CHAPTER - 1
NATURAL FATTY ACIDS, OLEOCHEMICALS AND PHARMACOLOGICAL ACTIVITY

INTRODUCTION

NATURAL FATTY ACIDS

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 seed oils have 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., Ricinus communis (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 processing.
Seed oils containing epoxy fatty acids are of potential interest as stabilizers in plastic formulations and in the preparation of other long-chain compounds\textsuperscript{3,3} e.g., *Vernonia anthelmintica* seed oil. Seed oils containing keto fatty acids are commercially exploited in paints and varnish industries\textsuperscript{4} e.g., *Licania rigida* seed oil. Seed oils containing cyclopropenoid fatty acids have attracted much attention owing to their biological effects in animals\textsuperscript{5-7} and co-carcinogenic properties\textsuperscript{8,9} e.g., *Sterculia foetida* seed oil. Thus, new and interesting unusual fatty acids present in high concentration of certain seed oils are being exploited for the commercial use\textsuperscript{10}.

The basic objective of the present investigation is to carry out a phytochemical survey and chemical screening of oilseeds of minor plants. The chemical screening of oilseeds will reveal the natural sources of unusual fatty acids along with the other normal fatty acids of their medicinal and industrial importance. In recent years, the structure and chemical transformation studies of unusual 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 fatty acids are chiefly straight chain compounds containing even and odd number of carbon atoms of unusual fatty acids along with other normal fatty acids.

**UNUSUAL FATTY ACIDS**

Cyclopropenoid fatty acids

Nunn has isolated the malvalic acid (1) and sterculic acid (2) as the cyclopropene fatty acids from *Sterculia foetida* seed oil. Morris and Hall have reported D-2-hydroxysterculic acid (3) 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 in animals and possess co-carcinogenic properties.

1. Malvalic acid
   
   \[
   \text{CH}_3\text{-}(\text{CH}_2)_7\text{-C}=\text{C}-(\text{CH}_2)_6\text{-COOH}
   \]
   
   [7-(2-Octylcyclopropen-1-yl) heptanoic acid]

2. Sterculic acid
   
   \[
   \text{CH}_3\text{-}(\text{CH}_2)_7\text{-C}=\text{C}-(\text{CH}_2)_7\text{-COOH}
   \]
   
   [8-(2-Octylcyclopropene-1-yl)-octanoic acid]

3. D-2-Hydroxysterculic acid
   
   \[
   \text{CH}_3\text{-}(\text{CH}_2)_7\text{-C}=\text{C}-(\text{CH}_2)_6\text{-CH-COOH}
   \]
   
   [OH]

(1) Malvalic acid
(2) Sterculic acid
(3) D-2-Hydroxysterculic acid.
Hydroxy fatty acids

Hydroxy fatty acids have a wide spread occurrence in nature. Ricinoleic acid (4) is known to occur in castor oil (*Ricinus communis*), which has been the sole commercial source of hydroxy fatty acid. The occurrence of this acid in appreciable amounts has also been reported in several other seed oils.

\[
\begin{align*}
\text{OH} \\
\text{CH}_3\text{-}(\text{CH}_2)_5\text{-CH-CH}_2\text{-CH}=\text{CH-}(\text{CH}_2)_7\text{-COOH} \\
(4) 12\text{-Hydroxyoctadec-}{\text{cis}}\text{-9-enolic acid}
\end{align*}
\]

Isoricinoleic acid (5) is known to occur in four genera of Apocynaceae plant family viz., *Hollarrheena*, *Nerium*, *Strophanhus*, and *Wrightia*. This isoricinoleic acid is also reported in the other seed oils. A new isomer (6) which has been reported in the seed oil of *Plantago major*.

\[
\begin{align*}
\text{OH} \\
\text{CH}_3\text{-}(\text{CH}_2)_4\text{-CH}=\text{CH-}(\text{CH}_2)_2\text{-CH-}(\text{CH}_2)_7\text{-COOH} \\
(5) 9\text{-Hydroxyoctadec-}{\text{cis}}\text{-12-enolic acid}
\end{align*}
\]

\[
\begin{align*}
\text{OH} \\
\text{CH}_3\text{-}(\text{CH}_2)_6\text{-CH}=\text{CH-CH}_2\text{-CH-}(\text{CH}_2)_7\text{-COOH} \\
(6) 9\text{-Hydroxyoctadec-}{\text{cis}}\text{-11-enolic acid}
\end{align*}
\]

Bohannon and Kleiman reported three α-hydroxy fatty acids, viz., α-hydroxyoleic acid (7), α-hydroxylinoleic acid (8) and α-hydroxylinolenic acid (9).
in *Salvia nilotica* seed oil. Smith and Wolff\textsuperscript{44} reported \(\alpha\)-hydroxylinolenic acid (9) in *Thymus vulgaris* seed oil.

\[
\begin{align*}
\text{OH} & \\
\text{CH}_3(\text{CH}_2)_7\text{CH=CH(CH}_2)_6\text{CH-COOH} & (7) \ \alpha\text{-Hydroxyoleic acid}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \\
\text{CH}_3(\text{CH}_2)_3(\text{CH}_2\text{-CH=CH(CH}_2)_6\text{CH-COOH} & (8) \ \alpha\text{-Hydroxylinoleic acid}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \\
\text{CH}_3(\text{CH}_2\text{-CH=CH(CH}_2)_6\text{CH-COOH} & (9) \ \alpha\text{-Hydroxylinolenic acid}
\end{align*}
\]

Mikolajczak et al.,\textsuperscript{45} have reported Lesquirolig acid (10) in twelve species of genera *Lesquerella*. Plattner et al.,\textsuperscript{46} have reported the same acid (10) and a trace of new hydroxy fatty acid (11) in the seed oil of *Heliophila amplexicaulis*. Smith et al.,\textsuperscript{47} have reported 9-hydroxy-trans-10, trans-12-octadecadienoic (Dimorphecolic) acid (12) in the seed oil of *Dimorphotheca aurantica*. Morris et al.,\textsuperscript{48} observed two new hydroxy fatty acids (13 & 14) along with dimorphecolic acid in *Dimorphotheca* seed oil.

\[
\begin{align*}
\text{OH} & \\
\text{CH}_3(\text{CH}_2)_5\text{-CH-CH}-\text{CH=CH(CH}_2)_9\text{-COOH} & (10) \ 14\text{-Hydroxyeicos-cis-11-enoic acid}
\end{align*}
\]
Badami and Morris\textsuperscript{49} isolated another hydroxy fatty acid (15) in \textit{Calendula officinalis} seed oil and this acid is also geometrically isomeric with the dimorphecolic acid. Smith et al.,\textsuperscript{50} have reported densipolic acid (16) in \textit{Lesquerella densipila} seed oil. Kleiman et al.,\textsuperscript{51} reported Auricolic acid (17).
Kamlolenic acid (18) has been reported in the seed oil of Mallotus philippensis\textsuperscript{52, 53} by Calderwood and Gunstone. Hanseen\textsuperscript{54} reported new hydroxy (Coriolic) acid (19) in the seed oil of Coriaria myristifolia.

Osman et al., have reported two new hydroxy fatty acids (20) and (21) in Mirabilis jalapa\textsuperscript{55} and Blepharis sindica\textsuperscript{56} seed oils respectively.

Cardamine impatiens\textsuperscript{57} seed oil contains four long-chain vicinal dihydroxy fatty acids (22-25). Badami and Kudari\textsuperscript{58} reported the same dihydroxy acid (22) in
Feronia elephantum seed oil. Ahmad et al.\textsuperscript{59} also reported dihydroxy acid (26) in Mucuna puriens seed oil.

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{CH}_3-(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_7-\text{COOH} \\
(22) 9,10-\text{Dihydroxyoctadecanoic acid}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{CH}_3-(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_9-\text{COOH} \\
(23) 11,12-\text{Dihydroxyeicosanoic acid}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{CH}_3-(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_11-\text{COOH} \\
(24) 13,14-\text{Dihydroxydocosanoic acid}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{CH}_3-(\text{CH}_2)_7-\text{CH-CH-(CH}_2)_13-\text{COOH} \\
(25) 15,16-\text{Dihydroxytetracosanoic acid}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{CH}_3-(\text{CH}_2)_4-\text{CH-CH-CH}_2-\text{CH=CH-(CH}_2)_7-\text{COOH} \\
(26) 12, 13-\text{Dihydroxyoleic acid}
\end{align*}
\]

Davis reported the non-vicinal dihydroxy acid (27) in Aleurites fordii\textsuperscript{60} seed oil (tung oil). Recently a new saturated dihydroxy acid (28) has been reported by Osman et al., in the seed oil of Peganum harmala\textsuperscript{61}. The seed oil of Baliospermum axillare\textsuperscript{62} contains a non-vicinal dihydroxy mono-unsaturated acid (29) as Axillarenic acid.

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{CH}_3-(\text{CH}_2)_3-\text{CH-CH=CH-CH=CH-(CH}_2)_7-\text{COOH} \\
(27) 9, 14-\text{Dihydroxyoctadeca-10, 12-dienoic acid}
\end{align*}
\]
Mikolajczak and Smith\textsuperscript{63} isolated two optically active tri-hydroxy fatty acids (30 and 31) from \textit{Chamaepeuce afra} 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. Gunstone reported vernolic acid (32) for the first time in \textit{Vernonia anthelmintica}\textsuperscript{64} seed oil. The considerable amount of vernolic acid has also been reported in several other seed oils\textsuperscript{65-81}.

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

\textit{(32)} cis-12, 13-Epoxyoctadec-cis-9-enoic acid
Smith et al.,\textsuperscript{82} reported an isomer of vemolic acid in \textit{Chrysanthemum coronarium} seed oil and named as coronaric acid (33). This coronaric acid is also found in the other seed oils\textsuperscript{83-86}.

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

\textit{Vernonia roxburghii}\textsuperscript{87} seed oil contains vemolic acid along with a new epoxy acid (34). The seed oil of \textit{Cephatocroton peuschelii}\textsuperscript{88} contains vemolic acid and also epoxy stearic acid (35), which is also reported in \textit{Tragopogon porrifolius}\textsuperscript{89} and \textit{Shorea robusta}\textsuperscript{90} seed oils.

\[
\text{CH}_3\text{(CH}_2\text{)}_5\text{-CH=CH-(CH}_2\text{)}_6\text{-CH-CH-CH}_2\text{-COOH} \\
(34) \text{cis-3, 4-Epoxy-cis-11-octadecenoic acid}
\]

\[
\text{CH}_3\text{(CH}_2\text{)}_7\text{-CH-CH-(CH}_2\text{)}_7\text{-COOH} \\
(35) \text{cis-9, 10-Epoyoctadecanoic acid}
\]

Ulchenko et al.,\textsuperscript{91} reported coronaric acid, vemolic acid and a trace of 9,10-epoxystearic acid in the seed oil of \textit{Artemisia absinthium}. Conacher and Gunstone\textsuperscript{92-93} reported coronaric acid, epoxyoctadecynoic acid and epoxystearic acid in \textit{Helichrysum bracteatum} seed oil. Spencer\textsuperscript{94} reported vemolic acid and a trace of epoxystearate, and two previously unknown acids (36) and (37) in \textit{Crepis conyzaefolia} seed oil.
Kleiman et al.\textsuperscript{95} reported new epoxy acid (38) in the seed oil of \textit{Stenachaeum macrocephalum} along with coronaric and epoxystearic acids. Gunstone and Morris\textsuperscript{96} reported 15,16-epoxylinoleic acid (39) in \textit{Camelina sativa} seed oil.

Kleiman et al.\textsuperscript{97} have reported a C-20 homologue of vernolic acid in \textit{Alchornea cordifolia} seed oil. This new epoxy fatty acid has been named as Alchomic acid (40).
Keto fatty acids

_Licania rigida_⁴ which has attained a commercial status as it contains an enormous amount of 4-keto-eleostearic acid and named as Licanic acid (41). This acid is used in paints and varnish industries for its drying property.

_Dimorphotheca sinuata_⁹⁸ seed oil contains a minor amount of keto acid (42). The two keto acids (41 & 43) have been reported by Gunstone and Subbarao from _Chrysobalanus icaco_⁹⁹ seed oil. Kaufmann et al.,¹⁰⁰ have reported α-Licanic acid in _Parinarium annamense_ seed oil. Later Philips et al.,¹⁰¹ reported two new keto acids (44 & 45) in the seed oil of _Monnina emerginata_.

\[
\text{CH}_3-(\text{CH}_2)_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{C}-(\text{CH}_2)_2-\text{COOH} \\
(41) \text{4-Keto-octadeca-cis-9, trans-11, trans-13-trienoic acid}
\]

\[
\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}-(\text{CH}_2)_7-\text{COOH} \\
(42) \text{9-Keto-trans-10, trans-12-octadecadienoic acid}
\]

\[
\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}=\text{CH})_2-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{C}-(\text{CH})_2-\text{COOH} \\
(43) \text{4-Keto-octadeca-cis-9, trans-11, trans-13, cis-15-tetraenoic acid}
\]

\[
\text{CH}_3-(\text{CH}_2)_4-\text{C}-\text{CH}=\text{CH}-\text{CH}-(\text{CH}_2)_7-\text{COOH} \\
(44) \text{13-Keto-octadeca-trans-9, trans-11-dienoic acid}
\]
Three keto acids (46, 47 & 48) have been reported by Smith\textsuperscript{102} in the seed oil of \textit{Cuspidaria pterocarpa}. Three new saturated keto acids (49, 50 & 51) have been reported in \textit{Costus specious}\textsuperscript{103} seed oil.

(46) 15-Keto-\textit{cis}-18-tetracosenoic acid

(47) 17-Keto-\textit{cis}-20-hexacosenoic acid

(48) 19-Keto-\textit{cis}-22-octacosenoic acid

(49) 14-Keto-tricosanoic acid

(50) 14-Keto-heptacosanoic acid

(51) 15-Keto-octacosanoic acid
Rukmini\textsuperscript{104} reported a new keto (Argemonic) acid (52) in the seed oil of *Argemone mexicana*. Mahato\textsuperscript{105} reported two new keto acids (53 & 54). Gunstone\textsuperscript{106} reported three-long-chain new keto acids (53, 55 & 56). The new keto acid (57) is reported in *Plantago ovata*\textsuperscript{107} and in *Cryptolepis buchnani*\textsuperscript{108} seed oils.

\[ \text{CH}_3-(\text{CH}_2)_{18}-\text{C-}(\text{CH}_2)_{9}-\text{C-}(\text{CH}_2)_{4}-\text{COOH} \]
\[ (52) \text{ (+)-6-Hydroxy-6-methyl-9-keto-octacosenoic acid} \]

\[ \text{CH}_3-(\text{CH}_2)_{18}-\text{C-}(\text{CH}_2)_{9}-\text{COOH} \]
\[ (53) 11-\text{Keto-triacontanoic acid} \]

\[ \text{CH}_3-(\text{CH}_2)_{18}-\text{CH-}(\text{CH}_2)_{9}-\text{COOH} \]
\[ (54) 11-\text{Hydroxytriacontanoic acid} \]

\[ \text{CH}_3-(\text{CH}_2)_{18}-\text{C-}(\text{CH}_2)_{7}-\text{COOH} \]
\[ (55) 9-\text{Keto-octacosanoic acid} \]

\[ \text{CH}_3-(\text{CH}_2)_{18}-\text{C-}(\text{CH}_2)_{9}-\text{COOH} \]
\[ (56) 11-\text{Keto-octacosanoic acid} \]
The other four new keto fatty acids (58), (59), (60) and (61) have been reported in *Lagerstroemia speciosa*\(^{109}\), *Gardenia lucida*\(^{110}\), *Cassia absus*\(^{111}\) and *Diospyros melanoxylon*\(^{112}\) seed oils, respectively.

\[
\text{CH}_3-(\text{CH}_2)_{5}-\text{CH}=\text{CH}-\text{CH}_2\text{-C-}(\text{CH}_2)_{7}\text{-COOH}
\]

(58) 9-Keto-octadec-*cis*-11-enoic acid

\[
\text{CH}_3-(\text{CH}_2)_{5}-\text{CH}=\text{CH}-\text{CH}-\text{CH}_2\text{-C-}(\text{CH}_2)_{5}\text{-COOH}
\]

(59) 7-Keto-octadec-*cis*-11-enoic acid

\[
\text{CH}_3\text{-CH}_2\text{-CH}=\text{CH}\text{-CH}_2\text{-C-}(\text{CH}_2)_{7}\text{-COOH}
\]

(60) 9-Keto-octadec-*cis*-15-enoic acid

\[
\text{CH}_3-(\text{CH}_2)_{3}\text{-CH}=\text{CH}\text{-CH}_2\text{-C-}(\text{CH}_2)_{7}\text{-COOH}
\]

(61) 9-Keto-octadec-*cis*-13-enoic acid
OLEO CHEMICALS

Interest in the biological and industrial potentialities of oleochemicals has resulted in the development of various synthetic procedures for the introduction of heterocyclic moiety into the hydrocarbon chain. Therefore, today oleochemicals have gained considerable momentum next only to petrochemicals in industry and technology of surfactants, lubricant additives, cosmetics, soaps, detergents, textiles, plastics, plasticizers, protective coatings, dispersants, intermediate chemicals, urethane derivatives, pharmaceuticals, organic pesticides and a variety of synthetic intermediates.

During the past decade production and utilization of oils and fats and their derivatives have grown both in size and diversity. In the industrial field there has been competition between oleochemicals and petrochemicals. The ever-increasing cost of petrochemicals has diverted the attention of chemists' to synthesize oleochemicals derived from natural oils and fats. These fat derived chemicals are essential to a variety of oleochemical industries. Thus, oleochemicals are manufactured starting with fatty acids and the most important being : (i) nitrogen derivatives, (ii) esters, (iii) metallic soaps, (iv) alcohols, (v) dimeric acids, (vi) ozonolysis products such as pelargonic and azelaic acids. In the world today, nitrogen derivatives and esters are the two most important classes of derivatives consuming more than 50 % of fatty acids \(^ {113}\).
Reactions of double bond in fatty acid chain:

A brief account of reactions in fatty acid chain has been described as follows.

Addition of Hydrogen cyanide and Nitriles

Ritter\textsuperscript{114-117} and others added hydrogen cyanide and a variety of nitriles to olefins in strong acid media to give substituted amides (62).

\[
\begin{align*}
\text{RCN} + \text{C} = \text{C} & \xrightarrow{\text{H}^+ / \text{H}_2\text{O}} \text{RCONHCH-CH} \\
\end{align*}
\]

(62)

Roe and Swem\textsuperscript{118} applied this reaction to oleic acid in strong acid media yielded substituted amido-stearic acids. In this reaction, sulphuric acid caused positional isomerisation through double bond migration. Under similar reaction conditions, different nitriles were successfully added to petroselinic acid\textsuperscript{119} and undecylenic acid\textsuperscript{120}.

Addition of Thiocyanogen

Kaufmann\textsuperscript{121} has reported that thiocyanogen adds quantitatively to the double bond of oleic acid, to one of the double bond of linoleic acid and to the two double bonds of linolenic acid to give the substituted thiocyanogen derivatives (63) of oleic, linoleic and linolenic fatty acids, respectively.

\[
\begin{align*}
\text{-CH=CH-} + (\text{SCN})_2 & \xrightarrow{} \text{-CH-CH-} \\
\text{SCN} & \text{SCN}
\end{align*}
\]

(63)
Addition of Phenols and Cresols

Phenols and cresols react with oleic acid in sulphuric acid to give both positional isomers with respect to the site of the rearranged bond in the fatty chain, and also with respect to ortho and para positions of both groups on the aromatic ring. The product (64) is exceedingly complex.

\[
\text{CH}_3(\text{CH}_2)_7\text{CH=CH(}\text{CH}_2)_7\text{COOH} + \text{CH}_3\text{OH,} \quad \text{CH}_3\text{CH(}\text{CH}_2)_7\text{COOH} \rightarrow
\]

Addition of Hydrogen sulphide and Mercaptans

Schwab, Gast, and Rohwedder\textsuperscript{122} were able to accomplish the nucleophilic addition of hydrogen sulphide to methyl oleate, methyl linoleate, and soyabean oil at \(-70\) °C to \(+25\) °C with boron triflouride. With excess \(\text{H}_2\text{S}\) and methyl oleate at \(-70\) °C the primary reaction products, as expected, is methyl 9-mercapto-stearate (65) and 10-mercapto-stearate (66). This has been applied for many industrial products; lubricants, synthetic rubbers, floatation collectors, and others.
Sulphation and Sulphonation

The unsaturated acids that react readily at the double bond with concentrated sulphuric acid with the introduction of either the sulphate (HSO₄⁻) group or sulphonate (HSO₃⁻) group at elevated temperature. The hydroxyl groups containing seed oils such as castor oil is readily sulphated to form esters followed by neutralization, which is carried out industrially, and extensively in the preparation of so-called sulphonated oils for the textile industry.

The α-sulphonation of saturated fatty acids is conveniently carried out with sulphur trioxide in dioxane. Stirton¹²³ et al., have prepared a series of them in order to evaluate the sodium salts as detergent materials. The preparation of sulphonated castor oil using sulphur trioxide¹²⁴ apparently affords a product with a somewhat higher degree of sulphation and sulphonation than the conventional product (Turkey red oil) usually prepared with sulphuric acid.

It is possible to increase the hydroxyl group content of unsaturated oils, and other esters by partially sulphating the unsaturated bonds, followed by hydrolysis to remove the sulphate group for the replacement of hydroxyl group¹²⁵.

Addition of Sulphur dichloride

Sulphur dichloride (SCl₂), reacts readily with olefins. Grimm¹²⁶ studied the addition of sulphur dichloride to various monoethenoid fatty materials (methyl oleate, methyl elaidate, oleonitrile) and ethyl linoleate and found that the products, β,β'-dichlorosulphides (67), could be easily oxidized with per-acetic
acid to the corresponding \( \beta,\beta' \)-dichlorosulphoxides (68), and \( \beta,\beta' \)-
dichlorosulphones (69).

\[
\begin{align*}
\text{RCH=CHR'} + \text{S} & \rightarrow \text{RSO}_{2}\text{Cl} \\
\text{RCH=CHR'} & \rightarrow \text{RCH=CHR'} \end{align*}
\]

(67) \hspace{1cm} (68) \hspace{1cm} (69)

R = -(CH\(_2\))\(_7\) CH\(_3\) or -(CH\(_2\))\(_7\) COOR, or -(CH\(_2\))\(_7\) CN

Where \( R' = -(CH\(_2\))\(_7\) COOR \) or -(CH\(_2\))\(_7\) CN or -(CH\(_2\))\(_7\) CH\(_3\), respectively.

\( \beta,\beta' \)-Dichlorosulphides are reactive intermediates with labile chlorines that
have been reacted with many nucleophiles to afford a series of potentially useful
sulphur-containing fatty derivatives\(^{126}\).

\[
\begin{align*}
\text{CH}_3\text{(CH}_2\text{)}_7\text{CH-CH(CH}_2\text{)}_7\text{COOH} + 2Z' & \rightarrow \text{CH}_3\text{(CH}_2\text{)}_7\text{CH-CH(CH}_2\text{)}_7\text{COOH} \\
\text{CH}_3\text{(CH}_2\text{)}_7\text{CH-CH(CH}_2\text{)}_7\text{COOH} & \rightarrow \text{CH}_3\text{(CH}_2\text{)}_7\text{CH-CH(CH}_2\text{)}_7\text{COOH}
\end{align*}
\]

Where \( Z = \text{OH}, \text{NH}_2, \text{RNH}, \text{many others} \) + positional isomers

**Addition of Maleic anhydride and other Dienophiles**

Fatty acids containing a conjugated diene system, in common with other
dienes, react with dienophiles such as maleic anhydride and this reaction (\textit{Diels-Alder}) is useful in the study of acids with conjugated unsaturation. Catalpic acid
and octadeca-trans-9, trans-11-dienoic acid, for example, readily form maleic anhydride adducts (70 & 71) which are identical products (72) after hydrogenation. This confirms that catalpic acid contains a 9-trans, 11-trans-diene system.

Hydrogen and Reduction

In the presence of suitable catalyst, hydrogen adds to the double bonds of unsaturated fatty acids. The partial reduction of double bond may be achieved by the use of hydrazine and oxygen.

\[
-\text{CH}=\text{CH}- + \text{NH}_2\text{NH}_2 + \frac{1}{2} \text{O}_2 \rightarrow -\text{CH}_2\text{CH}_2- + \text{N}_2 + \text{H}_2\text{O}
\]
Halogenation

Chlorine, bromine, iodine monochloride and iodine monobromide are added to the double bonds of unsaturated acids and their derivatives.

Halogenated fatty compounds are being used in several novel applications, viz., as textile additives, as reactive intermediates and in dehalogenation processes to increase the degree of unsaturation.

Addition of Carbon monoxide

The reaction of carbon monoxide with the double bonds of fatty acids confirms that, at least three modes of addition

1. Hydroformylation

\[
\text{Co}_2(\text{CO})_8 + \text{CH}=\text{CH} + \text{CO} + \text{H}_2 \rightarrow \text{CHCH}_2 \rightarrow \text{CHCH}_2
\]

\[
\underline{\text{CHO}} \quad \underline{\text{CH}_2\text{OH}}
\]

The products of all three reactions are usually mixtures of many positional isomers.

2. Koch reaction

\[
\text{H}_2\text{SO}_4 + \text{CH}=\text{CH} + \text{CO} + \text{ROH} \rightarrow \text{CHCH}_2 \rightarrow \text{CHCH}_2
\]

\[
\underline{\text{R}=\text{H, alkyl}} \quad \underline{\text{COOR}}
\]

3. Reppe reaction

\[
\text{Ni}(\text{CO})_4 + \text{CH}=\text{CH} + \text{CO} + \text{ROH} \rightarrow \text{CHCH}_2 \rightarrow \text{CHCH}_2
\]

\[
\underline{\text{R}=\text{H, alkyl}} \quad \underline{\text{COOR}}
\]
Reactions of carboxylic group in fatty acid chain:

A brief account of reactions of carboxylic group in fatty acid chain has been described as follows.

General methods of synthesis of 1,3,4-oxadiazoles

In the five membered ring system the presence of two nitrogen and one oxygen heteroatoms defines an interesting class of compounds known as oxadiazoles. These may be of four types viz., 1,2,3-oxadiazole (73), or 1,2,4-oxadiazoles (74), 1,2,5-oxadiazole (75) and 1,3,4-oxadiazole (76).

\[
\begin{align*}
1,2,3\text{-oxadiazole} & \quad & 1,2,4\text{-oxadiazole} \\
1,2,5\text{-oxadiazole} & \quad & 1,3,4\text{-oxadiazole}
\end{align*}
\]

Synthesis of oxadiazoles from thiosemicarbazides

Stolle and Gaertner\textsuperscript{127} synthesised 1,3,4-oxadiazoles (77) by cyclisation of thiosemicarbazides with PbO and NaN\textsubscript{3} in ethanol to give 2-substituted-5-aryl-1,3,4-oxadiazoles.

\[
R\text{CONHNHCSNHR}' \xrightarrow{\text{PbO/NaN}_3} \quad R-C\text{-}N\text{-}C-R'
\]

\(R=\text{aryl} \quad R'=\text{arylamino}\)
Hoggarth\textsuperscript{128} synthesized 2-amino-5-phenyl-1,3,4-oxadiazoles (78) by heating 1-benzoyl-s-methyl-isothiosemicarbazide for 10 minutes at 200 °C.

\[
\text{C}_6\text{H}_5\text{CONHN}=\text{C}-\text{NH}_2 \xrightarrow{200 \text{ C}} \text{H}_2\text{C}_6\text{C}=\text{C}\text{N}=\text{C}-\text{NH}_2
\]

(78)

Silberg and Cosma\textsuperscript{129} synthesised 1,3,4-oxadiazoles (79) by oxidative cyclisation of thiosemicarbazides with iodine in potassium iodide.

\[
\text{RCONHNHCNHC}_6\text{H}_5 \xrightarrow{\text{I}_2 \text{ in KI}} \text{N} \text{N} \text{C-NHC}_6\text{H}_5
\]

(79)

\[\text{R=C}_6\text{H}_5, \text{p(Cl) C}_6\text{H}_4, \text{p(NO}_2) \text{C}_6\text{H}_4, \text{o(OH) C}_6\text{H}_4\]

**Synthesis of oxadiazoles from hydrazines**

2,5-Diaryl-1,3,4-oxadiazoles (80) are prepared by the cyclisation of the corresponding 1,2-diarylhydrazines in the presence of dehydrating agent, such as acetic anhydride\textsuperscript{130}.

\[
\text{R-C-NH-NH-C-R'} \xrightarrow{\text{Ac}_2\text{O}} \text{N} \text{N} \text{C-C-R'}
\]

(80)
1,3,4-Oxadiazoles (81) are also prepared by the condensation of an acid hydrazide of aromatic carboxylic or carbothionic acid with ortho ester such as ethyl ortho formate\textsuperscript{131}.

$\begin{align*}
\text{R-C-NHNH}_2 + \text{HC(O}_2\text{C}_2\text{H}_5)_3
\rightarrow
\text{R-C-} \equiv \text{C-R'}
\end{align*}$

\begin{align*}
\text{R}=\text{C}_6\text{H}_5, \quad \text{R'}=\text{H} \\
\text{C}_2\text{H}_5 \quad \text{4-Pyridyl}
\end{align*}

Konig et al.,\textsuperscript{132} synthesized 2-hydroxy-5-(4-pyridyl)-1,3,4-oxadiazole (82) and 2-mercapto-5-(4-pyridyl)-1,3,4-oxadiazole (82) by reacting isonicotinic acid hydrazide with phosgene or thiophosgene.

$\begin{align*}
\text{Py}-\text{C} \equiv \text{C-NHNH}_2 + \text{CXCl}_2
\rightarrow
\text{Py} \equiv \text{C-} \equiv \text{C-XH}
\end{align*}$

Where, $X=\text{O}$ or $S$

**Synthesis of oxadiazoles from semicarbazones**

2-Amino-5-phenyl-1,3,4-oxadiazoles (83) are prepared from benzaldehyde semicarbazone and sodium hypoiodide or hypobromite\textsuperscript{133}.

$\begin{align*}
\text{Ph-CH=NH-NH-CONH}_2 + \text{NaOBr}
\rightarrow
\text{Ph-} \equiv \text{C-} \equiv \text{C-NH}_2
\end{align*}$

\begin{align*}
\text{Ph}=\text{C}_6\text{H}_5
\end{align*}
Synthesis of oxadiazoles from Schiff's bases

Saikachi\textsuperscript{134} synthesized 5-substituted-2-(2-furyl)-1,3,4-oxadiazoles (84) by oxidative cyclisation of Schiff's bases by lead tetra acetate.

\[
\text{CONHN=CHR} \xrightarrow{\text{Pb(OAc)}_4} \text{N-O}
\]

\[
R= \text{2-furyl, 2-thienyl and substituted phenyl}
\]

However, 1,3,4-oxadiazoles (85) are also prepared by heating appropriate hydrazides with carbon disulphide and alcoholic alkali\textsuperscript{135}.

\[
R - \text{CONHNH}_2 \xrightarrow{\text{CS}_2/\text{KOH}} R - \text{CONHNHC}_2\text{K}
\]

\[
R = \text{Substituted phenyl}
\]

General methods of synthesis of 1,2,4-triazoles

In the five membered ring systems the presence of three nitrogen heteroatoms defines an interesting class of compounds known as triazoles. These may be of two types viz., 1,2,3-triazoles or \(\nu\)-triazoles (86) and 1,2,4- triazoles or s-triazoles (87).

\[
\begin{align*}
\text{(86)} & \\
\text{(87)} & 
\end{align*}
\]
The widely applied methods for the synthesis of s-triazoles are the ring closure of acyl derivatives of aminoguanidines, semicarbazides and thiosemicarbazides in alkaline solutions.

**Synthesis of triazoles from formhydrazine and formamide**

The substituted triazoles can be (88) obtained by the fusion of N-formyl-N-alkyl or aryl hydrazine with formamide at 250 - 280 °C in poor yields. Because of difficulty in isolation of triazoles, this method has been modified by heating formamide with a substituted hydrazine hydrochloride and this general type of reaction is known as Pellizzari reaction¹³⁶.

\[
\begin{align*}
\text{RNHNHCHO} + \text{HCONH}_2 & \xrightarrow{\Delta} \text{N} \equiv \text{N} \\
& \xleftarrow{\text{HCONH}} \text{HCONH}_2 + \text{RNHNH}_2\text{HCl}
\end{align*}
\]

(88)

**Synthesis of 3-amino-1,2,4-triazoles (89) via formylamino guanidine**

The preparation of 3-amino triazoles via N-formylamino guanidine was really accomplished by heating a mixture of an amino guanidine salt (H₂CO₃, HCl, HNO₃, H₂SO₄) and formic acid in toluene¹³⁷,¹³⁸.

\[
\begin{align*}
\text{H}_2\text{N} \equiv \text{C} - \text{NH}_2 + \text{HCOOH} + \text{H}_2\text{O} & \xrightarrow{\text{HCOOH} \cdot \text{H}_2\text{O}} \text{H}_2\text{N} \equiv \text{C} - \text{NH}_2 \\
& \xrightarrow{\text{H}_2\text{O}} \text{N} \equiv \text{N} \equiv \text{N} - \text{NH}_2 \text{H}_2\text{O} \text{or} \text{H}_2\text{N} \equiv \text{C} - \text{NH}_2 \\
& \xleftarrow{\text{H}_2\text{N} \equiv \text{C} - \text{NH}_2} \text{N} \equiv \text{N} \equiv \text{N} - \text{NH}_2 \\
& \xrightarrow{\text{H}_2\text{N} \equiv \text{C} - \text{NH}_2} \text{N} \equiv \text{N} \equiv \text{N} - \text{NH}_2
\end{align*}
\]

(89)

**Synthesis of triazoles from aryl semicarbazides**

The aryl semicarbazide on boiling with anhydrous formic acid yielded 3-hydroxy-1-aryl-1,2,4-,1H-triazoles (90) which is on heating at 200 °C with P₂O₅ gave 80% of 1-aryl-1,2,4-1H-triazole(91)¹³⁹.
Synthesis of triazoles by cyclisation of acyl thiosemicarbazides

Hoggarth has reported the synthesis of 3-aryl-5-mercapto-1,2,4-triazole (92) by base catalysed cyclisation of 4-acylthiosemicarbazides\(^{140}\).

\[
\text{alkali} \quad \text{ArCONHNCSNH}_2 \quad \rightarrow \quad \text{Ar-CN-C-SH} \quad (92)
\]

Synthesis of triazoles from s-triazines

The substituted 1,2,4-trizole i.e., 1-phenyl-1,2,4-1H-triazole (93) is obtained by the reaction of substituted hydrazine salt with s-triazine in 83% yield. When phenyl hydrazine hydrochloride is treated with s-triazine which involves cleavage of a molecule of s-triazine to yield a substituted formimido hydrazone. This reacts immediately with another molecule of s-triazine to yield the substituted triazole\(^{141}\).

\[
\begin{align*}
\text{NNHR} & \quad + \quad 3\text{NH}_2\text{NHPHCl} \\
\text{HC} & \quad \rightarrow \quad \text{NH}_2\text{HCl} \\
\text{HC} & \quad \rightarrow \quad \text{NH}_4\text{Cl} \\
\text{NNHR} & \quad + \quad 3\text{NH}_4\text{Cl}
\end{align*}
\]
PHARMACOLOGICAL ACTIVITY

Medicinal chemistry is a science whose roots lie in all branches of chemistry and biology. It involves the mechanism of the actions of drugs to establish relationships between chemical structure and biological activity which links biodynamic behaviour to the chemical reactivity and physical properties of therapeutic agents. Medicinal chemistry also involves the isolation, characterization and synthesis of compounds that can be used in medicine for the prevention treatment and cure of disease. It prevents the chemical basis for the interdisciplinary field of therapeutics\textsuperscript{142}.

The amides and hydrazides have been known to be associated with antibacterial\textsuperscript{143}, antifungal\textsuperscript{144}, anthelmintic\textsuperscript{145} and anticonvulsant\textsuperscript{146} activities. The various thiosemicarbazide derivatives were reported to possess interesting pharmacological properties like antitubercular\textsuperscript{147-149}, antidepressant\textsuperscript{150}, anti-inflammatory and analgesic\textsuperscript{151} activities. In addition to the antibacterial activities\textsuperscript{152} exhibited by several triazole derivatives, they were also examined for their fungicidal, herbicidal\textsuperscript{153}, analgesic and anti-inflammatory\textsuperscript{154} activities. The oxadiazoles and their derivatives are well known chemotherapeutic agents for muscle relaxant\textsuperscript{155}, hypoglycemic\textsuperscript{156} and antibacteriostatic\textsuperscript{157}. 
GENERAL EXPERIMENTAL PROCEDURE

Sources of oilseeds

The seed samples belonging to different plant families were collected from various parts of Karnataka State.

Solvents and Chemicals

Petroleum ether (b.p. 40-60 °C), ethanol, methanol, benzene, acetone, acetic acid, diethyl ether, CHCl₃, CCl₄, CS₂, Ac₂O, HCl, HBr, H₂SO₄ and bromine were of reagent grade.

All the solvents were distilled. The anhydrous diethyl ether was prepared by distilling the commercial samples over anhydrous CaCl₂ and the distillate was stored in contact with sodium wire. The super dry ethanol and methanol were prepared using magnesium turnings and iodine.

Undecylenic acid (s.d-fine), nitriles (Aldrich, Acros and Lancaster), hexamethyl disilazane (Acros), trimethylchlorosilane (Acros), hydrazine hydrate, K₂CO₃, KOH, NaOH, KI, KCNS, pyridine and silver nitrate were used. All these chemicals were of synthetic grade.

Extraction of oils

The air-dried seeds were ground, powdered and extracted thoroughly with light petroleum ether (b.p. 40-60 °C) in a Soxhlet extractor for 24 hours. The petroleum ether extracts were dried over anhydrous sodium sulphate and solvent
was removed in vacuum at 40 °C to get the oil. The analytical values of oils were determined according to the AOCS methods.

Chromatographic Methods

Thin layer chromatography (TLC)$^{158}$

Analytical

The clean glass plates (20 x 10 cm) were coated with a slurry of silica gel ‘G’ in distilled water (1:2 w/v) to get the film of 0.2 mm thickness using a “Camag” applicator. The coated plates were air-dried and activated at 100 °C for 1 hour and cooled in a desiccator.

Preparative thin layer chromatography

Glass plates were coated to get a silica gel ‘G’ layer of 1mm thickness using “Camag” applicator. The coated plates were air-dried and activated at 100°C for 1 hour and cooled in a desiccator.

Development and Visualization

The plates after applying samples as spots or bands were developed with suitable solvent systems in a closed glass-developing chamber. The separated spots or bands were located by exposing to iodine vapours, ammonia fumes, spraying picric acid or 2,4 DNPH.
Direct thin layer chromatography

A thickness of 0.2 mm silica gel 'G' coated, activated glass plates of thickness 0.2 mm silica gel 'G' coated were used. After applying samples as spots or bands were developed with suitable solvent systems petroleum ether : diethyl ether (70 : 30 v/v) in a closed glass-developing chamber. The separated spots or bands were located by exposing to iodine vapours for few minutes.

Picric - acid thin layer chromatography\textsuperscript{159}

A thickness of 0.2 mm silica gel 'G' coated, activated glass plate was developed in a solvent system, petroleum ether : diethyl ether : acetic acid (75:25:1 v/v/v). It was sprayed thoroughly with 0.5M picric acid in 95\% ethanol and placed in a jar saturated with vapours of diethyl ether : ethanol : acetic acid (80:20:1 v/v/v). After 30 minutes, the plates were removed and exposed to ammonia fumes for few minutes. The orange spot on a yellow background of the plate indicated the presence of epoxy fatty acids.

2,4-Dinitrophenylhydrazine (2,4-DNPH) thin layer chromatography\textsuperscript{160}

A thickness of 0.2 mm silica gel 'G' coated, activated glass plate was developed in a solvent system, petroleum ether : diethyl ether : acetic acid (75:25:1 v/v/v). It was sprayed thoroughly with approximately 0.2M 2,4-DNPH solution. An orange spot on the plate indicated the presence of keto group.
Column chromatography

The oxygenated ester or acid was purified by using activated neutral alumina in a column. About 500 mg of ester or acid was transferred to a column (4 X 0.25") containing 40 gms of neutral alumina and petroleum ether. Then, it was further eluted with petroleum ether and diethyl ether (7 : 3 v/v). The pure material thus obtained was analyzed for IR, $^1$H NMR, $^{13}$C NMR and MS.

Gas liquid chromatography

The quantitative examination of the methyl esters was carried out on a “Perkin-Elmer Model Sigma Unit” using a stainless steel column coated with 15% DEGS on chromosorb, W, 45-60 mesh. The temperature at injection port, detector port and oven were 240 °C, 240 °C and 190 °C respectively. The machine recorded directly the weight percent of individual peaks. The peaks were identified by comparing their retention times with those of standard reference sample under the similar conditions.

Spectroscopic Methods

Ultraviolet (UV)

The UV spectra of the methyl esters of oils were taken on Hitachi 150-20 Model Instrument in methanol using cell of 1 cm path length was used. The concentration of solutions was 0.001%.
Infrared (IR)

The IR spectra of oils and their methyl esters were recorded on a Nicolet Impact-410 Model instrument. IR spectra were determined as liquid films and KBr pallets for liquid and solid samples, respectively.

Nuclear Magnetic Resonance $^1$H NMR and $^{13}$C NMR

The $^1$H NMR were recorded from deuterio chloroform and deuterio DMSO solutions on Bruker (300 MHz & 400 MHz) Model spectrophotometer. The chemical shifts (δ 0-20) were measured in ppm downfield from internal TMSi at δ=0.

Mass Spectrophotometry (MS)

The mass spectra of TMSi derivative, diacetyl derivative, keto fatty esters and novel oleochemicals were run on Auto Spec EI mass spectrophotometry. at 70 eV with a source temperature 250 °C.

Chemical Methods

Halphen test$^{161}$

This chemical test was specific for the cyclopropene functional group in fatty oils. A solution of sulphur (1% in CS$_2$) was mixed with equal volume of amyl alcohol and is known as Halphen reagent. The fatty oil and Halphen reagent were mixed and the reaction mixture was heated on a water bath (70-80 °C) for few minutes until all the carbon disulphide boiled off. Then the test tube was loosely
plugged with cotton and heated for 1-2 hours in an oil bath at 110-115°C. A development of red colouration indicated the presence of cyclopropene fatty acids.

**Saponification**

A known weight of the oil was saponified at room temperature by stirring overnight with 0.8N alcoholic potassium hydroxide solution. The excess of alcohol was removed by distillation under reduced pressure. It was then diluted with water. The non-saponifiable matter was removed by extraction with diethyl ether. After careful acidification of pH 5 with 0.5N sulphuric acid, the mixed fatty acids were extracted with diethyl ether. The ether solution was washed with water several times and the solvent was removed.

**Acetolysis**

A portion of oil (20gm) was stirred for 24 hours at room temperature with 200 ml of glacial acetic acid in 80 ml of 10% of sulphuric acid according to Wilson’s method. It was then diluted with distilled water and extracted with solvent ether repeatedly. The combined ether extracts were washed thoroughly with distilled water and dried over anhydrous sodium sulphate. The solvent was removed in a stream of nitrogen. The acetolyzed product was saponified as described above.
Isolation Procedure

a) Hydroxy fatty acids

The mixed fatty acids thus obtained were partitioned according to Gunstone’s method\textsuperscript{163} between equal volume of petroleum ether (b.p 40-60°C) and 80% methanol. The yields of oxygenated and non-oxygenated fatty acids were recorded.

b) Mono-hydroxy and di-hydroxy fatty acids

The mixed fatty acids methyl esters thus obtained were separated on a column of neutral alumina into non-hydroxy esters (eluted with benzene), mono-hydroxy ester (eluted with ether) and dihydroxy ester (eluted with ether containing 5% of methanol)\textsuperscript{164} The yields of oxygenated and non-oxygenated fatty acids methyl esters were recorded. The Concentrate of pure hydroxy and dihydroxy fatty acids methyl esters were obtained by preparative TLC techniques.

Esterification

Methyl esters of fatty acids were prepared by the following methods.

Transesterification method

The seed oil was transesterified with 1% sodium methoxide in methanol (50 ml) under reflux for 1 hour. Then, the reaction mixture was diluted with distilled water (25 ml) and extracted with diethyl ether (30 ml). The combined ether extracts were washed with distilled water, dried over anhydrous sodium sulphate and solvent was removed in a stream of nitrogen.
**Fischer esterification method**

The fatty acid samples were refluxed in a large excess of absolute methanol containing 1% sulphuric acid (v/v). In each case, the resulting mixture was diluted with water and then extracted repeatedly with diethyl ether. The combined ether extracts were dried over anhydrous sodium sulphate and solvent was removed in a stream of nitrogen.

**Preparation of cyclopropenoid derivatives**

The transesterified methyl esters or methyl esters of non-oxygenated fractions of seed oil (200 mg) were treated with absolute methanol (60 ml) saturated with silver nitrate. The reaction was allowed to proceed at room temperature (27 °C) with stirring for 24 hours. The normal fatty esters and the cyclopropenoid derivatives were recovered from the reaction mixture and subjected to GLC analysis using methyl esters of reference standard.

**Trimethylsilylation**

The hydroxy fatty acid methyl esters (10 mg) were converted into TMSi derivative by dissolving the fatty esters in dry pyridine (1 ml), 0.2 ml of hexamethyldisilazane and 0.1 ml of trimethylchlorosilane in an anhydrous condition. The mixture was shaken vigorously for 30 seconds and was allowed to stand for 5 minutes. Then the pyridine was removed in a stream of nitrogen and the resulting derivatives were used for MS and GLC analysis.
Acetylation\textsuperscript{167}

About 200 mg of dihydroxy fatty acid methyl esters were taken in a 250 ml round bottomed flask and a mixture of acetic anhydride and pyridine (15 ml) was added. The reaction mixture was refluxed on a water-bath for about 2 hours in an anhydrous condition. The product was cooled and diluted with water (50 ml). It was extracted with diethyl ether and dried over anhydrous sodium sulphate. The excess of pyridine was removed in a stream of nitrogen.

Hydrogenation\textsuperscript{167}

About 50 mg of fatty acid methyl ester(s) with 75 ml of methanol were subjected to catalytic hydrogenation with equal amount of palladium-charcoal (20\%) in a Parr-low pressure hydroginator for about 12 hours at 50-60 lbs/inch. The catalyst was filtered off and the solvent was removed to get the hydrogenated product.

Oxidation Methods

KMnO\textsubscript{4}/ Acetic acid method\textsuperscript{168}

The hydroxy acid (2 gm) dissolved in acetic acid, which was oxidized by gradual addition of powdered potassium permanganate (10 gm) at such a rate that temperature did not exceed 50\(^\circ\) C. After 3 hours, at this temperature the solvent was removed under reduced pressure and the residue distilled with water and acidified with dilute sulphuric acid. This was decolourised with sulphur dioxide and then steam distilled. Both the residue and the distillate were extracted with
diethyl ether to give crude dibasic acid (1.4 gms) and crude monobasic acid (0.5 gm) respectively. The former was extracted with boiling water and after the concentration of solution to 10 ml and cooling to 0°C gave azelaic acid (0.5 gm) m.p. 106-107°C (from ethyl acetate) underpresssed with authentic sample. The volatile acid (0.25 gm) was distilled under pressure, which readily gave p-bromophenacyl heptanoate m.p. 66-67°C.

**von Rudloff method**

The oxidation of the unsaturated keto acid was carried out in t-butanol (20 ml). A solution of keto acid in t-butanol (0.25%) was treated with a solution of sodium-metaperiodate (200 mg) in 20 ml of water and potassium permanganate (1 ml) in the presence of potassium carbonate 60 mg. The mixture was stirred at room temperature for 24 hours, and the solution then decolourised with NaHSO₃ followed by acidification with HCl. The mixed acids were extracted with diethyl ether. The ether was removed and the extracts were treated with 10% H₂SO₄ in absolute methanol. The mixture was refluxed for 1 hour and then extracted with diethyl ether. The ether extracts were dried over anhydrous Na₂SO₄. The solvent was removed in a stream of nitrogen.

The GLC analysis of the products as their methyl esters showed that the cleavage fragments were monobasic and dibasic acids, respectively.

**Analytical Methods**

Analytical data of oils were determined according to AOCS methods.
Iodine value (I.V.)

The fatty material was weighed accurately into an iodine flask (250 ml) and was dissolved in carbon tetrachloride (20 ml). Then Wijs’ solution (25 ml) was added. [Wijs’ solution was prepared by dissolving iodine monochloride (4 ml) in one litre of glacial acetic acid]. The weight of the sample was maintained in such a way that there would be an excess of Wijs’ solution of 100 to 150% over the amount required. After swirling, the iodine flask was kept in dark place for 30 minutes at room temperature. The flask was removed from dark storage.

Potassium iodide 15% solution (20 ml) and 100 ml of distilled water were added to the iodine flask. The contents of iodine flask were then titrated against 0.1N sodium thiosulphate solution using starch as an indicator. A blank titration was also carried out simultaneously.

\[
\text{Iodine value (I.V.)} = \frac{(A-B) \times N \times 12.69}{M}
\]

Where A and B are titre values of blank and samples, respectively. Similarly, M and N are weight of sample and normality of sodium thiosulphate solution, respectively.
Saponification value (S.V.)

1-2 gm of fatty material was weighed accurately and added to 0.5N alcoholic potassium hydroxide (25 ml) in a round bottom flask (250 ml) to which an air condenser was attached. The mixture was refluxed on a water bath for 1 hour and titrated against a standard 0.5N hydrochloric acid using phenolphthalein as an indicator. Simultaneously a blank reading was also carried out.

\[
\text{Saponification Value (S.V.)} = \frac{56.1 \times N \times (A-B)}{M}
\]

Where A and B are titre values of blank and sample, respectively. Similarly, M and N are weight of sample and normality of HCl, respectively.

Durbetaki titration\textsuperscript{171}

Preparation of Durbetaki reagent (0.1 N HBr in HAc)

20 gms of red phosphorus and 40ml of water were taken in a flask. To this 40ml of liquid bromine was added drop by drop from tap funnel. On addition of first few drops of bromine lambent green flame appeared but not when the air was displaced. At the end of the reaction, the flask was gently heated and the liberated HBr was passed through a U tube loosely fitted with broken glass smeared with moist red phosphorus (to remove bromine vapours) and was bubbled at a slow rate through 1 litre of glacial acetic acid until desired normality was attained.
Standardization of the reagent

About 0.4 gms of potassium phthalate was weighed and was dissolved in 10 ml glacial acetic acid. Then it is titrated with HBr solution using 5 drops of 1% crystal violet indicator (0.1 gm in 100 ml acetic acid) to a bluish green end point. Normality of HBr was calculated as follows.

\[
\text{Normality of HBr} = \frac{\text{Weight of pot. phthalate}}{0.2042 \times \text{Titration in ml}}
\]

Stepwise titration

About 300-500 mg of the oil sample was weighed in a 50 ml conical flask and was dissolved in 5 ml of distilled benzene. Four to five drops of indicator were added. Durbetaki reagent (HBr in acetic acid 0.1N) was taken in a semi-microburette and was added to the conical flask slowly with constant stirring at 3°C and 55°C, separately. The end point was observed by bluish green colouration.

The amount of HBr reactive fatty acid(s) present in the oil sample were calculated as follows.

\[
\begin{align*}
\% \text{ of cyclopropenoid fatty acid(s) (CPFAs) at 55°C} &= \frac{A \times N}{M} \times 28.8 \\
\% \text{ of epoxy fatty acid(s) (EFAs) at 3°C} &= \frac{A \times N}{M} \times 31.4
\end{align*}
\]

Where A is titre value in ml, M and N are weight of sample(s) and normality of HBr, respectively.
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