CH}_2\text{)}_6\text{-CH=CH-CH}_2\text{-CH-(CH}_2\text{)}_7\text{-COOH} \\
(3) \ 9\text{-Hydroxyoctadec-cis-11-enoic acid}
\end{align*}
\]
Bohannon and Kleiman\textsuperscript{28} reported three $\alpha$-hydroxy fatty acids, viz., $\alpha$-hydroxyoleic acid (4), $\alpha$-hydroxylinoleic acid (5) and $\alpha$-hydroxylinolenic acid (6) in \textit{Salvia nilotic\textit{s}} seed oil. Smith and Wolff\textsuperscript{29} reported of $\alpha$-hydroxylinolenic acid (6) in \textit{Thymus vulgar\textit{s}} seed oil.

\begin{center}
\begin{tabular}{c}
\centering
\begin{tikzpicture}
\node at (0,0) {$\text{CH}_3\cdot(\text{CH}_2)_7\cdot\text{CH}=\text{CH}\cdot(\text{CH}_2)_6\cdot\text{CH}\cdot\text{COOH}$};
\end{tikzpicture}
\end{tabular}
\end{center}

\textbf{(4) $\alpha$-Hydroxyoleic acid}

\begin{center}
\begin{tabular}{c}
\centering
\begin{tikzpicture}
\node at (0,0) {$\text{CH}_3\cdot(\text{CH}_2)_3\cdot(\text{CH}_2\cdot\text{CH}=\text{CH})_2\cdot(\text{CH}_2)_6\cdot\text{CH}\cdot\text{COOH}$};
\end{tikzpicture}
\end{tabular}
\end{center}

\textbf{(5) $\alpha$-Hydroxylinoleic acid}

\begin{center}
\begin{tabular}{c}
\centering
\begin{tikzpicture}
\node at (0,0) {$\text{CH}_3\cdot(\text{CH}_2\cdot\text{CH}=\text{CH})_3\cdot(\text{CH}_2)_6\cdot\text{CH}\cdot\text{COOH}$};
\end{tikzpicture}
\end{tabular}
\end{center}

\textbf{(6) $\alpha$-Hydroxylinolenic acid}

Mikolajczak et al.,\textsuperscript{30} have reported twelve species of genera \textit{Lesquerella} which contain Lesquirolic acid (7). Plattner et al.,\textsuperscript{31} have reported the same acid (7) and a trace of new hydroxy fatty acid (8) in the seed oil of \textit{Heliophila amplexicaulis}. Smith et al.,\textsuperscript{32} have reported 9-hydroxy-trans-10, trans-12-octadecadienoic (Dimorphecolic) acid (9) in the seed oil of \textit{Dimorphotheca aurant\textit{ica}}. Morris et al.,\textsuperscript{33} observed two new hydroxy fatty acids along with dimorphecolic acid in Dimorphotheca seed oil. They characterized these acids as 9-hydroxy-trans-10, \textit{cis}-12-octadecadienoic acid (10) and 13-hydroxy-cis-9, \textit{trans}-11-octadecadienoic acid (11). This acid is isomeric with dimorphecolic acid.
Badami and Morris\textsuperscript{34} isolated another hydroxy fatty acid (12) in \textit{Calendula officinalis} seed oil and this acid is also geometrically isomeric with the dimorphecolic acid. Smith et al.,\textsuperscript{35} have reported densipolic acid (13) in \textit{Lesquerella densipila} seed oil. Kleiman et al.,\textsuperscript{36} reported Auricolic acid (14).
The seed oil of *Mallotus philippinensis*\(^{37,38}\) contains Kamlolenic acid and has been characterized as a 18-hydroxy-octadeca-cis-9, *trans*-11, *trans*-13-trienoic acid (15). Hanseen\(^{39}\) reported new hydroxy acid (16) in the seed oil of *Coriaria myristifolia* and named as Coriolic acid.

\[
\text{OH} \\
\text{CH}_3\text{-CH}_2\text{-CH=CH-(CH}_2\text{)}_2\text{-CH-CH}_2\text{-CH=CH-(CH}_2\text{)}_2\text{-COOH}
\]

(15) 18-Hydroxyoctadeca-cis-9, *trans*-11, *trans*-13-trienoic acid

Osman and co-workers have reported two new hydroxy fatty acids (17) and (18) in *Mirabilis jalapa*\(^{40}\) and *Blepharis sindica*\(^{41}\) seed oils respectively.

\[
\text{OH} \\
\text{CH}_3\text{-CH}_2\text{-CH=CH-(CH}_2\text{)}_2\text{-CH-CH}=\text{CH-CH}=(\text{CH}_2\text{)}_2\text{-CH}-(\text{CH}_2\text{)}_6\text{-COOH}
\]

(17) 8-Hydroxyoctadeca-cis-11, *cis*-14-dienoic acid

\[
\text{OH} \\
\text{CH}_3\text{-CH}_2\text{-CH}-(\text{CH}_2\text{)}_2\text{-COOH}
\]

(18) 9-Hydroxydodecanoic acid
Cardamine impatiens\textsuperscript{42} seed oil contains four long-chain vicinal dihydroxy fatty acids (19-22). Badami and Kudari\textsuperscript{43} reported the same dihydroxy acid (19) in Feronia elephantum seed oil. Ahmad and co-workers\textsuperscript{44} also reported dihydroxy acid (23) in Mucuna puriens seed oil.

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {OH OH} ;
\node (b) at (1,0) {\text{CH}_3(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_7\text{-COOH}} ;
\node (c) at (0,-1) {9,10-Dihydroxyoctadecanoic acid} ;
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {OH OH} ;
\node (b) at (1,0) {\text{CH}_3(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_9\text{-COOH}} ;
\node (c) at (0,-1) {11,12-Dihydroxyeicosanoic acid} ;
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {OH OH} ;
\node (b) at (1,0) {\text{CH}_3(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_{11}\text{-COOH}} ;
\node (c) at (0,-1) {13,14-Dihydroxydocosanoic acid} ;
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {OH OH} ;
\node (b) at (1,0) {\text{CH}_3(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_{13}\text{-COOH}} ;
\node (c) at (0,-1) {15,16-Dihydroxytetraicosanoic acid} ;
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {OH OH} ;
\node (b) at (1,0) {\text{CH}_3(\text{CH}_2)_{14}-\text{CH-CH-CH=CH-(CH}_2)_7\text{-COOH}} ;
\node (c) at (0,-1) {12, 13-Dihydroxyoleic acid} ;
\end{tikzpicture}
\end{center}

Davis reported the non-vicinal 9, 14-dihydroxy-10, 12-octadecadienoic acid (24) in Aleurites fordii\textsuperscript{45} seed oil (tung oil). Recently a new saturated dihydroxy acid (25) has been reported by Osman and co-workers in the seed oil of Peganum harmala\textsuperscript{46}. The seed oil of Baliospermum axillare\textsuperscript{47} contains a non-vicinal dihydroxy mono-unsaturated acid (26) as Axillarenic acid.
Mikolajczak and Smith isolated two optically active tri-hydroxy fatty acids (27 and 28) from *Chamaepeuce afr* seed oil.

Epoxy fatty acids

The epoxy fatty acids may be regarded as the derivatives of oleic, linoleic, linolenic and other unsaturated fatty acids, in which one of the double bond is epoxidised through metabolism. The seed oils rich in epoxy acids are of potential interest as stabilizers in plastic formulations and in the preparation of other long-chain compounds.
Gunstone reported vemolic acid (29) for the first time in *Vernonia anthelmintica* seed oil. The considerable amount of vemolic acid has also been reported in several other seed oils.

\[
\text{CH}_3(\text{CH}_2)_4\text{CH}==\text{CH}-(\text{CH}_2)_7\text{COOH} \quad (29) \text{cis-12, 13-Epoxyoctadec-cis-9-enoic acid}
\]

Smith et al.,\textsuperscript{71} reported an isomer of vemolic acid in *Chrysanthemum coronarium* seed oil and named as coronaric acid (30). This coronaric acid is also found in the other seed oils.

\[
\text{CH}_3(\text{CH}_2)_4\text{CH}==\text{CH}-\text{CH}-(\text{CH}_2)_7\text{COOH} \quad (30) \text{cis-9,10-Epoxyoctadec-cis-12-enoic acid}
\]

*Vernonia roxburghii* seed oil contains vemolic acid along with a new epoxy acid (31). The seed oil of *Cephatocroton peuscheli*\textsuperscript{77} contains vemolic acid and also epoxy stearic acid (32), which is also reported in *Tragopogon porrifolius*\textsuperscript{78} and *Shorea robusta* seed oils.

\[
\text{CH}_3(\text{CH}_2)_6\text{CH}==\text{CH}-(\text{CH}_2)_7\text{COOH} \quad (31) \text{cis-3, 4-Epoxy-cis-11-octadecenoic acid}
\]

\[
\text{CH}_3(\text{CH}_2)_7\text{CH}==\text{CH}-(\text{CH}_2)_7\text{COOH} \quad (32) \text{cis-9, 10-Epoxyoctadecanoic acid}
\]
Ulchenko et al., reported coronaric acid, vernolic acid and a trace of 9, 10-epoxystearic acid in the seed oil of *Artemisia absinthium*. Conacher and Gunstone reported coronaric acid, epoxy-octadecynoic acid and epoxystearic acid in *Helichrysum bracteatum* seed oil. Spencer reported vernolic acid and a trace of epoxystearate, and two previously unknown acids (33) and (34) in *Crepis conyzaefolia* seed oil.

\[
\text{CH}_3-(\text{CH}_2)_4-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_4\text{-COOH} \\
(33) (+) \text{cis-12, 13-Epoxyoctadec-trans-6, cis-9-dienoic acid}
\]

\[
\text{CH}_3-(\text{CH}_2)_4-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_4\text{-COOH} \\
(34) \text{cis-12, 13-Epoxyoctadec-cis-6, cis-9-dienoic acid}
\]

Kleiman, and others reported new epoxy acid (35) in the seed oil of *Stenachaenium macrocephalum* along with coronaric and epoxystearic acids. Gunstone and Morris reported 15,16-epoxylinoleic acid (36) in *Camelina sativa* seed oil.

\[
\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}-(\text{CH}_2)_4\text{-CH=CH-CH}_2\text{-COOH} \\
(35) 9, 10-Epoxy-trans-3, cis-12-octadecadienoic acid
\]

\[
\text{CH}_3\text{-CH}_2\text{-CH-CH}_2\text{-CH=CH-CH}_2\text{-CH=CH-(CH}_2)_7\text{-COOH} \\
(36) 15, 16-Epoxylinoleic acid
\]
A C-20 homologue of vernolic acid has been reported in *Alchornea cordifolia* seed oil by Kleiman and others\textsuperscript{86}. This new epoxy fatty acid has been named as Alchornic acid (37).

\[
\text{CH}_3\text{-}(\text{CH}_2)_4\text{-}\text{CH}\text{-CH}\text{-CH}_2\text{-CH=CH-}(\text{CH}_2)_9\text{-COOH}
\]

(37) (+) *cis*-14, 15-*Epoxy-cis*-11-eicosenoic acid

**Keto fatty acids**

The occurrence of keto fatty acids in natural seed oils is rare\textsuperscript{87-88}, although naturally occurring long-chain hydroxy fatty acids are widely distributed in plants\textsuperscript{89-90}. *Licania rigida*\textsuperscript{91} which has attained a commercial status as it contains an enormous amount of 4-keto-eleostearic acid and named as Licanic acid (38). This acid is popular for its drying properties and hence it is used in paints and varnish industries.

*Dimorphotheca sinuata*\textsuperscript{92} seed oil contains a minor amount of keto fatty acid (39). The two keto fatty acids (38) and (40) have been reported by Gunstone and Subbarao from *Chrysobalanus icaco*\textsuperscript{93} seed oil. Kaufmann and co-workers\textsuperscript{94} have reported \(\alpha\)-Licanic acid in *Parinarium annamense* seed oil. Later Philips and co-workers\textsuperscript{95} reported two new keto fatty acids (41) and (42) in the seed oil of *Monnina emerginata*.

\[
\text{CH}_3\text{-}(\text{CH}_2)_3\text{-CH}=\text{CH-CH=CH-CH=CH-}(\text{CH}_2)_4\text{-C-}(\text{CH}_2)_2\text{-COOH}
\]

(38) 4-Keto-octadeca-*cis*-9, *trans*-11, *trans*-13-trienoic acid
Three new and unusually exceptional long-chain keto fatty acids (43), (44) and (45) have been reported by Smith in the seed oil of *Cuspidaria pterocarpa.*
Gupta and co-workers\textsuperscript{97} have reported the occurrence of three new saturated keto fatty acids (46), (47) and (48) in \textit{Costus specious} seed oil.

\[ \text{O} \]
\[ \begin{array}{c}
\text{CH}_3(\text{CH}_2)_7\text{-CH}_2\text{-CH}_2\text{-}(\text{CH}_2)_{11}\text{-COOH}
\end{array} \]
\begin{align*}
(46) & \quad \text{14-Keto-tricosanoic acid}
\end{align*}

\[ \text{O} \]
\[ \begin{array}{c}
\text{CH}_3(\text{CH}_2)_{11}\text{-CH}_2\text{-CH}_2\text{-}(\text{CH}_2)_{11}\text{-COOH}
\end{array} \]
\begin{align*}
(47) & \quad \text{14-Keto-heptacosanoic acid}
\end{align*}

\[ \text{O} \]
\[ \begin{array}{c}
\text{CH}_3(\text{CH}_2)_{11}\text{-CH}_2\text{-CH}_2\text{-}(\text{CH}_2)_{12}\text{-COOH}
\end{array} \]
\begin{align*}
(48) & \quad \text{15-Keto-octacosanoic acid}
\end{align*}

Rukmini\textsuperscript{98} reported an unusual keto fatty acid (49) in the seed oil of \textit{Argemone mexicana} and designated as Argemonic acid. Lata Mahato\textsuperscript{99} reported two keto fatty acids (50) and (51). Gunstone\textsuperscript{100} reported three-long-chain keto fatty acids (50), (52) and (53). The new keto fatty acid (54) is reported in \textit{Plantago ovata}\textsuperscript{101} and in \textit{Cryptolepis buchmani}\textsuperscript{102} seed oils.

\[ \text{O} \quad \text{OH} \]
\[ \begin{array}{c}
\text{CH}_3(\text{CH}_2)_{18}\text{-C-(CH}_2)_2\text{-C-(CH}_2)_4\text{-COOH}
\end{array} \]
\begin{align*}
(49) & \quad (+)-6-Hydroxy-6-methyl-9-keto-octacosenoic acid
\end{align*}

\[ \text{O} \]
\[ \begin{array}{c}
\text{CH}_3(\text{CH}_2)_{18}\text{-C-(CH}_2)_9\text{-COOH}
\end{array} \]
\begin{align*}
(50) & \quad \text{11-Keto-triacontanoic acid}
\end{align*}
The other four new keto fatty acids (55), (56), (57) and (58) have been reported in *Lagerstroemia speciosa*<sup>103</sup>, *Gardenia lucida*<sup>104</sup>, *Cassia absus*<sup>105</sup> and *Diospyros melanoxylon*<sup>106</sup> seed oils, respectively.
Cyclopropane fatty acids

Lactobacillic acid (59) was the first cyclopropane fatty acid to be found in nature. The occurrence of a C\textsubscript{17} cyclopropane fatty acid (60) was reported in the lipids of the bacterium \textit{Escheria coli}\textsuperscript{107-109}.

\[
\text{CH}_3-(\text{CH}_2)_6-\text{CH-CH-(CH}_2)_6\text{COOH}
\]

(59) Lactobacillic acid

\[
\text{CH}_3-(\text{CH}_2)_5-\text{CH-CH-(CH}_2)_7\text{COOH}
\]

(60) \textit{cis}-9, 10-Methylene-hexadecanoic acid
[8-(2-Hexylcyclopropyl)-octanoic acid]

Several authors\textsuperscript{110-112} have reported dihydromalvalic acid (61) and dihydrosterculic acid (62) in the seed oils of Anacardiaceae, Celastraceae, Sapotaceae, Sapindaceae, Elaeocarpaceae plant families and plant order Malvales\textsuperscript{113}. The dihydrosterculic acid is a major constituent in the seed oil of \textit{Dimocarpus longans}\textsuperscript{114}.

\[
\text{CH}_3-(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_6\text{COOH}
\]

(61) Dihydromalvalic acid
\textit{cis}-8, 9-Methylene-heptadecanoic acid
[7-(2-Octylcyclopropyl) heptanoic acid]

\[
\text{CH}_3-(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_7\text{COOH}
\]

(62) Dihydrosterculic acid
\textit{cis}-9, 10-Methylene-octadecanoic acid
[8-(2-Octylcyclopropyl) octanoic acid].
Cyclopropene fatty acids

Nunn has isolated the malvalic acid (63) and sterculic acid (64) as the cyclopropene fatty acids from *Sterculia foetida* seed oil. Morris and Hall have reported D-2-hydroxysterculic acid (65) in the *Pachira insignis* and *Bombacopsis glabra* seed oils. Recently, cyclopropene fatty acids have also been reported in several seed oils. These cyclopropene fatty acids have significant biological effects on animals and possess co-carcinogenic properties.

\[
\text{CH}_3-(\text{CH}_2)_7\text{C}==\text{C}-(\text{CH}_2)_6\text{COOH}
\]

(63) Malvalic acid

[7-(2-Octylcyclopropen-1-yl) heptanoic acid]

\[
\text{CH}_3-(\text{CH}_2)_7\text{C}==\text{C}-(\text{CH}_2)_7\text{COOH}
\]

(64) Sterculic acid

[8-(2-Octylcyclopropene-1-yl)-octanoic acid]

\[
\text{CH}_3-(\text{CH}_2)_7\text{C}==\text{C}-(\text{CH}_2)_6\text{CH-COOH}
\]

(65) D-2-Hydroxysterculic acid.

Cyclopentenoid fatty acids

The fixed oils extracted from the seeds of most members of Flacourtiaceae plant family are extensively used in the treatment of leprosy and other cutaneous diseases. These oils contain the following types of unsaturated cyclic fatty acids...
(66 - 72). Spencer and Mangold\textsuperscript{129} examined the seed oils of \textit{Calanchoba echinata} and \textit{Hydnocarpus anthelmintica} and reported several new cyclopentyl fatty acids.

\[ \text{CH-(CH}_2\text{)}_{10}\text{-COOH} \]

(66) [11-(2-Cyclopentene-1-yl) undecanoic acid]

(\text{Hydnocarpic acid})

\[ \text{CH-(CH}_2\text{)}_{12}\text{-COOH} \]

(67) [13-(2-Cyclopentene-1-yl) tridecanoic acid]

(\text{Chaulmoogric acid})

\[ \text{CH-(CH}_2\text{)}_{18}\text{-CH=CH-(CH}_2\text{)}_4\text{-COOH} \]

(68) [13-(2-Cyclopenten-1-yl) tridec-6-enoic acid]

(\text{Gorlic acid})

\[ \text{CH-(CH}_2\text{)}_{14}\text{-COOH} \]

(69) 15-(2-Cyclopenten-1-yl) pentadecanoic acid

(\text{Hormelic acid})

\[ \text{CH-(CH}_2\text{)}_6\text{-CH=CH-(CH}_2\text{)}_6\text{-COOH} \]

(70) 15-(2-Cyclopenten-1-yl) pentadec-8-enoic acid

(\text{Oncobic acid})

\[ \text{CH-(CH}_2\text{)}_3\text{-CH=CH-(CH}_2\text{)}_7\text{-COOH} \]

(71) 13-(2-Cyclopenten-1-yl) tridec-9-enoic acid

\[ \text{CH-(CH}_2\text{)}_6\text{-CH=CH-(CH}_2\text{)}_4\text{-COOH} \]

(72) 11-(2-Cyclopenten-1-yl) undec-6-enoic acid

(\text{Manoaic acid})
Acetylenic fatty acids

The occurrence of triple bonds in several fatty acids from vegetable seed oils of Simarubaceae plant family are reported. The simplest example is “Tariric acid” which is structurally related to petroselenic acid. Arnaud\textsuperscript{130} first reported tariric acid (73) in *Picramnia tariri* seed oil. Later, this tariric acid has been reported in the seed oils of *Picramnia linderiana*\textsuperscript{131}, *Picramnia sellowii*\textsuperscript{132} and *Picramnia sous*\textsuperscript{133}.

\[
\text{CH}_3-(\text{CH}_2)_{10}-\text{C}==\text{C}-(\text{CH}_2)_{4}-\text{COOH} \\
(73) \text{Octadec-6-ynoic acid}
\]

Pearl and others\textsuperscript{134} reported two acetylenic fatty acids (74) and (75) previously unknown in *Alvadora amorphoides* seed oil. Later, the crepenynic acetylenic fatty acid (76) has been reported in the seed oils of *Crepis foetida*\textsuperscript{135}, *Crepis* species\textsuperscript{136} and *Saussurea candicans*\textsuperscript{137}.

\[
\text{CH}_2=\text{CH}-(\text{CH}_2)_9-\text{C}==\text{C}-(\text{CH}_2)_4-\text{COOH} \\
(74) \text{Octadec-17-en-6-ynoic acid}
\]

\[
\text{CH}_3-(\text{CH}_2)_{12}-\text{C}==\text{C}-(\text{CH}_2)_4-\text{COOH} \\
(75) \text{6-Eicosynoic acid.}
\]

\[
\text{CH}_3-(\text{CH}_2)_4-\text{C}==\text{C}-\text{CH}_2-\text{CH}==\text{CH}-(\text{CH}_2)_7-\text{COOH} \\
(76) \text{cis-9-Octadecen-12-ynoic}
\]

Madurnath and Manjunath\textsuperscript{138,139} have reported Santalbic acid in the seed oil of *Santalum album*. This santalbic acid is identical with ximenynic acid, which has
been characterized as octadec-11-en-9-ynoic acid (77) by Gunstone and McGee\textsuperscript{140}. This ximenynic acid has been reported in the seed oils of \textit{Exocarpus cupressiformis} and \textit{Exocarpus strictus}\textsuperscript{141}. The root oils of these \textit{Exocarpus} plants and \textit{Ximenia americana}\textsuperscript{141} contain substantial amounts of \textit{trans}-13-octadecen-9, 11-diynoic acid (78). Hopikins and others\textsuperscript{142} have reported several acetylenic fatty acids (79 - 82) from Santalaceae plant family.

\begin{align*}
\text{CH}_3\text{-}(\text{CH}_2)_5\text{-CH=CH-C}==\text{C-(CH}_2)_7\text{-COOH} & \quad \text{(77) Octadec-11-en-9-dynoic acid} \\
\text{(Santalbic or Ximenynic acid)}
\end{align*}

\begin{align*}
\text{CH}_3\text{-}(\text{CH}_2)_3\text{-CH=CH-C}==\text{C-C==C-(CH}_2)_7\text{-COOH} & \quad \text{(78) Octadec-13-en-9, 11-diynoic acid} \\
\text{(Exocarpic acid)}
\end{align*}

\begin{align*}
\text{CH}_2\text{=CH-(CH}_2)_3\text{-CH=CH-C}==\text{C-(CH}_2)_7\text{-COOH} & \quad \text{(79) Octadeca-\textit{trans}-11, 17-dien-9-ynoic acid}
\end{align*}

\begin{align*}
\text{CH}_3\text{-}(\text{CH}_2)_7\text{-C==C-(CH}_2)_7\text{-COOH} & \quad \text{(80) Octadec-9-ynoic acid} \\
\text{(Stearolic acid)}
\end{align*}

\begin{align*}
\text{CH}_3\text{-}(\text{CH}_2)_5\text{-CH=CH-C}==\text{C-(CH}_2)_6\text{-COOH} & \quad \text{(81) Heptadec-10-en-8-ynoic acid} \\
\text{(Pyrulic acid)}
\end{align*}

\begin{align*}
\text{CH}_2\text{=CH-(CH}_2)_4\text{-CH=CH-C}==\text{C-CH-(CH}_2)_5\text{-COOH} & \quad \text{(82) 7-Hydroxyheptadeca-\textit{trans}-10, 16-dien-8-ynoic acid}
\end{align*}
The seed oils of *Ongokea gore* contain isanic acid (83). The isano oil contains isanic acid (84) and isanolic acid (85). When isano oil is heated above 200°C it explodes violently owing to the intensely fast thermal polymerization of these acetylenic acids.

\[
\text{CH}_2\text{=CH-(CH}_2)_4\text{CH=CH-C}==\text{C-}(\text{CH}_2)_7\text{-COOH} \\
\text{(83) Octadec-trans-11,17-dien-9-ynoic acid}
\]

\[
\text{CH}_2\text{=CH-(CH}_2)_4\text{C}==\text{C}==\text{C-}(\text{CH}_2)_7\text{-COOH} \\
\text{(84) Octadec-cis-17-en-9, 11-diynoic acid} \\
\text{(Isanic or Erythrogenic acid)}
\]

\[
\text{CH}_2\text{=CH-(CH}_2)_4\text{C}==\text{C}==\text{C-CH-(CH}_2)_6\text{-COOH} \\
\text{(85) 8-Hydroxyoctadec-17-en-9, 11-diynoic acid} \\
\text{(Isanolic acid).}
\]

The further research work on the seed oil of *Ongokea gore* is of both academic and commercial importance because it contains a large number of acetylenic fatty acids (86-93) four of which have hydroxyl substituents. Badami, Gunstone, Sealy and Morris published the most definitive characterization work on these acetylenic fatty acids.

\[
\text{CH}_2\text{-(CH}_2)_5\text{-CH=CH-C}==\text{C-}(\text{CH}_2)_7\text{-COOH} \\
\text{(86) Octadec-9-yn-11-eonic acid}
\]

\[
\text{CH}_3\text{-(CH}_2)_5\text{-C}==\text{C}==\text{C-}(\text{CH}_2)_7\text{-COOH} \\
\text{(87) Octadec-9-11-diynoic acid}
\]

\[
\text{CH}_3\text{-(CH}_2)_3\text{-CH=CH-C}==\text{C}==\text{C-}(\text{CH}_2)_7\text{-COOH} \\
\text{(88) Octadec-13-en-9, 11-diynoic acid}
\]
Miller and others\textsuperscript{153} re-investigated the isano oil and isolated four new oxygenated acetylenic fatty acids (94-97) in this seed oil. These structures have been determined by $^1$H NMR, $^{13}$C NMR and MS studies.
A monohydroxyenyne acid (98) has been reported in the seed oil of *Ximenia caffra*\(^{154}\). Hopkins and Chisolm\(^{155}\) reported octadec-trans-11-en-9, 11-diynoic acid (99) in the seed oil of *Buchleya distichophylla*. Powell and co-workers\(^{156,157}\) reported hydroxyacetylenic acid (100). Conacher and Gunstone\(^{158}\) reported epoxyacetylenic fatty acid (101) in *Helichrysum bracteatum* seed oil. Jeavens and Hopkins\(^{159}\) have discovered new sterculynic (102) in the seed oil of *Sterculia alata*.

\[
\text{CH}_2=\text{CH}-(\text{CH}_2)_3\text{C}==\text{C}\equiv\text{C}-\text{CH}-(\text{CH}_2)_6\text{COOH}
\]

(97) 8-Hydroxyoctadec-17-en-10, 12-diynoic acid

\[
\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}-\text{C}==\text{C}-\text{CH}-(\text{CH}_2)_6\text{COOH}
\]

(98) 8-Hydroxy-trans-11-octadec-9-ynoic acid

\[
\text{CH}_2=\text{CH}-(\text{CH}_2)_4\text{C}==\text{C}\equiv\text{C}-(\text{CH}_2)_7\text{COOH}
\]

(99) Octadec-trans-17-en-9, 11-diynoic acid

\[
\text{CH}_3(\text{CH}_2)_4\text{C}==\text{C}-\text{CH}=\text{CH}-\text{CH}-(\text{CH}_2)_7\text{COOH}
\]

(100) 9-Hydroxy-trans-octadec-10-en-12-ynoic acid

(Helenynolic acid)

\[
\text{CH}_3(\text{CH}_2)_4\text{C}==\text{C}-\text{CH}_2\text{CH}-(\text{CH}_2)_7\text{COOH}
\]

(101) Cis-9, 10-Epoxyoctadec-12-ynoic acid

\[
\text{HC}==\text{C}-(\text{CH}_2)_6\text{C}==\text{C}-(\text{CH}_2)_7\text{COOH}
\]

(102) 7-(2-Non-8'-ynylcyclopropene-1-yl) octanoic acid

(Sterculynic acid)
**Furanoid fatty acids**

The occurrence of furanoid fatty acids in commercial fish oils was reported by several workers\textsuperscript{160-164}. A minor source of furanoid fatty acid (103) was reported in *Exocarpus cupressiformis*\textsuperscript{165} seed oil.

\[
\text{CH}_3\text{-(CH}_2\text{)}_5\text{-} \backslash \text{-} \text{(CH}_2\text{)}_7\text{-COOH} \\
(103) \text{ 8-(5-Hexylfuryl-2-)octanoic acid}
\]

**Flouro fatty acids**

The seed oil of ratsbane, *Dichapetalum toxicarum* which is the most unusual of all fatty oils, which contains \(\omega\)-flourofatty acids. Peters et al., reported \(\omega\)-flourofatty acid (104) and a small of solid \(\omega\)-flouro-palmitic acid (105) from this seed oil\textsuperscript{166-168}.

\[
\text{F-CH}_2\text{-(CH}_2\text{)}_7\text{-CH}=\text{CH-(CH}_2\text{)}_7\text{-COOH} \\
(104) \text{ \(\omega\)-Flouro-oleic acid}
\]

\[
\text{F-CH}_2\text{-(CH}_2\text{)}_{14}\text{-COOH} \\
(105) \text{ \(\omega\)-Flouro-palmitic acid}
\]
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