CHAPTER II

SYNTHESIS OF SUBSTITUTED UNDECANOIC ACIDS,
OXADIAZOLES AND TRIAZOLE DERIVATIVES
INTRODUCTION

During the last decade production and utilisation 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 industries such as coatings, surfactants, plasticizers, lubricant additives, cosmetics, pharmaceuticals, soaps, detergents, textiles, plastic and organic pesticides.

Starting with glyceride oils one can obtain products such as brominated oils, epoxidized oils, polymerized oils, sulphurised oils, sulphated and sulphonated oils, dehydrated castor oil, monoglycerides etc. These products were perhaps the first range of oleochemicals to be manufactured in our country.

Oleochemistry, now regarded as a mature branch of Chemistry, deals with synthesis of fatty chemicals, production of pharmaceuticals, soaps, detergents and protective coatings. A special strength of oleochemical industry is that it generates valuable products from non-edible oils or lower quality fats. Much larger amounts of oils and fats are transformed by chemical reaction into basic fatty materials for use in the important oil based industries. The fundamental reactions are saponification, hydrolysis, polymerisation,
interesterification and hydrogenation. Many oleochemicals are manufactured starting with fatty acids, the most important being (i) Nitrogen derivatives (ii) Esters (iii) Metallic soaps (iv) Alcohols (v) Dimeric acids and (vi) Ozonolysis products such as Pelargonic acid and Azelaic acids. In the world today nitrogen derivatives and esters are the two most important class of derivatives consuming more than 50 per cent of fatty acids

Reactions in the fatty acid chain

The reactions in fatty acid chain are described in brief.

Hydrogenation and Reductions

In the presence of suitable catalyst such as nickel, platinum or palladium, gaseous hydrogen adds to the double bonds of unsaturated fatty acids, transforming them to the corresponding saturated acids or reducing degree of unsaturation

The partial reduction of double bond may be achieved by the use of hydrazine and oxygen which, unlike partial hydrogenation does not involve the migration of bonds. The reaction has been assumed to be represented by the following equation.

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

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

\[
\begin{array}{c}
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{C} = \text{C} \quad \text{C} \\
\text{H} \quad \text{H}
\end{array}
\quad + \quad \begin{array}{c}
\text{Br}_2
\end{array}
\quad \rightarrow \quad \begin{array}{c}
\text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\end{array}
\quad \begin{array}{c}
\text{H} \quad \text{H} \quad \text{H} \\
\text{Br} \quad \text{Br}
\end{array}

Addition takes place readily but in quantitative yield only under special conditions, because the halogens tend to add incompletely or to replace hydrogen atoms (substitution reactions).

Halogenated fatty compounds have several uses: a) they have use in several novel applications, for example, brominated fatty acid derivatives contribute anti-flammability properties to textile additives, b) they are reactive intermediates for the preparation of other compounds by replacement of the halo groups with hydroxyl, cyano, sulphonic acid, or phosphonic acid groups, c) those prepared by substitution offer the possibility of yielding chains of increased unsaturation by dehydrohalogenation processes.

Addition of sulphur dichloride

Sulphur dichloride, \( \text{SCl}_2 \), reacts readily with olefins (reaction with ethylene affords "mustard gas"\(^2\)) Grimm\(^3\) studied the addition...
of sulphur dichloride to various monoethenoid fatty materials (methyl oleate, methyl elaidate, oleomtriile) and ethyl linoleate and found that the products, $\beta, \beta'$-dichlorosulphides (I), could be easily oxidized with peracetic acid to the corresponding $\beta, \beta'$-dichlorosulphoxides (II), and $\beta, \beta'$-dichlorosulphones (III):

$$2RCH=CHR + SCl_2 \rightarrow [O] \rightarrow R'Cl R'Cl R'Cl R'Cl$$

(I)

$$R\begin{array}{c} \text{CH} \\ \text{CH} \end{array} \begin{array}{c} \text{S} \\ \text{S} \end{array} \begin{array}{c} \text{CH} \\ \text{CH} \end{array} \begin{array}{c} \text{R} \\ \text{R} \end{array} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array}$$

(II)

$$R\begin{array}{c} \text{CH} \\ \text{CH} \end{array} \begin{array}{c} \text{S} \\ \text{S} \end{array} \begin{array}{c} \text{CH} \\ \text{Cl} \end{array} \begin{array}{c} \text{CH} \\ \text{Cl} \end{array}$$

(III)

$$R=CH_3(CH_2)_7-, -(CH_2)_7COOR, \text{ or } -(CH_2)_7CN$$

When $R' = -(CH_2)_7COOR, -(CH_2)_7CN, \text{ or } CH_3(CH_2)_7-, \text{ respectively.}$

The products from monoethenoids were definite and characterizable, those from ethyl linoleate were complex, darkly coloured polymeric materials $\beta, \beta'$-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.

\[
\text{\begin{align*}
\text{Cl} & \\
\text{CH}_3\text{(CH}_2\text{)}_2\text{CH} & - \text{CH(CH}_2\text{)}_7\text{COOH} \\
\text{S} & \\
\text{Cl} & \\
\text{CH}_3\text{(CH}_2\text{)}_7\text{CH} & - \text{CH(CH}_2\text{)}_7\text{COOH}
\end{align*}}
\]

+ positional isomers

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

\[Z = \text{OH}, \text{NH}_2, \text{RNH}, \text{many others}\]

Addition of hydrogen cyanide and nitriles

Ritter\textsuperscript{4-6} and others\textsuperscript{7} added hydrogen cyanide and a variety of nitriles to olefins in strong acid media to give substituted amides in excellent yields

\[
\text{RCN} + \text{C} = \text{C} \xrightarrow{(1) \text{H}^+} \xrightarrow{(2) \text{H}_2\text{O}} \text{RCONHCH} - \text{CH}
\]

Roe and Swern applied this reaction to oleic acid\textsuperscript{8} and noted, in general, that sulphuric acid undoubtedly caused positional
isomerization through double bond migration, and that the products were slow to crystallize during the hydrolysis step. They postulated the existence of an intermediate (IV) •

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_x \text{CH(\text{CH}_2)}_y & \text{COOH} \\
\text{N} & \\
\text{R} - \text{C-O-SO}_3 \text{H} \\
(\text{IV})
\end{align*}
\]

\[x + y = 15\]

Which must hydrolyze and tautomerize to yield the substituted amide product. Under similar reaction conditions, hydrogen cyanide, acetonitrile, acrylonitrile, propionitrile and benzonitrile were successfully added to petroselinic acid but small amounts of sulphur apparently remained in some of the products.

**Addition of thiocyanogen**

Kaufmann discovered that thiocyanogen adds smoothly and quantitatively to isolated double bonds, and since that time it has been shown to add nearly quantitatively to the double bond of oleic acid, to one of the two double bonds of linoleic acid, and to two of the three double bonds of linolenic acid.

\[
\begin{align*}
-\text{CH} = \text{CH} - & \quad + (\text{SCN})_2 \\
\text{SCN} & \quad \text{SCN}
\end{align*}
\]
Silbert, Russell, and Showell\textsuperscript{11} examined the addition of thiocyanogen to both cis- and trans-9-octadecene and methyl oleate. Subsequently they and others studied other olefinic species, solvent effects, and other reaction variables\textsuperscript{12}. They separated a number of products from the addition reaction and elucidated the stereochemistry of the reactions to cis and trans olefins, and also showed that a complex mixture of products was obtained, including dithiocyanates, thiocyanates-isothiocyanates, and products that involved solvent incorporation in some cases. The reaction is more complex than originally reported\textsuperscript{9}.

**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 (Diels-Alder) is useful in the study of acids with conjugated unsaturation. Its value for structural interpretation is increased by the fact that it only occurs readily with trans-trans-diene systems. Catalpic acid and octadeca-trans-9-, trans-11-dienoic acid, for example, readily form maleic anhydride adducts which are identical after hydrogenation. This confirms that catalpic contains a 9t,11t-diene system.

\[
\begin{align*}
\text{Maleic anhydride} & \rightarrow \text{Maleic anhydride adduct} \\
\text{Catalpic acid} & \rightarrow \text{Hydrogenation product}
\end{align*}
\]
The Friedel-Crafts reaction of aromatic compounds with oleic acid acting as an olefin has been known for many years. Benzene reacts with oleic acid with highly acidic catalysts, such as sulphuric acid, to give mixed phenylstearic acids consisting of 12 different positional isomers. The 13-, 15-, 16-, and 17-phenylstearic acids have actually separated out of such complex mixtures.

10-Undecenoic acid reacts with benzene in the Friedel-Crafts reaction to give mixed phenylundecanoic acids that consists of 11.6% of a mixture of 5- and 6-phenyl isomers, and 15.1%, 17.0%, 21.0% and 35.3% of the 7-, 8-, 9-, and 10-isomers, respectively. Thus it is to be expected that the relatively smooth addition of phenols and cresols to the oleic acid double bond is accompanied by substantial double bond migration.
The reaction of long chain olefins with phenol proceeds in the temperature range 200-425°C without a catalyst, and the products are characterized structurally as predominantly straight-chain (addition at 1-position of the olefin) and branched-chain (addition at 2-position of the olefin) with the alkyl group in the product occupying the ortho position of the aromatic ring. Methanesulphonic acid functions as both catalyst and solvent in the addition of phenol and its homologues to methyl linoleate. Cresol reacts 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 is exceedingly complex.

\[
\text{CH}_3 \left( \text{CH}_2 \right)_7 \text{CH} = \text{CH} \left( \text{CH}_2 \right)_7 \text{COOH} + \text{CH}_3 \left( \text{CH}_2 \right)_x \text{CH} \left( \text{CH}_2 \right)_y \text{COOH} \rightarrow
\]

\[
x + y = 15
\]

(One of a series of isomers)

**Addition of hydrogen sulphide and mercaptans**

Within the last 10 years detailed work has been carried out on the addition of hydrogen sulphide and mercaptans to the unsaturated...
bonds of fatty materials. It has been appreciated for some time that the addition of mercaptans to double bonds is feasible, especially since the use of mercaptans in the elaidimization of methyl oleate to methyl elaidate indicated that a small amount of sulphur remains bound in the methyl elaidate product. Practically, the reaction has been applied for many industrial products, lubricants, synthetic rubbers, flotation collectors, and others. However, there has been an effort to understand the reaction mechanisms and the structures of the several products that are obtained.

Schwab, Gast, and Rohwedder were able to accomplish the nucleophilic addition of hydrogen sulphide to methyl oleate, methyl linoleate, and soybean oil at -70 to +25°C with boron trifluoride. With excess H₂S and methyl oleate at -70°C the primary reaction product, as expected, is methyl 9(10)-mercapto-stearate.

\[
\text{SH} \\
\text{CH}_3(\text{CH}_2)_7\text{CH}((\text{CH}_2)_8\text{COOH}_3 \\
\text{CH}_3(\text{CH}_2)_8\text{CH}(\text{CH}_2)_7\text{COOH}_3 \\
\text{SH}
\]

Sulphation and sulphonation

Unsaturated acids react readily at the double bond with concentrated sulphuric acid with the introduction of either the sulphate group OSO₂OH or, at elevated temperatures, the sulphonate group SO₃OH.
Hydroxyl groups, if present, as in the case of castor oil or monoglycerides, are readily sulphated to form esters. This reaction, followed by neutralization of the resulting sulphuric ester with sodium carbonate, is carried out industrially and extensively in the preparation of so-called sulphonated oils for the textile industry.

The \( \alpha \)-sulphonation of saturated fatty acids is conveniently carried out with sulphur trioxide in dioxane. Stirton \(^{19}\) et al. have prepared a series of them in order to evaluate the sodium salts as detergent materials. Ault \(^{20}\) et al prepared a series of branched-chain fatty acids by the free radical addition of \( \alpha \)-olefins to saturated acids and showed that the products were easily \( \alpha \)-sulphonated. Simple directions for the \( \alpha \)-sulphonation of palmitic and stearic acids in carbon tetrachloride and dioxane using sulphur trioxide have been given by Stirton \(^{21}\).

The preparation of sulphonated castor oil using sulphur trioxide\(^{22}\) 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, acids, and other esters by partially sulphating the unsaturated bonds, followed by hydrolysis to remove the sulphate group for replacement by the hydroxyl group\(^{23}\). Oleic-rich oils or fatty acids afford hydroxy products corresponding to 50-70% of
the original monoene content Safflower oil is partially sulphated, without side reactions with 78-79% (wt/wt) sulphuric acid. The hydrolyzed products show hydroxyl values of about 35 for a loss of 13 units of iodine value.

Addition of carbon monoxide

The reaction of carbon monoxide with the double bonds of fatty acids conforms to at least three modes of addition:

1 Hydroformylation

\[
\text{CHO} + \text{H}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_2\text{CHO} + \text{CH}_2\text{OH}
\]

2 Koch reaction

\[
\text{CHO} + \text{H}_2 \xrightarrow{\text{Ni(CO)}_4} \text{CH}_2\text{R} + \text{CH}_2\text{OH}
\]

3 Reppe reaction

\[
\text{CHO} + \text{ROH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_2\text{R}
\]

The products of all three reactions are usually mixtures of many positional isomers.
A. General methods of synthesis of 1,2,4-triazoles

In 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 the 1,2,3-triazoles or v-triazole (I) and 1,2,4-triazoles or s-triazoles (II).

\[
\begin{align*}
\text{I} & : & \begin{array}{c}
\text{HC} \quad \text{N} \\ \text{HC} \quad \text{N} \\ \text{HC} \quad \text{N}
\end{array} & \quad \begin{array}{c}
\text{HC} \quad \text{N} \\ \text{HC} \quad \text{N} \\ \text{HC} \quad \text{N}
\end{array} \\
\text{II} & : & \begin{array}{c}
\text{HC} \quad \text{N} \\ \text{HC} \quad \text{N} \\ \text{HC} \quad \text{N}
\end{array} & \quad \begin{array}{c}
\text{HC} \quad \text{N} \\ \text{HC} \quad \text{N} \\ \text{HC} \quad \text{N}
\end{array}
\end{align*}
\]

Ring closure of acyl derivatives of aminoguanidines, semicarbazides or thiosemicarbazides in alkaline solutions is a method widely applied for the preparation of s-triazoles.

1. Triazoles from formhydrazine and formamide

The fusion of an N-formyl-N-alkyl or aryl hydrazine with formamide at 250-280°C results in the formation of substituted triazoles in poor yield. 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 reaction.24
2. Preparation of 3-aminotriazoles via formylaminoguanidine

The preparation of 3-aminotriazoles via N-formylaminoguanidine was readily accomplished by heating a mixture of an aminoguanidine salt (H₂CO₃, HCl, HNO₃, H₂SO₄) and formic acid in toluene²⁵, ²⁶

\[
RNHNCONH₂ + HCHO + HCOOH \xrightarrow{\Delta} RNHNCONH₂ + HCONH₂ + RNHN₂HCl
\]

3. Triazoles from arylsemicarbazides

1-arylsemicarbazide on boiling with anhydrous formic acid yielded 3-hydroxy-1-aryl-1,2,4-1H-triazoles. The removal of hydroxy group was accomplished by heating (III) to over 200°C with P₂S₅. 1-aryl-1,2,4-1H-triazole is obtained in 80% yield.²⁷

\[
RNHNCONH₂ + HCOOH \quad \xrightarrow{\text{H₂O}} \quad RNHNCONH₂ + HCOOH \quad \xrightarrow{\text{H₂O}} \quad RNHNCONH₂ + HCOOH \quad \xrightarrow{\text{H₂O}} \quad RNHNCONH₂ + HCOOH \quad \xrightarrow{\text{H₂O}} \quad RNHNCONH₂ + HCOOH
\]

\[
R = C₆H₅
\]
4. Cyclisation of acythiosemicarbazides

Base catalysed cyclisation of 4-acylthiosemicarbazides resulted to give 3-aryl-5-mercapto-1,2,4-triazoles as reported by Hoggarth.\(^2\)

\[
\text{ArCONHNCSNH} \xrightarrow{\text{alkali}} \text{Ar} - \text{C} - \text{C} - \text{SH}
\]

5. Triazoles from s-triazines

Reaction of substituted hydrazine salt with s-triazine resulted in the formation of substituted 1,2,4-triazoles\(^2\) : for example 1-phenyl-1,2,4-1H-triazole is obtained in 83% yield when phenylhydrazine hydrochloride is treated with s-triazine. This reaction involves a cleavage of a molecule of s-triazine to yield a substituted formamidrazono, which reacts immediately with another molecule of s-triazine to yield the substituted triazole and ammonia.

\[
\text{+ 3NH}_2\text{NPhHCl} \xrightarrow{} \text{3HC} \text{NH}_2\text{HCl} \xrightarrow{\text{NH}_4\text{Cl}} \text{R} = \text{C}_6\text{H}_5
\]
B. General methods of synthesis of 1,3,4-oxadiazoles

In five membered ring systems the presence of two nitrogen and one oxygen heteroatoms makes the nucleus known as oxadiazoles. The four possible structures are as follows

1. Oxadiazoles from thiosemicarbazides

Stolle and Gaertner synthesized 1,3,4-oxadiazoles by cyclisation of thiosemicarbazides with PbO and NaN₃ in ethanol to give 2-substituted-5-aryl-1,3,4-oxadiazoles.

\[
\text{RCONHNHCSNHR'} \xrightarrow{\text{PbO/NaN}_3} \quad \begin{array}{c}
\text{N} \\
\text{C-R}
\end{array}
\]

\[
R = \text{aryl, } \quad R' = \text{arylamino}
\]
Hoggarth\textsuperscript{31} synthesised 2-amino-5-phenyl-1,3,4-oxadiazoles by heating 1-benzoyl-s-methyliso-thiosemicarbazide for 10 minutes at 200°C.

\[
\begin{align*}
C_6H_5{-}\text{CONH-N=C-NH}_2 & \xrightarrow{200°C} H_5C_6{-}\text{C-N=C-NH}_2 \\
\text{S-CH}_3
\end{align*}
\]

Silberg and Cosma\textsuperscript{32} prepared 1,3,4-oxadiazoles by oxidative cyclisation of thiosemicarbazides with iodine in potassium iodide.

\[
\begin{align*}
\text{RCONHNHC}_{6}H_5 & \xrightarrow{I_2 \text{in KI}} \text{R-C-} \text{C-NHC}_{6}H_5 \\
\text{R = C}_6H_5, \text{p(Cl)}C_6H_4, \text{o(OH)}C_6H_4, \text{p(NO}_2)C_6H_4
\end{align*}
\]

2 Synthesis of oxadiazoles from hydrazines

2,5-Diaryly-1,3,4-oxadiazoles are prepared by the cyclisation of the corresponding 1,2-diarylhydrazine in the presence of dehydrating agent, such as acetic anhydride\textsuperscript{33}.

\[
\begin{align*}
\text{O} & \text{O} & \xrightarrow{\text{Ac}_2O} \text{N} & \text{N} \\
\text{R-C-NH-NH-C-R'} & \xrightarrow{\text{Ac}_2O} \text{R-C-} \text{C-R'}
\end{align*}
\]

1,3,4-oxadiazoles are also prepared by the condensation of an acid hydrazide of aromatic carboxylic or carbothionic acid with orthoester such as ethyl ortho formate\textsuperscript{34}.
Konig\textsuperscript{35} et al. prepared 2-hydroxy-5-(4-pyridyl)-1,3,4-oxadiazoles and 2-mercapto-5-(4-pyridyl)-1,3,4-oxadiazole by reacting isonicotinic acid hydrazide with phosgene or thiophosgene.

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

3. **Synthesis of oxadiazoles from semicarbazones**

2-amino-5-phenyl-1,3,4-oxadiazoles are prepared from benzaldehyde semicarbazone and sodium hypoiodide or hypobromite\textsuperscript{35}.

4. **Oxadiazoles from Schiff's bases**

Saikachi\textsuperscript{37} synthesized 5-substituted-2-(2-furyl)-1,3,4-oxadiazoles by oxidative cyclisation of Schiff's bases by lead tetracetate.
R = 2-furyl, 2-thienyl and substituted phenyl.

However, 1,3,4-oxadiazoles are also prepared by heating appropriate hydrazides with carbon disulfide and alcoholic alkali.\(^{38}\)
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PRESENT WORK

The reactions between phenols and unsaturated compounds have been known for a long time. The addition of phenols and phenyl ethers to oleic acid has been reported by Roe and co-workers. The derivatives of this type are of a great interest as lubricant additives. Keeping these facts in view, the present investigation describes the novel type of acid-catalyzed addition of phenols such as phenol, m-cresol, m-amino phenol and anisole, to undec-10-enoic acid. There are no reports in the literature on the reactions of these phenols with undec-10-enoic acid.

Phenols and phenyl ether have been added to undec-10-enoic acid, using 95% sulphuric acid. The products formed on addition, resulted in low yields and were difficult to purify. The chromatographic techniques were used for the purification and separation of the compounds. However, the present investigation describes the characterisation and identification of the only major products (p-isomers).

The newly synthesised substituted arylundecanoic fatty acids were converted into corresponding methyl esters and were further converted into oxadiazole and triazole derivatives. These were characterised by IR, NMR and elemental analyses.
RESULTS AND DISCUSSION.

Scheme I

\[ CH_2 = CH - (CH_2)_8 - COOH \xrightarrow{1) 95\% H_2SO_4} CH_3 - CH - (CH_2)_8 - COOH \_H_3 \]

11) Phenols/phenylether  
111) At 18-22°C  
iv) Hydrolysis  
v) Esterification

\[ R = \]

(a)  \[ \text{OH} \]  
(b)  \[ \text{OCH}_3 \]  
(c)  \[ \text{and} \]  
(d)  \[ \text{NH}_2 \]

Mechanism

\[ H_2SO_4 \xrightarrow{\text{H}^+ + HSO_4^-} \]

\[ R' - CH=CH_2 + H_2SO_4 \xrightarrow{} R' - CH - CH_3 + HSO_4^- \]

where  
\[ R' = -(CH_2)_8-COOH \]

(p-isomer) Major product  
[0-isomer] Negligible
Spectral studies

The structures of newly synthesised aryl substituted undecanoic acids (Ia to Id) were characterised by IR, NMR and elemental analysis. IR spectra of all the compounds were taken on Hitachi 270-30 model instrument using KBr pallets. The 1H NMR spectra of all the compounds were recorded on Varian T-60 model instrument using CDCl₃ as solvent and TMSi as internal standard.

Methyl-10-(4-hydroxyphenyl)undecanoate.

The methyl-10-(4-hydroxyphenyl)undecanoate (B.P. 138-140°C) gave infrared absorption bands at 3460 cm⁻¹ and 1705 cm⁻¹ for hydroxyl and ester functional groups respectively. The n.m.r. spectra exhibited signal at δ 5.25-6.35 for hydroxyl proton which disappeared on addition of D₂O. Aromatic protons multiplet integrating were observed at δ 6.85-7.35 and at δ 3.69-3.78 for -C-OCH₃. The elemental analysis showed carbon 73.90% and hydrogen 9.51%.

Methyl-10-(p-methoxyphenyl)undecanoate.

The methyl-10-(p-methoxyphenyl)undecanoate (B.P. 120-122°C) showed infrared absorption bands at 1705 cm⁻¹ for ester functional group. The n.m.r. spectrum gave signal at δ 6.75-7.20 (aromatic protons), δ 3.80-3.90 (-OCH₃) and δ 3.69-3.75 (-C-OCH₃). The elemental analysis showed carbon 74.40% and hydrogen 9.69%.
Methyl-10-(2-methyl-4-hydroxyphenyl)undecanoate

The methyl-10-(2-methyl-4-hydroxyphenyl)undecanoate (B.P. 100-102°C) showed infrared absorption bands at 3450 cm\(^{-1}\) and 1710 cm\(^{-1}\) for hydroxyl and ester functional groups respectively. The n.m.r spectra exhibited signal at \(\delta\) 5.75-6.20 for hydroxyl proton which disappeared on addition of D\(_2\)O. The other signals appeared at \(\delta\) 3.65-3.70 for \(-\text{OCH}_3\) at \(\delta\) 6.8-7.3 for aromatic protons and at \(\delta\) 2.75-2.90 for m-CH\(_3\). Elemental analysis showed carbon 74.41\% and hydrogen 9.70\%.

Methyl-10-(2-amino-4-hydroxyphenyl)undecanoate

The 10-(2-amino-4-hydroxyphenyl)undecanoate (B.P. 228-230°C) showed infrared absorption bands at 3450 cm\(^{-1}\), 3320 cm\(^{-1}\), and 1705 cm\(^{-1}\) for hydroxyl, amino and ester functional groups respectively. The n.m.r. signals exhibited at \(\delta\) 5.35-6.20 and 6.8-7.25 for hydroxyl and amino protons which disappeared on addition of D\(_2\)O. The other signals showed at \(\delta\) 3.69-3.80 and 7.85-8.35 for ester and aromatic protons respectively. The elemental analysis showed carbon 70.31\%, hydrogen 9.41\% and nitrogen 4.51\%.

These results together with elemental analysis, established the substitution and protonation at C\(_{10}\) and C\(_{11}\) respectively in the undec-10-enoic acid.
The newly prepared substituted arylundecanoic fatty esters were further converted into oxadiazole and triazole derivatives and were characterised by IR, NMR and elemental analyses. The details are given in Scheme II.

Scheme II

R - COOCH₃ → RCONNH₂ → RCONHNH₂

KOH

CS₂

(II)

KCNS/CH₃OH/HCl

R - CONHNHCSNH₂ → R - CONHNHCSNH₂

KOH

pH, 5-6

(IV)

(II)

(III)

(thiol)

(thione)

(thiol)

(thione)

R =

(a) CH₃ - CH - (CH₂)₈ -

(b) CH₃ - CH - (CH₂)₈ -

(c) CH₃ - CH - (CH₂)₈ -

(d) CH₃ - CH - (CH₂)₈ -
The IR spectra of mercapto-triazole derivatives showed the characteristic band 3396-3198 cm\(^{-1}\) for (-NH) group. A band around 1600-1525 cm\(^{-1}\) was observed due to (C=N) stretching. The mercapto-oxadiazole and mercapto-triazole derivatives showed band at 1138-1100 cm\(^{-1}\) for (C=S) and absence of any band around 2600-2550 cm\(^{-1}\) revealed that these compounds exist in thione form rather than thioles. Mercapto-oxadiazoles showed characteristic band at 1260-1050 cm\(^{-1}\) for (=O-C=) However, the other usual bands were also observed in different compounds.

\(^1\)HNMR spectra (CDCl\(_3\)) of oxadiazole derivatives showed broad peaks (-NH) at δ 6.5-8.5 which disappeared on shaking with D\(_2\)O. Similarly, the triazole derivatives showed the expected chemical shifts due to -NH. The absence of an up-field chemical shift due to -SH group, supported the thione structure instead of the thiol structure.
1 Roe, E.T., Parker, W.E., & Swern, D.,

EXPERIMENTAL

Preparation of methyl (p-hydroxyphenyl)undecanoate

A homogeneous mixture of undec-10-enolic acid (0.115 mole) and of phenol (0.45 mole) was added in 45 minutes to 95% sulphuric acid (0.99 mole) with rapid stirring. The temperature was maintained between 18-22°C by external cooling. After complete addition, the mixture was poured into crushed ice and water and extracted with ether. The solvent was removed. The methyl esters were prepared and were distilled. The major fractions were collected and purified by the preparative t.l.c.

Similarly corresponding esters were prepared by using anisole, m-cresol, m-aminophenol and undec-10-enolic acid.

Preparation of hydrazides

To a solution of an appropriate acid ester (0.1 mole) in 150 ml ethanol was added to 95% hydrazine hydrate (0.2 mole) and the mixture was heated under reflux for 4-5 hours. It was allowed to cool and the solid that separated was collected, washed with ethanol and dried.

For analytical purpose, the crude compound was recrystallised from ethanol.
Preparation of 2-substituted-5-mercapto-1,3,4-oxadiazoles³

To a solution of an appropriate hydrazide (0.01 mole) in 10 ml of ethanol, a solution of carbon disulphide (2 ml) in 3 ml of water and 1 gm of potassium hydroxide was added, and the mixture was refluxed for 8-10 hours until the H₂S is ceased. It was cooled and acidified with dilute hydrochloric acid. The solid mass that separated was collected. It was filtered, washed with distilled water and dried.

For analytical purpose the crude mass was recrystallised from ethanol.

Preparation of thiosemicarbazides⁴

To a solution of an appropriate acid hydrazide (0.02 mole) in 50 ml methanol, a solution of potassium thiocyanate (0.03 mole) and 3 ml hydrochloric acid was added with constant stirring. The mixture was immediately evaporated to dryness on a steam bath and heated for an additional hour with another 50 ml of methanol. The resulting solid was treated with distilled water, and with little ethanol.

For analytical purpose, the crude compound was recrystallised from ethanol.
Preparation of 3-substituted-5-mercapto 4H-1,2,4-triazoles

To a solution of an appropriate thiosemicarbazide (0.01 mole) in 15 ml of ethanol, a solution of 10.0% potassium hydroxide (20 ml) was added and the reaction mixture was refluxed immediately for 8-10 hours on boiling water-bath. It was cooled and acidified with dilute hydrochloric acid at pH 5-6. The resulting solid is filtered off, washed with distilled water and dried.

For analytical purpose the crude compound was recrystallised from ethanol.

Elemental analyses, yield and melting points of all the compounds are given in Table I. Melting points were determined by open capillary method and are uncorrected.
## Table I

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Compound</th>
<th>Yield %</th>
<th>M.P °C/ B.P. °C</th>
<th>Carbon %</th>
<th>Hydrogen %</th>
<th>Nitrogen %</th>
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<tbody>
<tr>
<td>1</td>
<td>Ia</td>
<td>56</td>
<td>B.P. 138-140 °C</td>
<td>73.97</td>
<td>73.90</td>
<td>9.59</td>
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<tr>
<td>2</td>
<td>Ib</td>
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<td>B.P. 120-122 °C</td>
<td>74.51</td>
<td>74.40</td>
<td>9.80</td>
</tr>
<tr>
<td>3</td>
<td>Ic</td>
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<td>B.P. 100-102 °C</td>
<td>74.51</td>
<td>74.42</td>
<td>9.80</td>
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<tr>
<td>4</td>
<td>Id</td>
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<td>B.P. 226-228 °C</td>
<td>70.36</td>
<td>70.31</td>
<td>9.45</td>
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<tr>
<td>5</td>
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<td>M.P. 56-58 °C</td>
<td>69.86</td>
<td>69.71</td>
<td>9.59</td>
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<tr>
<td>6</td>
<td>IIb</td>
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<td>M.P. 52-54 °C</td>
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<td>70.51</td>
<td>9.80</td>
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<td>65.00</td>
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<td>8.03</td>
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</table>
SPECTRUM NO.

\[
\text{CH}_3\text{CH}-(\text{CH}_2)_8\text{CH}_2\text{NH}_2
\]

\[
\text{H}_2\text{O}
\]
REFERENCES


