CHAPTER 3

PRESENT INVESTIGATION
RESULT AND DISCUSSION

PRESENT INVESTIGATION RESULTS

AND DISCUSSION

Any chemical used to destroy or inhibit plant growth, especially of weeds or other undesirable vegatation is termed as herbicide. The concept of modern herbicide technology began to develop about 1900 and accelerated rapidly with the discovery of dichlorophenoxy acetic acid (2,4-D) as a growth-regulator type herbicide in 1944-45. Since the introduction of 2,4-D a wide variety of organic herbicides have been developed and have received wide usage in agriculture, forestry and other industries. Today, the development of highly specific herbicides that are intended to control specific weed types continues. Modern usage often combines two or more herbicides to provide the desired weed control. Worldwide usage of herbicides continues to increase, making their manufacture and sale a major industry.

2,4-D, 2,4DB butyl/Ethylester of 2,4-D as well as butoxyethanol ester of 2,4-D are widely used to control weeds in cereals, milo, corn, aquatic and general weed, soybeans & other broad leafed crops, cotton, legumes, flax, sugarcane, rice etc.

CNSL is an indigenously available raw material a byproduct of cashew processing industries in India. In order to make it's valuable use, a study was undertaken for synthesis of (3-pentadecyl) phenoxy acetic acid (1) which possesses long straight chain alkyl group besides the phenoxy acetic acid moiety. It was expected that the low volatility of ester/amide derivatives of (1) would be an important factor in usefulness of these new

potential herbicides.

The unique feature of cardanol, a meta-substituted long chain alkylphenol containing an average of two double bonds in the alkyl side chain and obtained by distillation of cashewnut shell liquid (CNSL) under reduced pressure is that on catalytic hydrogenation it gives 3-pentadecylphenol (tetrehydroanacardol, THA) which offers a great chemical maneuverability for the synthesis of a variety of compounds.

In view of the availability of CNSL in abundance, and the biological activity shown by various aryloxyacetic acids[1], 3-pentadecylaryloxy acetic acid, 4-chloro-3-pentadecyl aryloxyacetic acid, 4,6-dichloro-3-pentadecyl aryloxyacetic acid[40] and corresponding 1-(3-pentadecylaryloxyacetamido) -2, 5-dimethylpyrroles etc, it was considered of interest to synthesise esters and amides incorporating a THA moiety and characterise them spectroscopically . It has been shown that presence of a long alkyl chain ($C_{15}H_{31}$) renders the compounds to be less toxic[4] as evidenced by higher values of their LD_{50} as compared to corresponding methyl substituted derivatives. Further THA containing moieties showed significant anti inflammatory activity in rats.

Thus, the present investigation was undertaken with a view to synthesize two new series of derivatives :esters and amides of (3-pentadecyl) phenoxy acetic acid from naturally occuring renewable resource, Cashewnut shell liquid (CNSL), as a basic raw material. The present study includes the synthesis and characterisation of following.

1. (3-pentadecyl)- phenoxyacetic acid. Ester, and Amide derivatives were prepared because at present widely used herbicides

are alkyl esters of 2,4-D and 2,4-D acetamides.

2. a (3-pentadecyl)-phenoxy methylacetate

   b (3-pentadecyl)-phenoxy ethylacetate

   c (3-pentadecyl)-phenoxy isopropylacetate

   d (3-pentadecyl)-phenoxy butylaectate

   e (3-pentadecyl)-phenoxy amylacetate

3. a (3-pentadecyl) -phenoxy -(N-phenyl) acetamide

   b (3-pentadecyl) -phenoxy [N-(m-nitrophenyl)] acetamide

   c (3-pentadecyl) -phenoxy [N-(p-nitrophenyl)] acetamide

   d (3-pentadecyl) -phenoxy [N-(p-bromophenyl)] acetamide

   e (3-pentadecyl) -phenoxy [N-(α-naphthyl)] acetamide

   f (3-pentadecyl) -phenoxy [N-(m-methylphenyl)] acetamide

   g (3-pentadecyl) -phenoxy [N-(p-methoxyphenyl)] acetamide
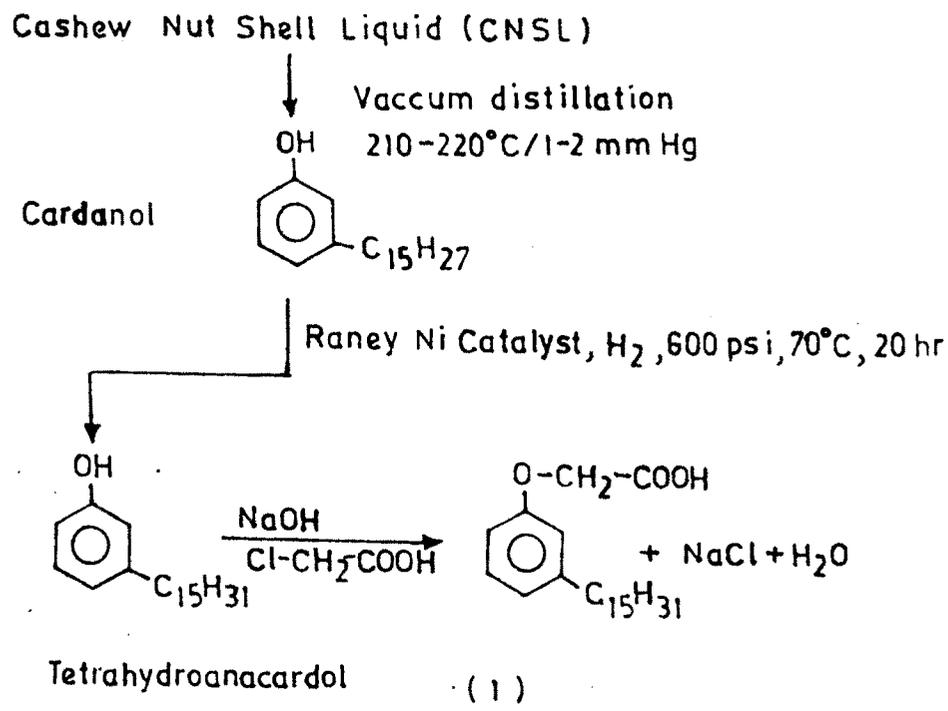
Compound Nos 2b to 2e and 3a to 3g (total 11) have been synthesized for the first time, whereas though compound No. 1 have been reported it's detailed C-13 characterisation has been performed in the present studies. Similarly all esters (2a to 2e) and amides (3a to 3g) have been analysed for IR, PMR, CMR, and mass spectroscopy to ellucidate the structural moieties. All above compounds are potential herbicides.

Commercially available CNSL was distilled under reduced pressure to obtain pale yellow coloured cardanol which was further hydrogenated as described in literature. The hydrogenation was carried out at 70°C using Raney Nickel catalyst in pressure reactor till there is no more hydrogen absorption[31]. TLC of the product gave a single spot and melted at 51°C on crystallisation from petroleum ether (60-80).

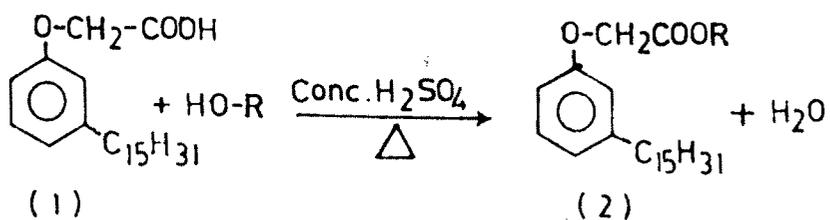The THA was characterised by IR, and PMR. The proton

SCHEME -1

Synthesis of 3-pentadecyl phenoxy acetic acid

Cashew Nut Shell Liquid (CNSL)

$\downarrow$ Vaccum distillation
210-220°C/1-2 mm Hg

Cardanol

OH
$C_{15}H_{27}$

Raney Ni Catalyst, H_2, 600 psi, 70°C, 20 hr

OH
$C_{15}H_{31}$

$\xrightarrow[Cl-CH_2COOH]{NaOH}$

$O-CH_2-COOH$
$C_{15}H_{31}$ $+ NaCl + H_2O$

Tetrahydroanacardol   (1)

SCHEME - 2

Syntheses of (3-pentadecyl) phenoxy alkyl acetates

$O-CH_2-COOH$
$C_{15}H_{31}$ $+ HO-R$ $\xrightarrow[\triangle]{Conc.H_2SO_4}$ $O-CH_2COOR$
$C_{15}H_{31}$ $+ H_2O$

(1)   (2)

$R = -CH_3$ 2 a
$= -C_2H_5$ 2 b
$= -CH(CH_3)_2$ 2 c
$= -CH_2-CH_2-CH_2-CH_3$ 2 d
$= -CH(CH_3)(C_3H_7)$ 2 e

NMR spectrum of THA showed aromatic protons signal over the region of 6.5 to 7.25 δ (m,4H). The methylene protons of the pentadecyl side chain directly attached to the benzene nucleus appear at 2.5 δ (t,2H). The other methylene protons of the pentadecyl side chain appeared at 1.25 δ(s,26H). The methyl protons showed at $\emptyset$.9 δ(t,3H). The phenolic hydroxyl proton appered at 4.6 δ (bs,1H).

3.1 Synthesis and Characterisation of (3-pentadecyl) phenoxy acetic acid :-

The derivatization of THA into (3-pentadecyl) phenoxy acetic acid (1) was effected with chloroacetic acid using tetra-alkyl ammonium halide catalyst in aq. sodium hydroxide in good yields[32]. It was observed that the reaction does not take place without catayst. The compound was characterised by IR, NMR spectroscopy and mass spectrometry.

The IR spectrum of (1) showed the carbonyl absorption (of -COOH) at 1727 cm^{-1} (fig.1) indicating formation of aryloxyacetic acid derivative of THA. Mass spectrum of (1) showed peak at m/e 362 corresponding to molecular ion peak. Loss of $C_{15}H_{31}$ gave peak at m/e 12$\emptyset$ (Table VI). Loss of CH_2 units successively is evident by peaks at regular interval of 14 units. Compound (1) was converted into a number of acid derivatives belonging to class of ester and amide.

3.2 Synthesis and Characterisation of (3-pentadecyl) Phenoxy alkylacetates (2a) to (2e) :-

Esterification reactions on (1) were performed using concentrated sulfuric acid catalyst with excess of lower alcohols containing C_1 to C_5 viz. methanol, ethanol, isopropanol, butanol

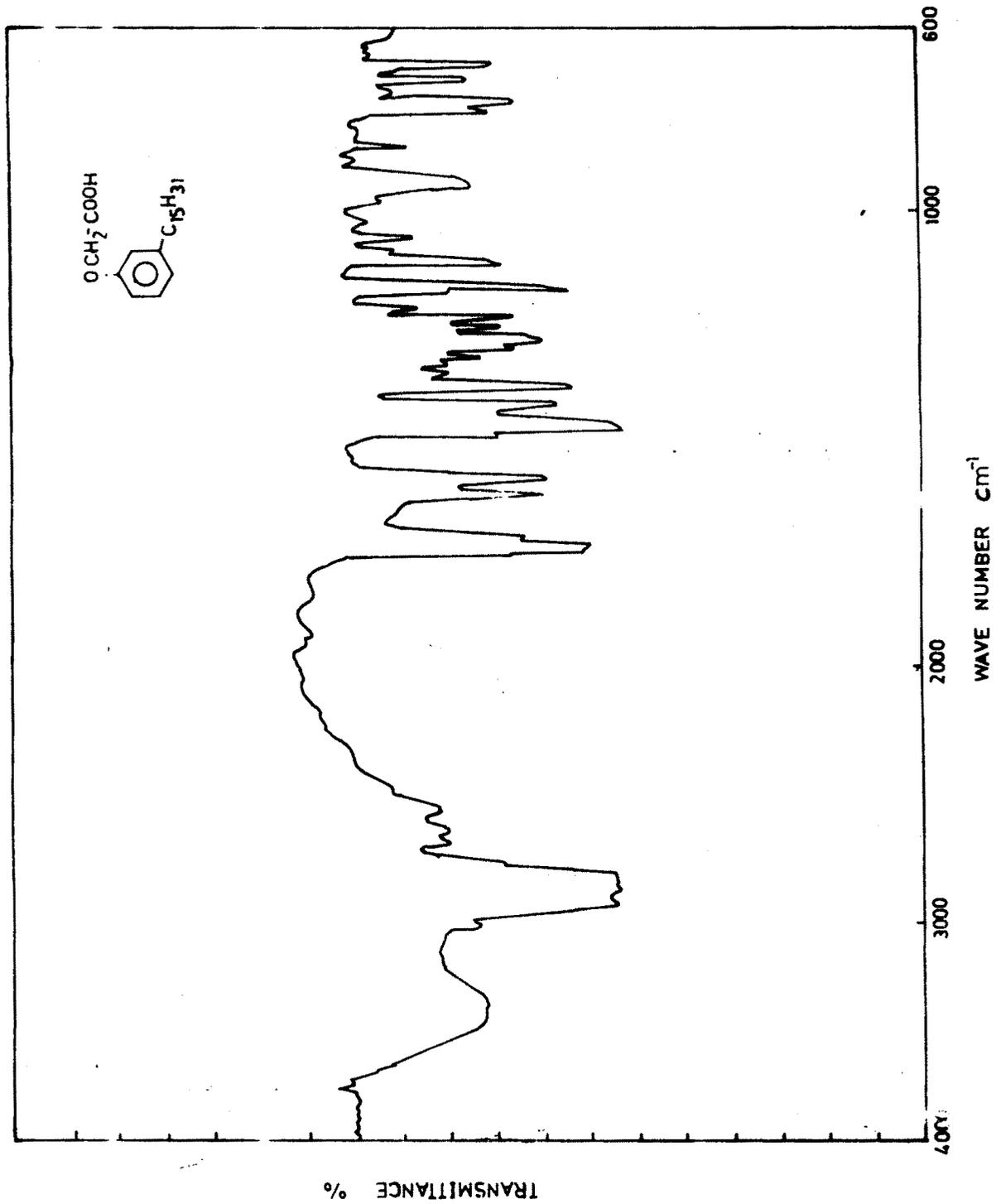FIG. 1 : IR SPECTRUM OF (3 PENTADECYL) PHENOXY ACETIC ACID.

Table VI

A Mass Spectrum of 3-pentadecyl phenoxy acetic acid (1)

m/e	% of base Peak	m/e	% of base Peak
55	43	133	22
57	3Ø	147	8
69	14	166	1ØØ
91	26	178	8
1Ø7	54	362(M+)	3
12Ø	96		

Table VII

A Mass spectrum of (3-pentadecyl) phenoxy methylacetate (2a)

m/e	% of base Peak	m/e	% of base Peak
		148	11
55	43	161	8
57	33	193	4
69	16	221	3
77	13	222	2
91	4Ø	376(M+)	3.3
1Ø7	31	M+1	Ø.88
121	1ØØ	M+2	Ø.16
133	23		

Table VIII

A Mass spectrum of (3-pentadecy) phenoxy ethylacetate (2b)

m/e	% of base Peak	m/e	% of base Peak
55	84	148	15
57	69	161	12
69	32	193	1Ø
77	2Ø	194	81
91	51	195	1Ø
1Ø7	48	206	6
12Ø	1ØØ	39Ø (M+)	32
121	54	(M+1)	8
133	25	(M+2)	1

and isoamylalcohol (scheme-2). Formation of desired ester (2a to 2e) was identified by IR, NMR and mass spectrometry.

Thus, IR spectrum of methylester of 3-pentadecyl phenoxy acetic acid (fig.2), showed strong absorption at 1755 cm^{-1} corresponding to ester carbonyl[33] and absence of broad medium absorption in range of 3600-3200 cm^{-1}.

The PMR spectrum of (2a) (fig.3) showed aromatic protons of 7.2 to 6.6 δ(m,4H) signed at 7.16 (t,1H) is assignable to H meta to both $C_{15}H_{31}$ and -OCH_2-COOMe, whereas peak at 6.71 δ (s,1H) is due to H ortho to both these substitutents . The remaining two protons appear at 6.83 (d,1H) and 6.61 δ (d,1H) due to H ortho to OCH_2-COOMe and ortho to $C_{15}H_{31}$ respectively. Methylene protons (-OCH_2-COO) appeared at 4.6 δ, (s,2H), whereas methoxy (OCH_3) appeared at 3.77 δ (s,3H). The protons of $C_{15}H_{31}$ alkyl substi- tuent are benzylic protons at 2.53 δ (t,2H benzylic CH_2), at 1.5 (qn,2H,CH_2) next to benzylic CH_2), at 1.32 δ (s,24H $CH_2)_{12}$) and methyl group at 0.9 δ (t,3H) as expected. The presence of OCH_3 at 3.77 δ (s,3H) clearly indicated formation of methylacetate derivative (2a) from phenoxyacetic acid.

The integrated intensity ratio was consistant with the molecular formula.

The structure of esters was also confirmed by C13 NMR spectroscopy, in which improvement was achieved by decoupling the protons from C13. In such H1 decoupled spectra every magnetic site (i.e.C13) is represented by an individual signal, because under these conditions C-C and C-H scalar interactions are not detected. Therefore the spectrum is simplified. Relatively large chemical shift ($\approx$200 ppm) compared to PMR has made C13 NMR a
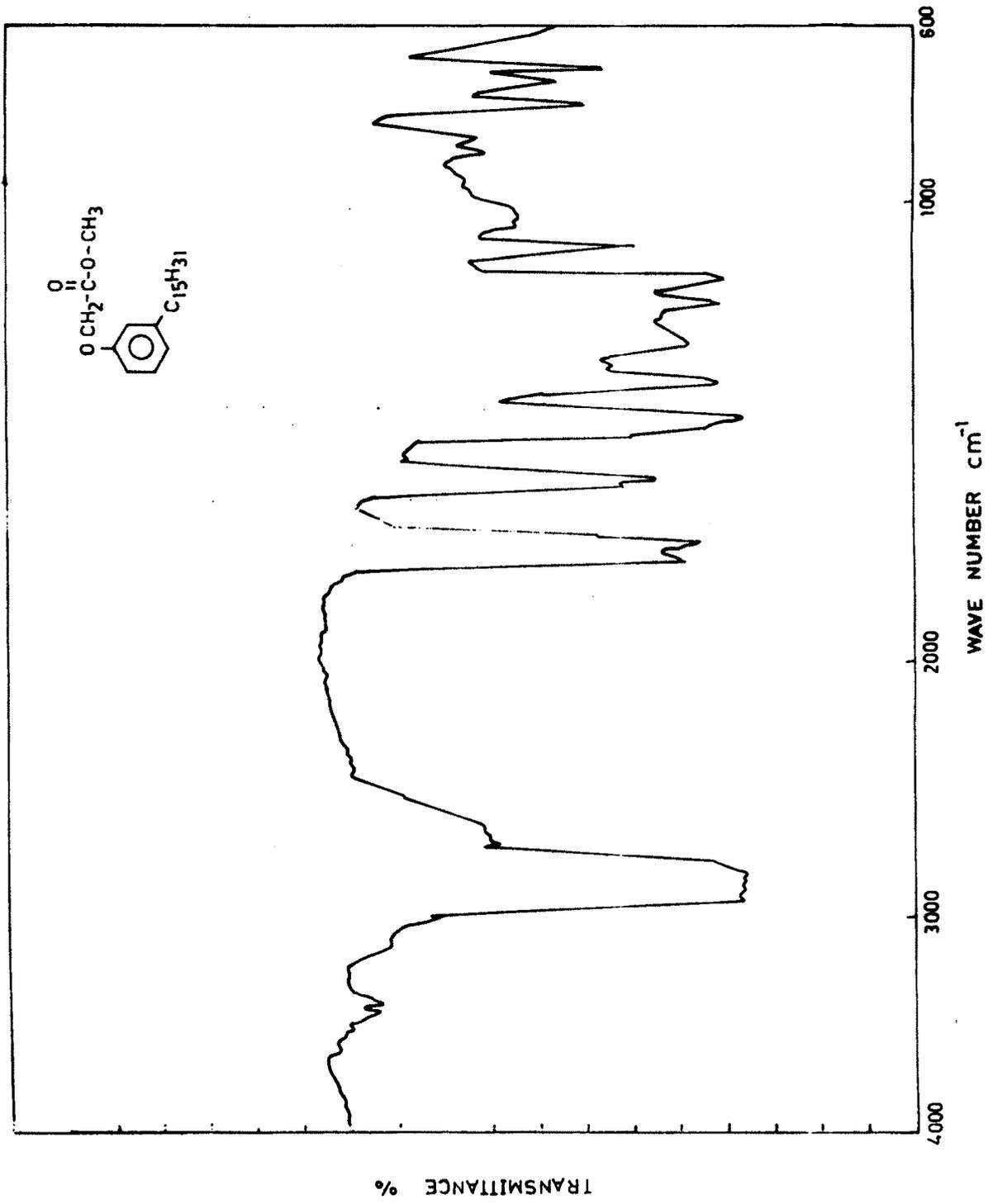
FIG. 2 : IR SPECTRUM OF (3-PENTADECYL) PHENOXY METHYLACETATE.
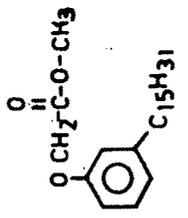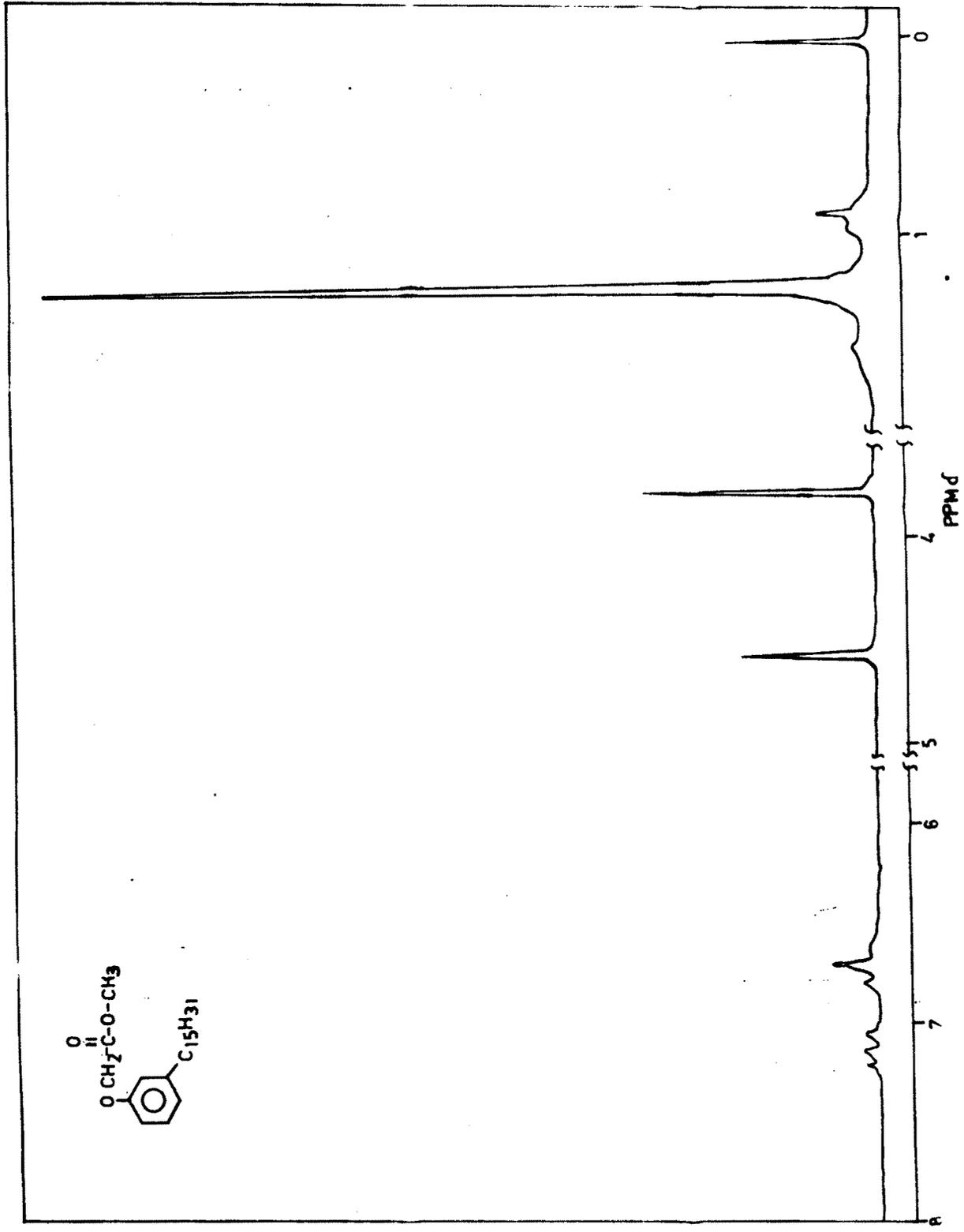
FIG. 3 : H-1 NMR SPECTRUM OF (3 PENTADECYL) PHENOXY METHYL ACETATE.

powerful technique in an elucidation of the structure.

Because of the lack of multiplicity in the conventional C13-H1 decoupled spectrum, it is not an easy matter to identify which carbon signals are which, although C13 signal and H1 signals are approximately equally affected in their chemical shifts by their surrounding. It is very useful in assigning C13 spectrum to be able to say with more certianty than simply a chemical shift argument that a particular C13 signal comes from the carbon atom that carries an identificable proton. Several multiphase experiments make this possible.

The first thing is to know whether the carbon atom in question is a quaternary, methine, methylene or methyl carbon. This can be done using off-resonance decoupling wherein incomplete collapse of the multiplicity occurs, and singlets, doublets, triplets and quartets are observed for C, CH, CH_2 and CH_3 carbons respectively.

More elaborate procedures allow the seperate plotting of subspecta from CH, CH_2 and CH_3 carbons (quaternery carbons are not observed and plotted). Such spectrum is termed as DEPT C13, one containing only the methine, one only the methylenes and one only the methyls are recorded. Correlation of DEPT with H1 decoupled C13 NMR spectrum enabled to identify the individual signals pertaining to the structure of esters and amides investigated in the present studies.

C-13 NMR, H-1 decoupled spectrum of (2a) is given in fig.4, in which carbonyl carbon appear at 169.52 δ whereas aromatic carbons showed signals at 158.82, 144.86, 129.35, 122.07, 115.23 and 111.52 δ. Methylene carbon of $-OCH_2$ - and methylcarbon of
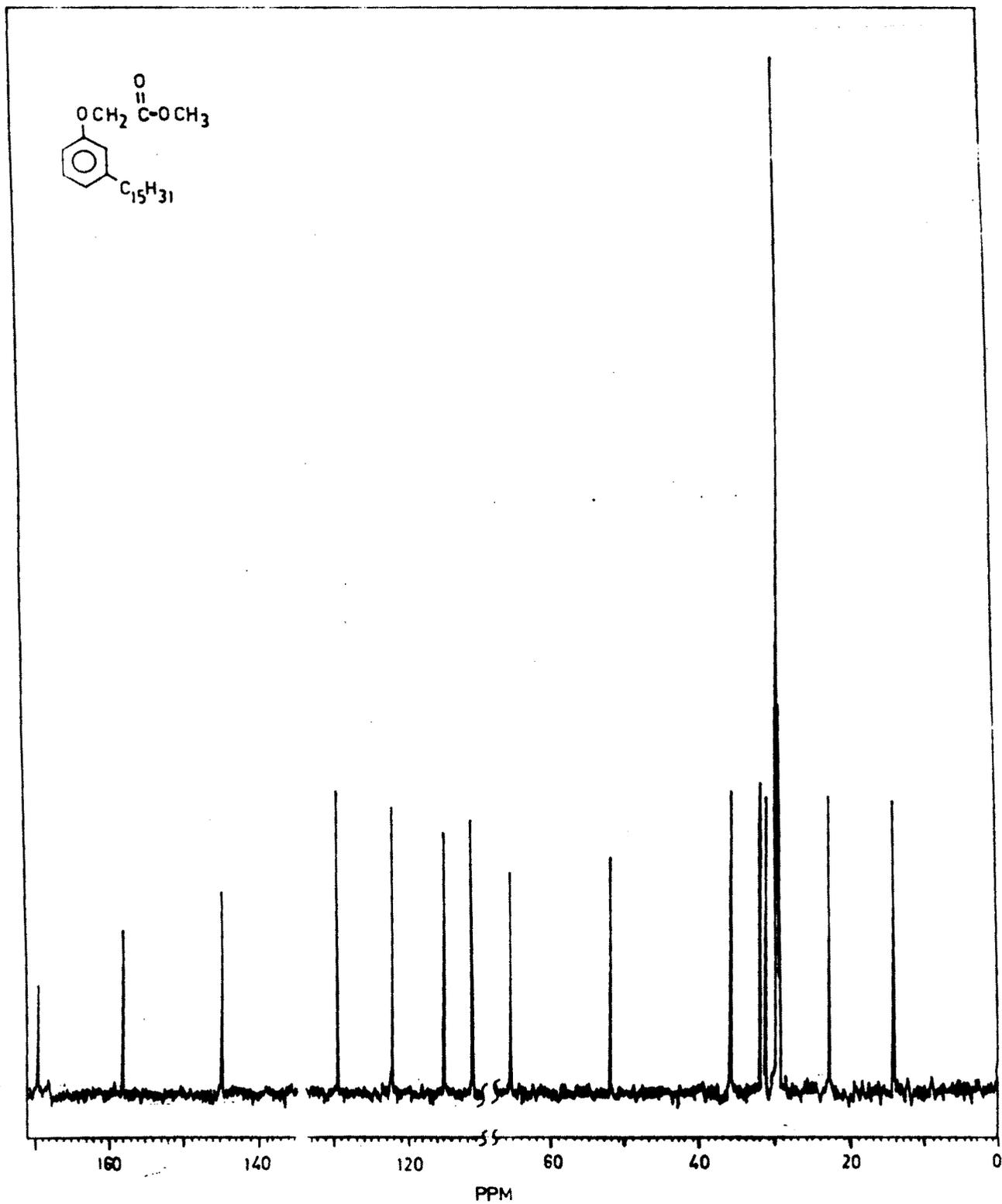
FIG.4: C-13 NMR SPECTRUM -H-1 DECOUPLED- OF (3-PENTADECYL) PHENOXY METHYL ACETATE

methoxy (OCH$_3$) showed NMR peaks at -64.40- and 52.13 δ respectively. The carbon signal due to C$_{15}$H$_{31}$, appeared at 36.11, 32.10, 31.44, 29.86, 29.69, 29.52, 22.84 and 14.24 corresponding to the alkyl moiety.

C-13 DEPT-NMR spectrum of (2a) in fig.5 confirms the assignments, giving 4 NMR peaks for CH of aromatic at 129.35, 122.07, 115.23 and 111.52 δ. Hence NMR signal at 158.82 and 144.86 are assigned to tertiary carbon of aromatic ring. The OCH$_3$ and CH$_3$ of (CH$_2$)$_{14}$ CH$_3$ appeared at 52.13 and 14.24 δ respectively.

All methylene carbons are differentiated by inverse flip. The peak at 64.40 δ is due to -OCH$_2$- , whereas (CH$_2$)$_{14}$ appeared at 36.11, 32.11, 31.44, 29.86, 29.69, 29.52 and 22.84δ. The assignment of PMR and CMR are supported by literature [34] values for similar functional groups of the analogus structural moieties.

Mass spectrum of (2a) showed molecular ion at m/e 376, corresponding to the molecular formula weight and the peak data is presented in (Table VII), base peak being at m/e 120.

Similarly catalytic esterification of (1) with ethyl alcohol gave the desired product (2b).

(3-Pentadecyl) -phenoxy- ethylacetate (2b), melted at 36°C and its IR spectrum (fig.6) indicated the disappearance of carbonyl of COOH (1720 cm^{-1}) and the appearance of ester-carbonyl group at 1763 cm^{-1}.

The PMR spectrum of (2b) scanned in CDCl$_3$ is shown in fig.7 and it showed -OCH$_2$- protons at 4.65 δ, (s,2H) whereas ethyl group is easily distinguished at 4.3 δ (q,2H,CH$_2$) and at 2.6 δ (t,3H,CH$_3$). Aromatic protons appeared in range of 6.7 to 7.3 δ.
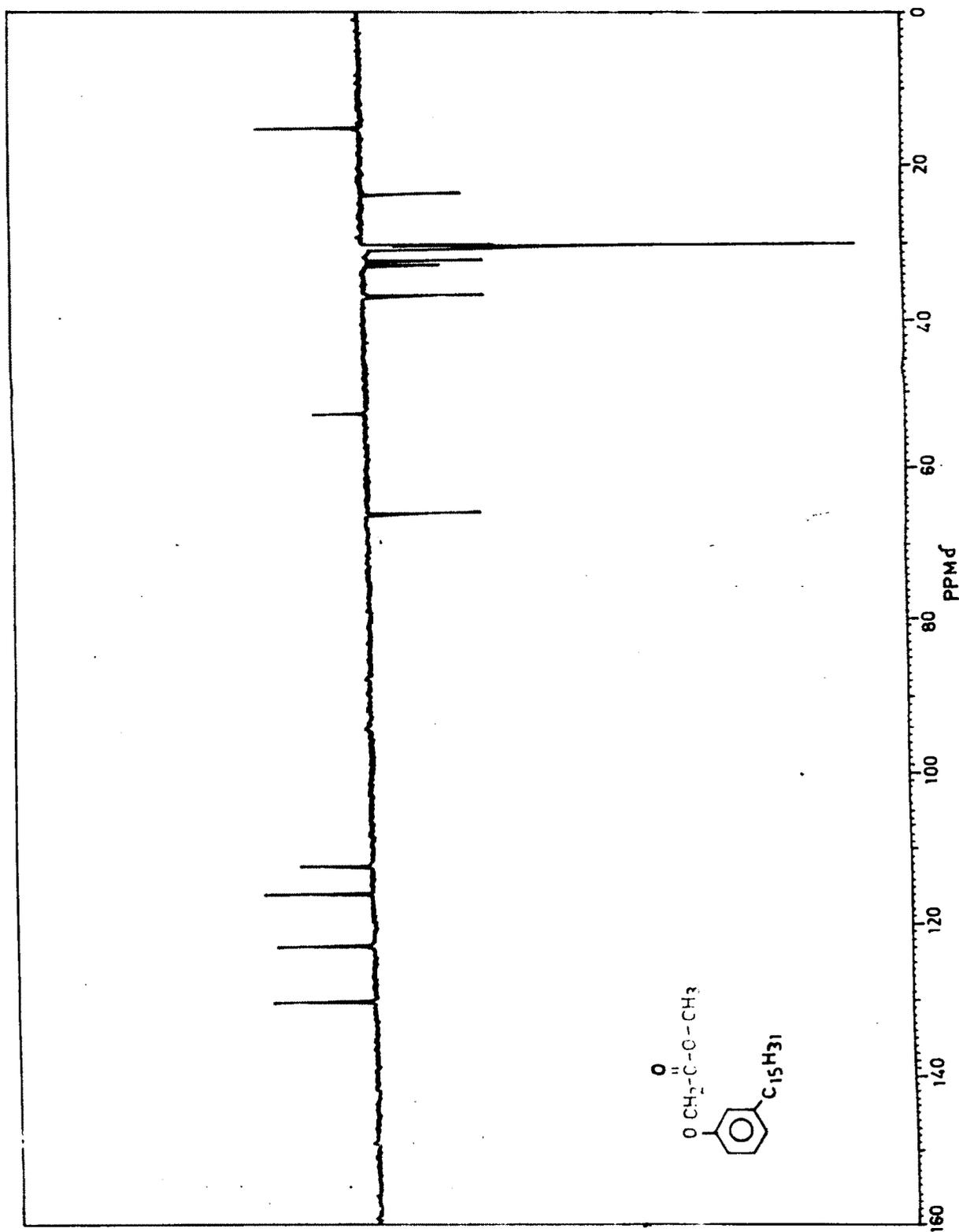
FIG. 5 : C-13 NMR SPECTRUM - DEPT - OF (3-PENTADECYL) PHENOXY METHYLACETATE.

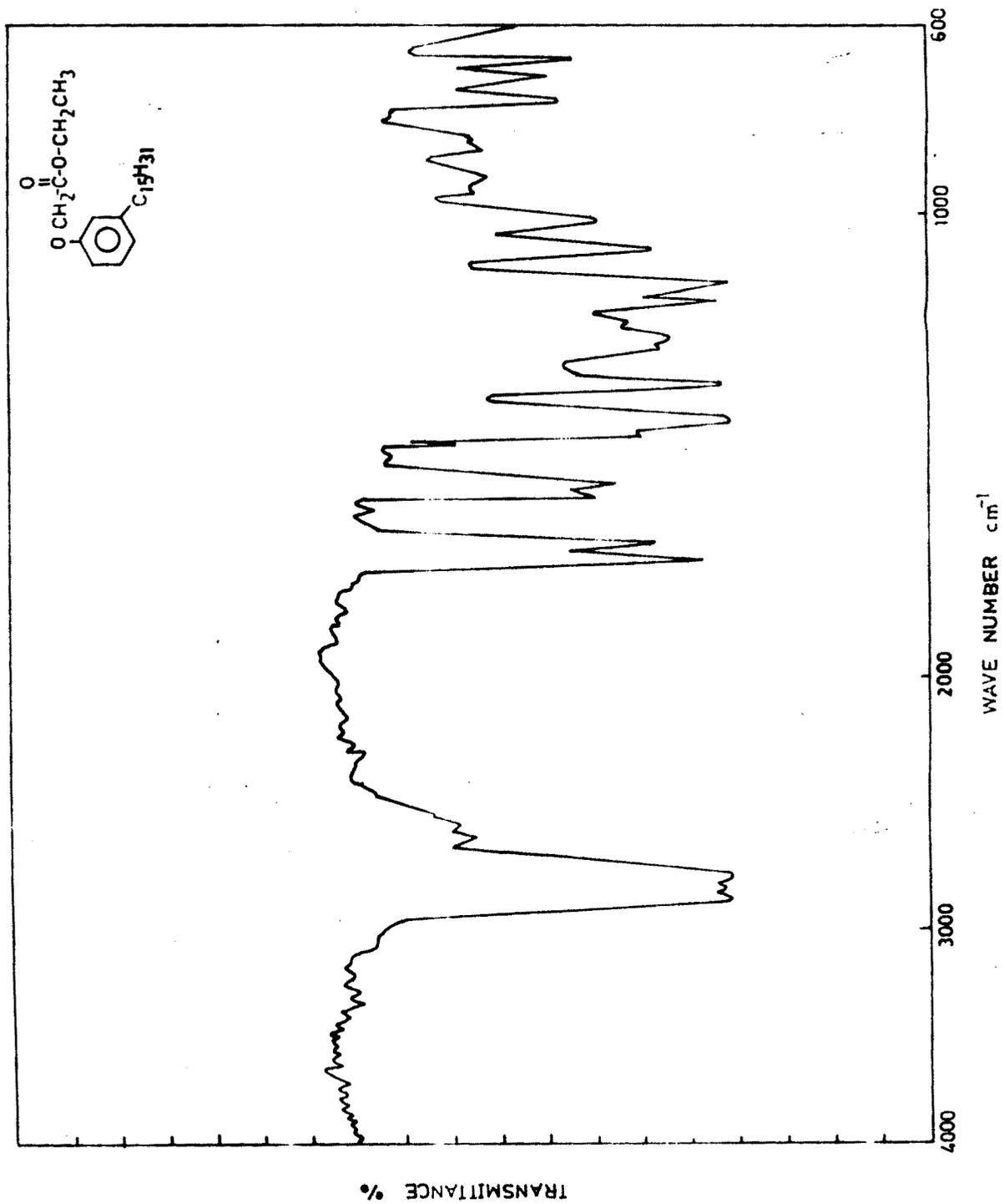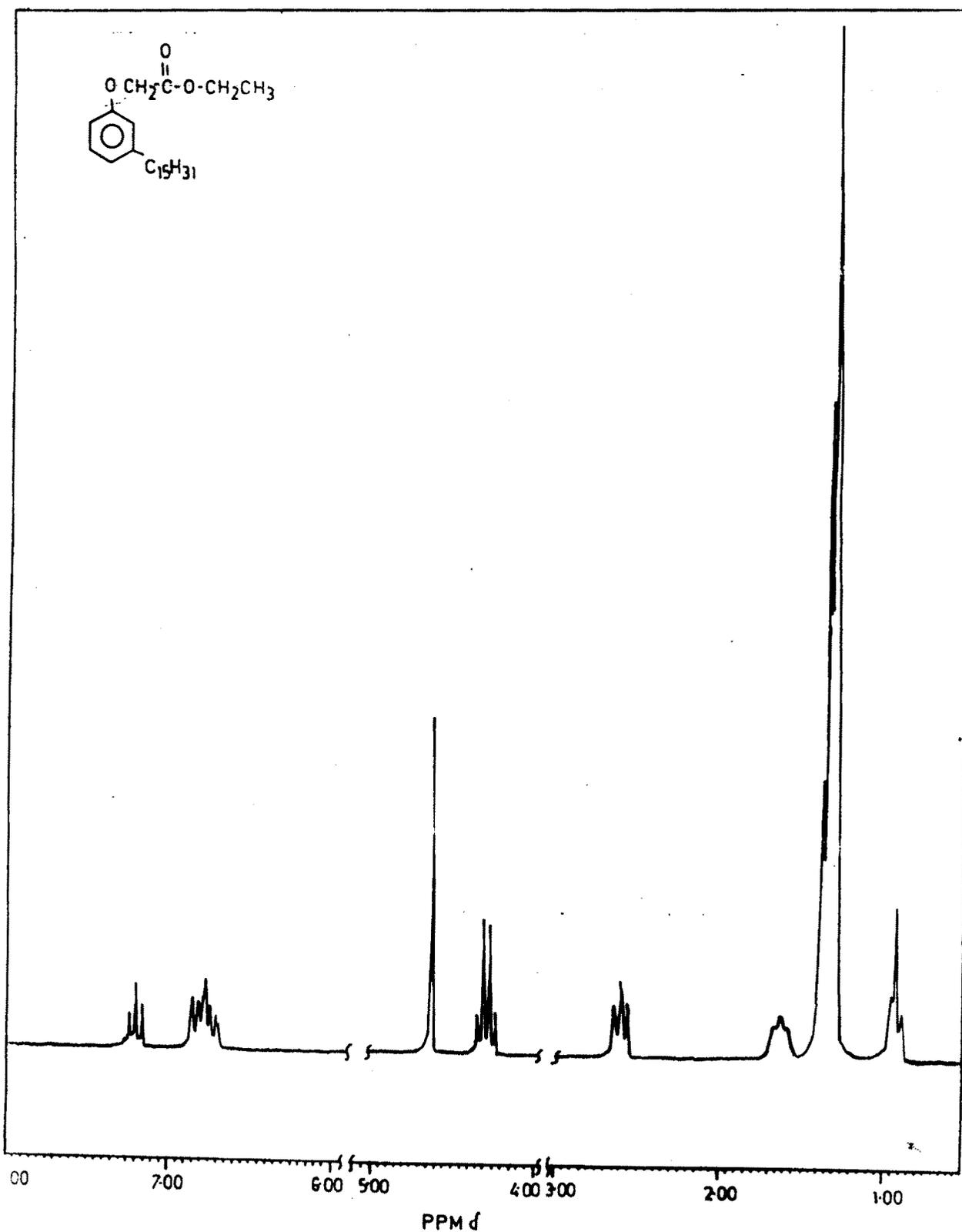FIG. 6 : IR SPECTRUM OF (3-PENTADECYL) PHENOXY ETHYLACETATE.

FIG.7: H-1 NMR SPECTRUM OF (3-PENTADECYL) PHENOXY ETHYLACETATE.

The signal at 7.2 δ (t,1H) is assigned to H meta to both $C_{15}H_{31}$ and OCH_2 moiety. The H ortho to both $C_{15}H_{31}$ and OCH_2 appeared at 6.8 δ (s,1H) along with two peaks at 6.85 δ (d,1H) and 6.75 δ (d,1H). Aliphatic protons of $C_{15}H_{31}$, Ar-CH_2 CH_2 $(CH_2)_{12}$ CH_3 of which methyl proton appear at 0.9δ (t,3H) whereas benzylic methylene proton at 2.6 δ (t,2H) and at 1.65 (qn,2H), whereas remaining methylene protons $(CH_2)_{12}$ appeared around 1.4 δ (s,24H).

C-13 NMR spectrum H1 decoupled, of (2b) is presented in fig.8. The signal most down field at 169.22 δ is due to C=O of ester carbonyl. The six carbons of aromatic ring appeared at 158.13, 144.94, 129.39, 122.11, 115.31 and 111.70 δ.

The signal at 65.69 δ is assigned to methylene carbon of -OCH_2 whereas methylene carbon of -CH_2CH_3 (ethyl group) appeared at 61.42 δ.

C-13 NMR-DEPT- of (2b) is given in fig.9. which showed 4 aromatic carbons of CH type at 129.39, 122.11, 115.31 and 111.70 δ. Hence the carbons of tertiary type are those at 158.13 and 144.94 δ. Methylene carbons of -OCH_2 and OCH_2 CH_3 appeared at 65.69 and 61.42 δ respectively.

Methyl carbons appeared at 14.34 δ. All other methylene cabons of $C_{15}H_{31}$ appeared at 36.17, 32.14, 31.48, 29.89, 29.56 and 22.90 δ.

Mass spectrum of (2b) showed strong molecular ion peak at m/e 390 and m/e 120 is the base peak. The detailed data is given in Table VIII.

Thus combination of IR, PMR, C-13- NMR (H1 decoupled and DEPT) spectra along with mass spectrometry helped in ellucidation
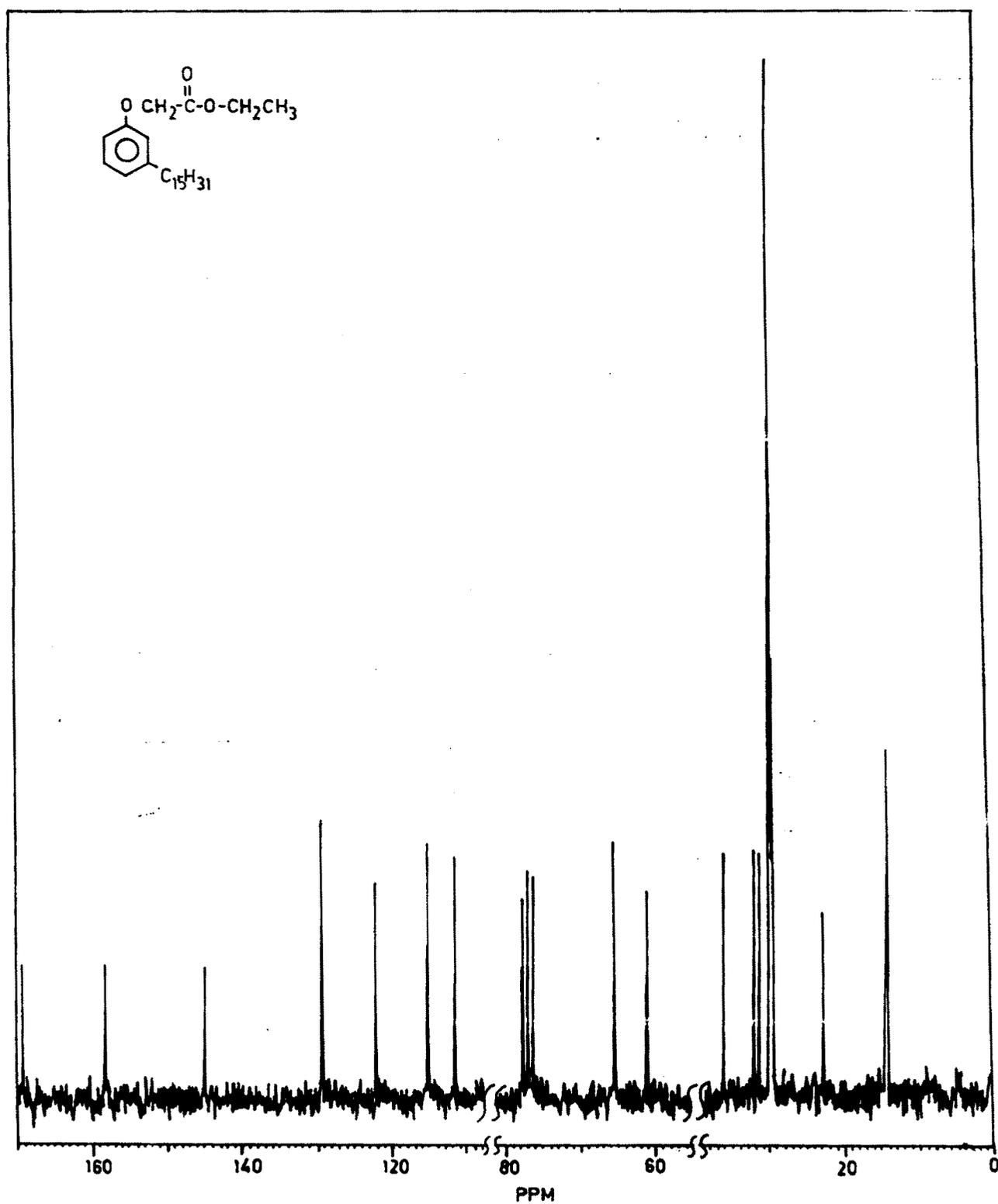
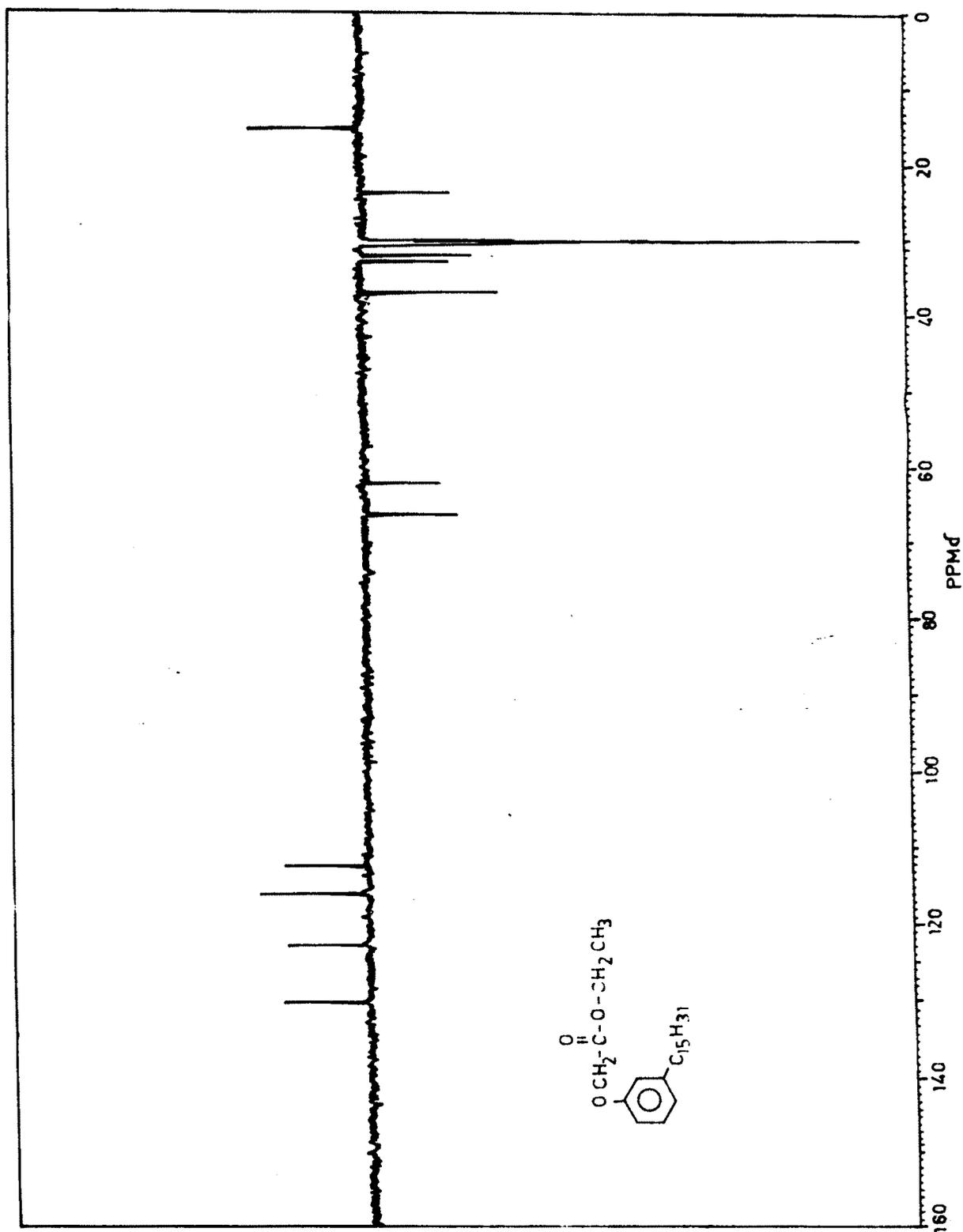FIG. 8 : C-13 NMR SPECTRUM — H-1 DECOUPLED - OF(3-PENTADECYL) PHENOXY ETHYLACETATE

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FIG. 9 : C-13 NMR SPECTRUM   -DEPT - OF (3-PENTADECYL) PHENOXY ETHYLACETATE.

of the assigned structures of esters (2a and 2b) i.e (3-pentade-cyl) phenoxy methylacetate and (3-pentadecyl)-phenoxy ethyla-cetate.

Esterification of (1) with isopropanol yielded (3-pentadecyl) phenoxy isopropylacetate.

Fig.10, presents IR spectrum of the ester (2c), which showed strong absorption at 1761 cm^{-1} due to ester carbonyl. The absorption in the region 3200-3500 cm^{-1} (OH) is absent.

Proton NMR spectrum of (2c) is depicted in fig.11 and is in accordance to the structure corresponding to isopropyl ester. Aromatic protons appeared at 7.25 (t,1H) 6.75 (s,1H), 6.8(d,1H) and 6.7 δ (d, 1H). Methine proton of isopropyl appeared at 5.2 δ (h,1H) whereas methyl group proton signals are masked in $C_{15}H_{31}$ proton signal at 2.2 to 1.1 δ range. Benzylic methylene protons appeared at 2.6 (t,2H) whereas peak at 0.9 (t,3H) is due to methyl group of $(CH_2)_{14}$ CH_3. NMR signal at 4.6 δ (s,2H) is as-signable to -OCH_2 moiety. Mass spectral data of (2c) is presented in Table IX where in very strong molecular ion peak appeard at m/e 404.

Esterification of (3-pentadecyl) phenoxy acetic acid with n-butanol gave butylester in good yields. Fig.12 presents IR spec-trum of (3-pentadecyl)phenoxy butylacetate (2d) and showed strong absorption at 1767 cm^{-1} due to ester carbonyl and disappearance of -OH (3600-3200 cm^{-1}) absorption of -COOH functonal group.

Fig.13 gives PMR spectrum of (2d) and the pattern is conforming to butylester structure. Aromatic protons appeared at 7.2 (t, 1H), 6.85 (d, 1H), 6.8 (s, 1H), 6.75 δ(d, 1H). The signal at 4.65 δ (s, 2H) is assigned to -OCH_2-COO unit's methylene
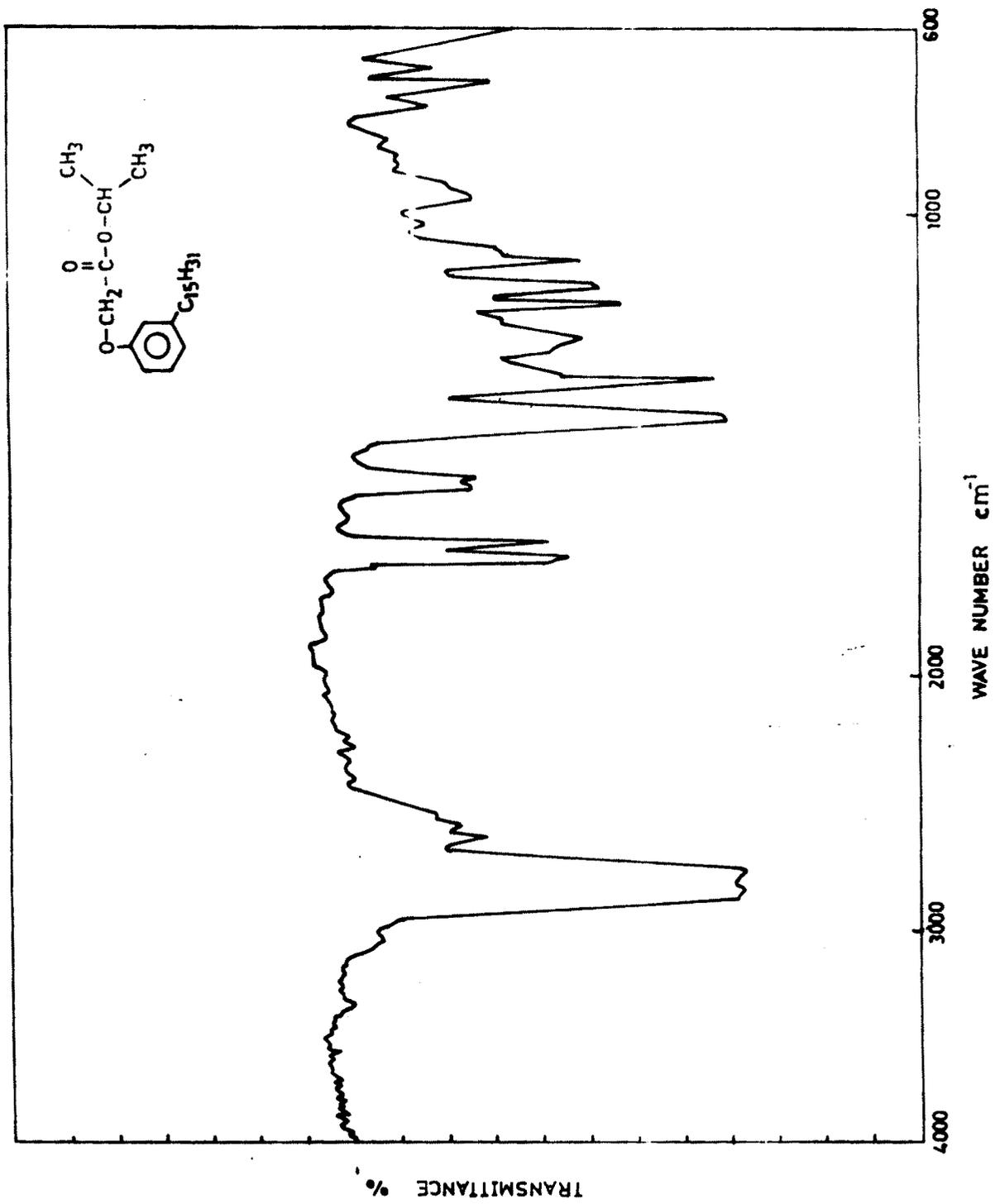
FIG. 10 : IR SPECTRUM OF (3-PENTADECYL) PHENOXY ISOPROPYLACETATE.

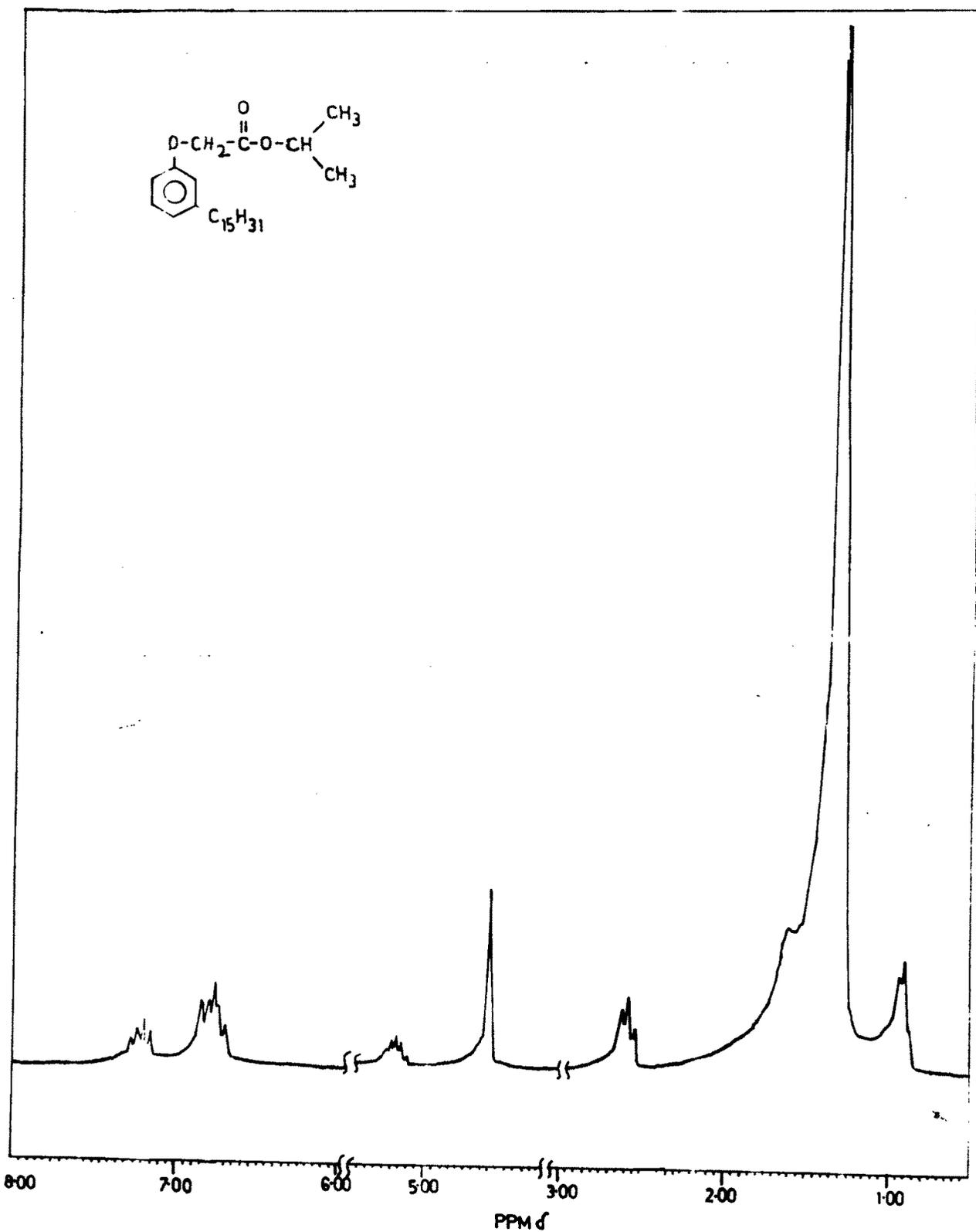FIG.11   NMR SPECTRUM OF (3·PENTADECYL) PHENOXY ISOPROPYLACETATE (PROTON).

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Table IX

A Mass spectrum of (3-pentadecyl) phenoxy isopropylacetate (2c)

m/e	% of base Peak	m/e	% of base Peak
55	100	133	18
57	91	147	12
69	36	161	10
90	30	165	42
91	50	166	82
107	60	208	40
108	55	404(M+)	52
120	51	(M+1)	12
121	78	(M+2)	02

Table X

A Mass spectrum of (3-pentadecyl) phenoxy butylacetate (2d)

m/e	% of base Peak	m/e	% of base Peak
55	60	121	30
56	55	133	10
57	100	147	7
69	28	161	7
91	20	166	40
107	22	179	4
108	20	222	23
120	37	418(M+)	0.4

Table XI

A Mass spectrum of (3-pentadecyl) Phenoxy amylacetate (2e)

m/e	% of base Peak	m/e	% of base Peak
55	38	133	05
57	28	147	04
69	30	161	02
71	100	165	6
91	12	166	22
107	15	179	01
108	17	236	5
120	13	432(M+)	35
121	21	(M+1)	0.1

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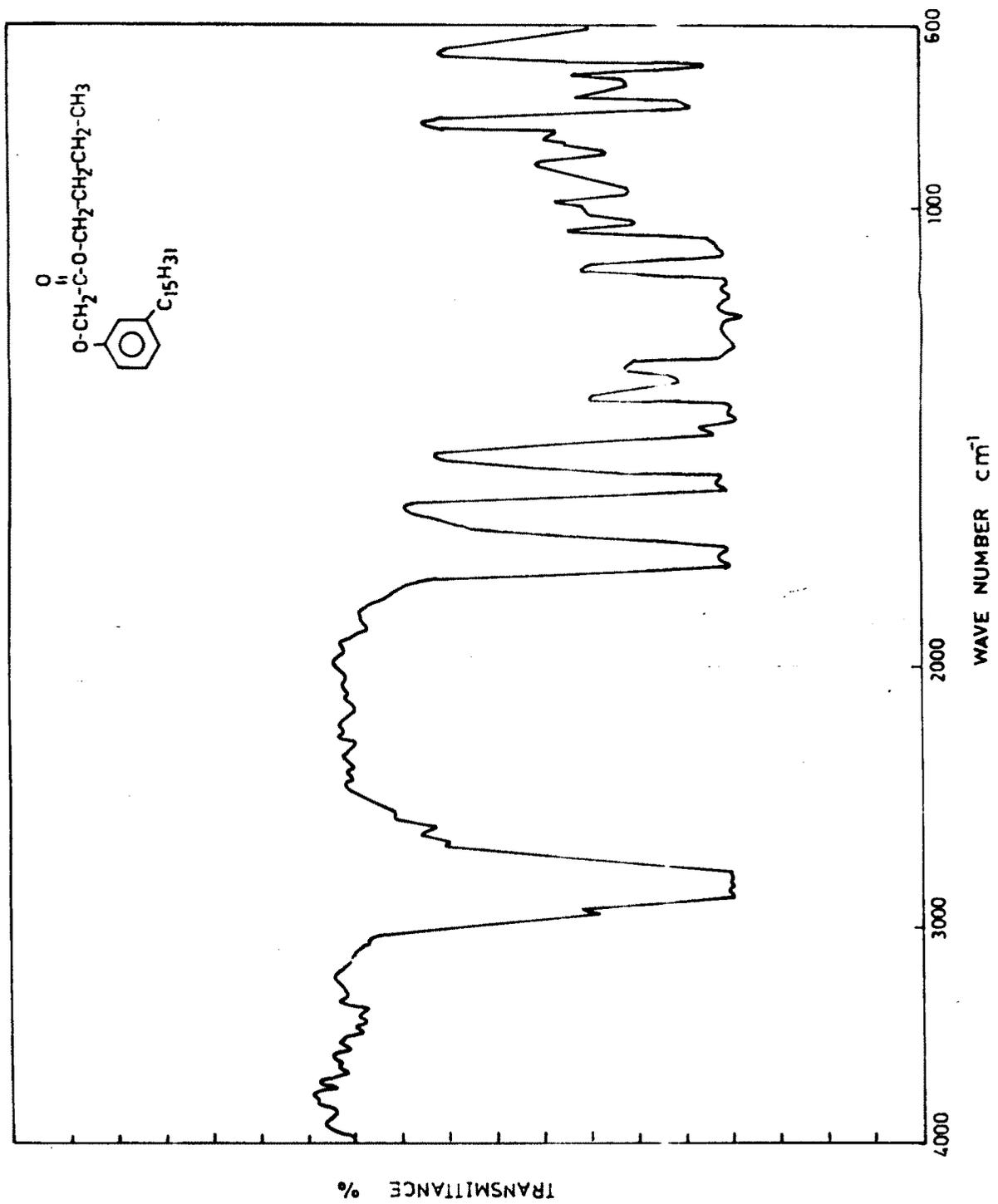
FIG. 12 : IR SPECTRUM OF (3-PENTADECYL) PHENOXY BUTYLACETATE
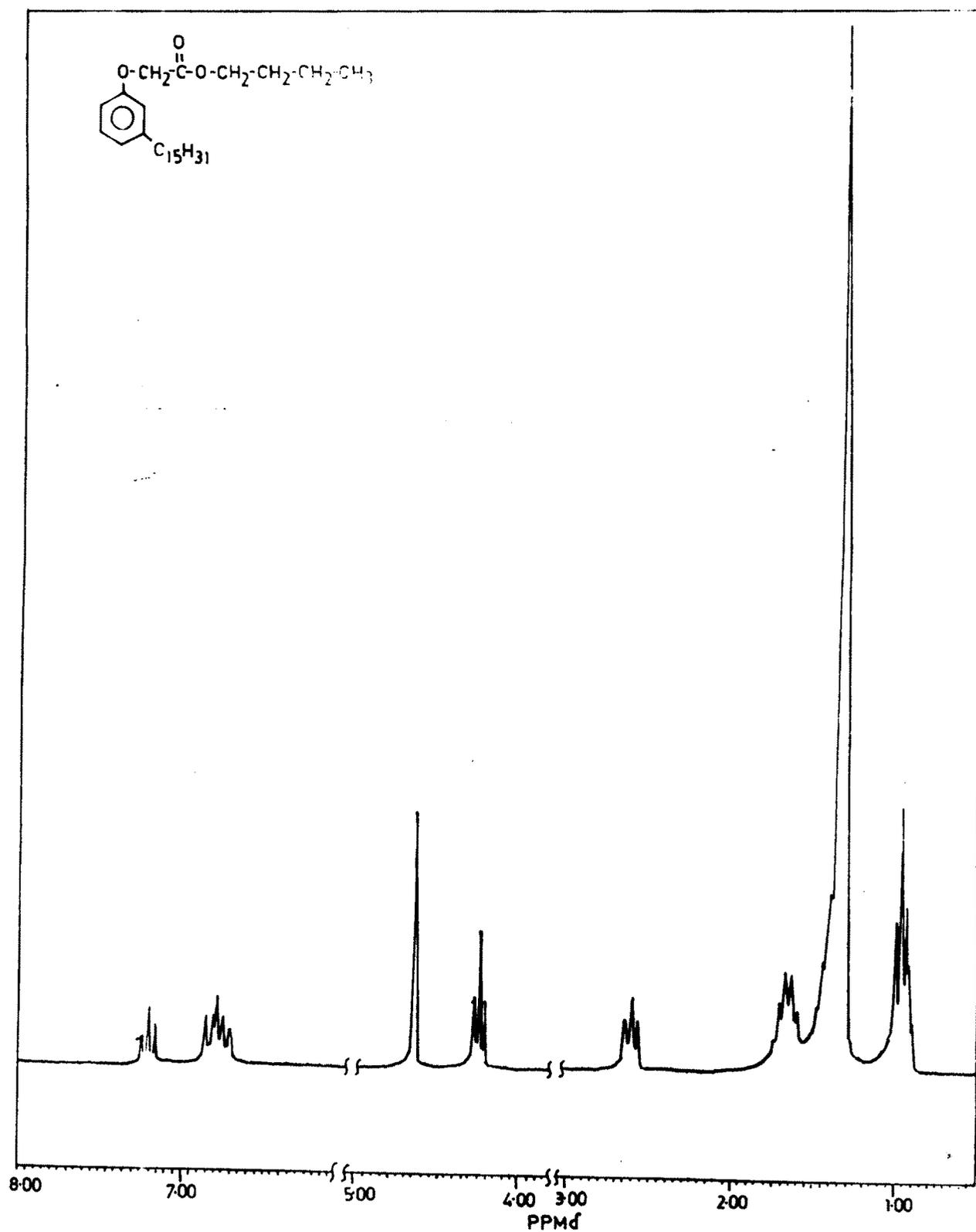
FIG.13:H1 NMR SPECTRUM OF (3-PENTADECYL) PHENOXY BUTYLACETATE.

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protons. Peaks at 4.2 δ (t, 2H) and 2.6 δ(t, 2H) are due to -COO-
CH_2-C_3H_7 butyl unit's methylene directly attached to oxygen and
benzylic methylene group of Ar-CH_2 $(CH_2)_{13}$ CH_3. There is overlap-
ping of NMR signal due to -C_3H_7 unit from butyl group with those
of $C_{15}H_{31}$ unit's peak in the range of 1.8 to 0.9 δ values.

Mass spectrum of (2d) gave weak molecular ion peak at m/e
418 and base peak being 57 corresponding to C_4H_9 fragment (Table
X). The reaction of (1) with isoamylalchohol gave the desired
ester product.

IR spectrum of ester (2e) (fig.14) indicated formation of
-COO- as evidenced by strong absorption at 1758 cm^{-1}, whereas
proton NMR spectrum (fig.15) gave required NMR signals as per
assigned structure.

Mass spectrum of (2e) is shown in Table XI indicating
molecular ion peak at m/e 432 and base peak being at m/e 71 which
corresponds to C_5H_{11} fragment.

Thus all (2a-2e) these alkylester of (1) have been
completely characterised by IR, PMR, CMR, (H1 decoupled and DEPT)
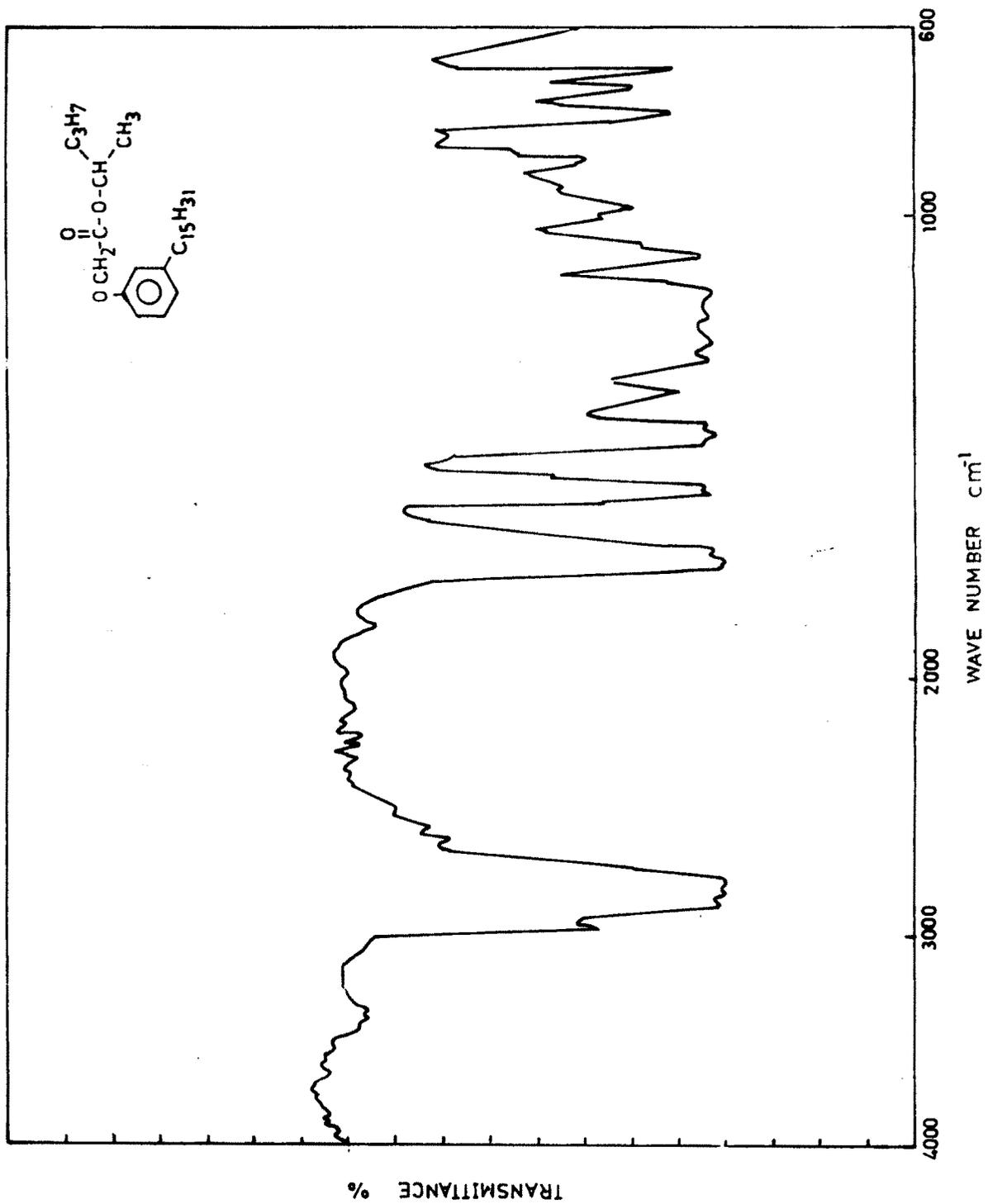and mass spectral techniques.

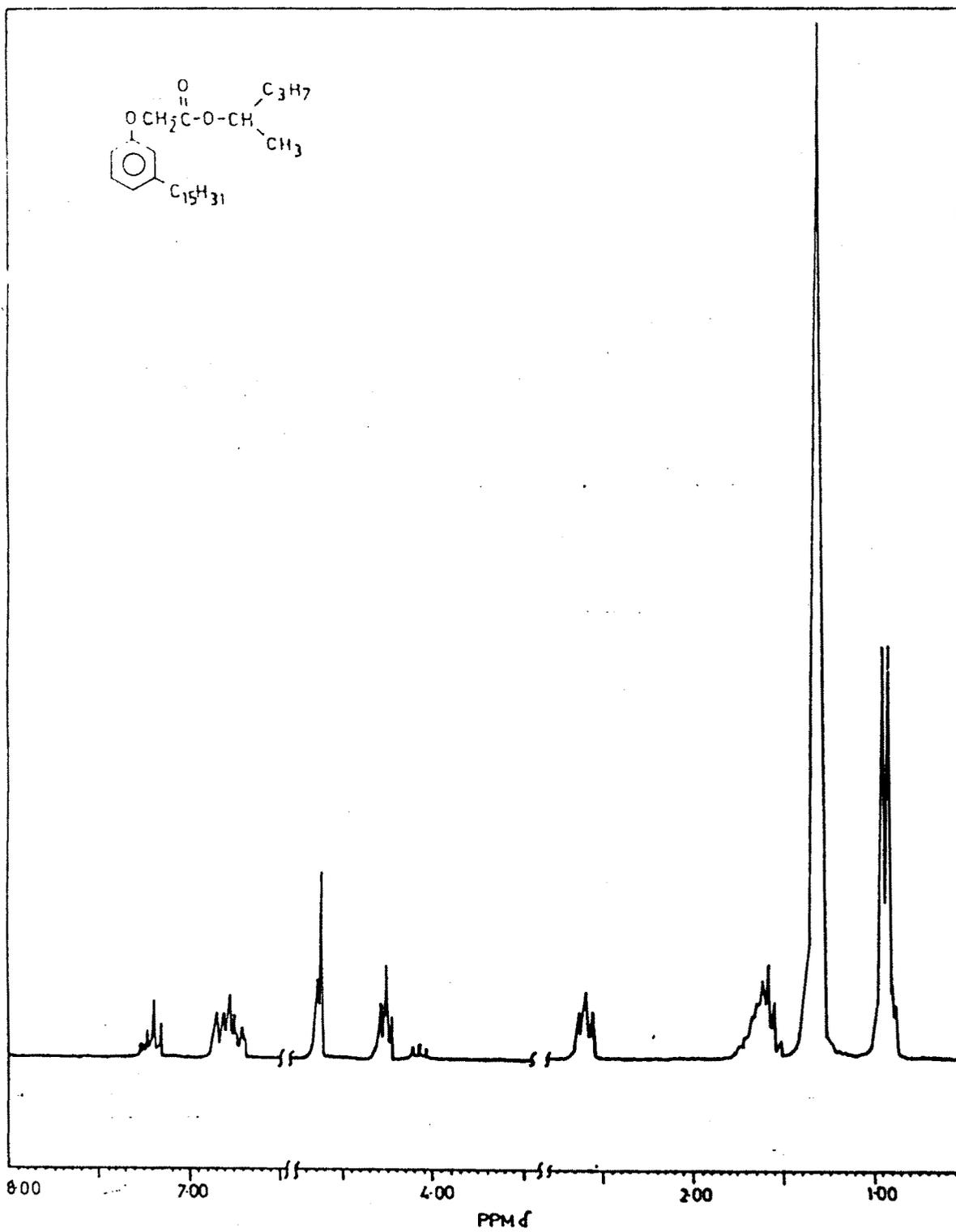FIG.14 : IR SPECTRUM OF (3-PENTADECYL) PHENOXY ISOAMYLACETATE.

FIG.15:H 1 NMR SPECTRUM OF (3 PENTADECYL) PHENOXY ISOAMYLACETATE

3.3 Synthesis and Characterisation of (3-pentadecyl) phenoxy (N-Aryl) Acetamides (3a to 3g) :-

Acid amides may be regarded as compounds derived from acid by replacing -OH group of -COOH by an amino group i.e. NH_2. There are many methods of preparation of the amides such as

a)   by heating ammonium salt of the acid

b)   by heating acid with urea

c)   by amminolysis i.e. by action of ammonium on ester, anhydrides

d)   by the action of ammonium or amine on acid chloride

Generally amides are prepared by the above method (d). The acid chloride derivatives of the acids are prepared by reaction of carboxylic acid and thionyl chloride. Then acid chlorides are treated with amines to get corresponding amides.

$$R - COOH + SOCl_2 \longrightarrow R - COCl + HCl + SO_2$$

$$R - COCl + R - NH_2 \longrightarrow R - CONH - R + H_2O$$
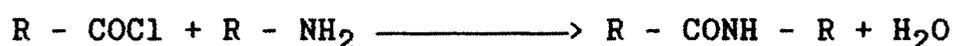
For the preparation of amide by using acid chloride, the acid chloride must be in pure form and the synthesis of acid chloride is tedious and expensive. The purification of acid chloride requires dry media and solvent. The yield of arylmethylene acid chlorides are less and purification is major problem, For example $PHCH_2COCl$, in addition to environmentally unacceptable evolution of HCl and SO_2 gases.

Again it is reported that in many cases it is difficult to prepare the corresponding carboxylic acid chloride derivatives. These are the problem [a] overcoming of condensation of acid chloride and organic base and [b] particularly when active

methylene group is present viz $-CH_2$ COOH, halogenation of $-CH_2$ group also may takes place.

In the year 1975 Yamazaki et al[35,36], and Ogata et al[37,38] used the condensing agent such as di- or triarylphosphites in the polycondensation reaction of dicarboxylic acids and aromatic diamines in N-methyl-2-pyrrolidone (NMP) and pyridine containing metal salts. We had applied same condensing agent[39] for the polycondensation of diacid and diamide by using pyridine and DMAC as a solvent. Similarly S.H.Hsian and C.P.Yang[40] applied the method for the preparation of polyamide imide.

In the present studies this type of phosphorylation reaction has been utilized to condense the carboxylic acid and organic base. Thus we have used condensing agent, triphenyl phosphite (TPP) and metal salt, LiCl (anhydrous) to synthesise a series of amide derivatives of (1) which can be used as active herbicide.

In light of limitation of acid chloride synthesis from Ar-CH_2 COOH, we have employed the so called condensing agent (viz TPP+LiCl) leading to the activation of acid and its subsequent in situ. condensation with amine under mild conditions, in organic solvent, leading to direct condensation of carboxylic acid with amines to form amides.

The reaction has been proposed to proceed via an aryloxy-N-phosphonium salt of pyridine formed by dephenoxylation of triphenyl phosphite followed by aminolysis.

In direct condensation reactions, addition of metal salt is very important. In the presence of metal salt the solvating power of aprotic solvent increase and side reactions are suppressed. The addition of LiCl in present reactions increased the yields.

The advantages of the present reaction for amide synthesis over melt/low temperature methods are :

1.   The condensation is carried out at moderate temperature without removing the side products and

2.   avoided the tedious acid chloride preparation step.

In view of above, a series of different substituted amides were prepared by direct amidation of (3-pentadecyl) phenoxy acetic acid by reacting with aromatic primary amines. The reactant amine, code No. of amide, physical constant and % yield of the products is presented in Table V.

Each of the product (3a to 3g) was characterised. Thus the structure of amide products 3a to 3g were identified with the help of spectroscopic techniques.

The fig.16 is representative IR spectra of (3-pentadecyl)-phenoxy (N-pheoyl) acetamide (3a) wherein the absorption at 3364 cm^{-1} (NH) and 1682 cm^{-1} (CONH) amide are characteristic of secondary amide, and hence confirm the formation of amide. Absence of 1727 cm^{-1} due to C=O of acid group suggest complete

SCHEME - 3

Syntheses of (3 pentadecyl) phenoxy N-aryl acetamide

$$\text{(1)} \quad + \ H_2N\text{-Ar} \ \xrightarrow[\substack{\text{Catalyst} \\ \text{TPP}}]{\substack{\text{NMP} \\ \triangle}} \quad \text{(3)} \quad + \ H_2O$$
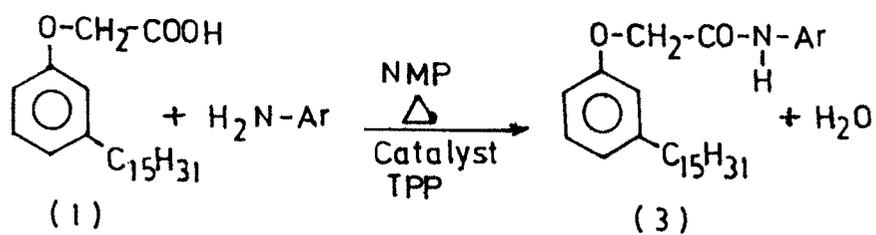
$-Ar$	$=$	C_6H_5	3 a
	$=$	$m - C_6H_4 - NO_2$	3 b
	$=$	$p - C_6H_4 - NO_2$	3 c
	$=$	$p - C_6H_4 - Br$	3 d
	$=$	$\alpha - C_{10}H_7$	3 e
	$=$	$m - C_6H_4 - CH_3$	3 f
	$=$	$p - C_6H_4 - OCH_3$	3 g
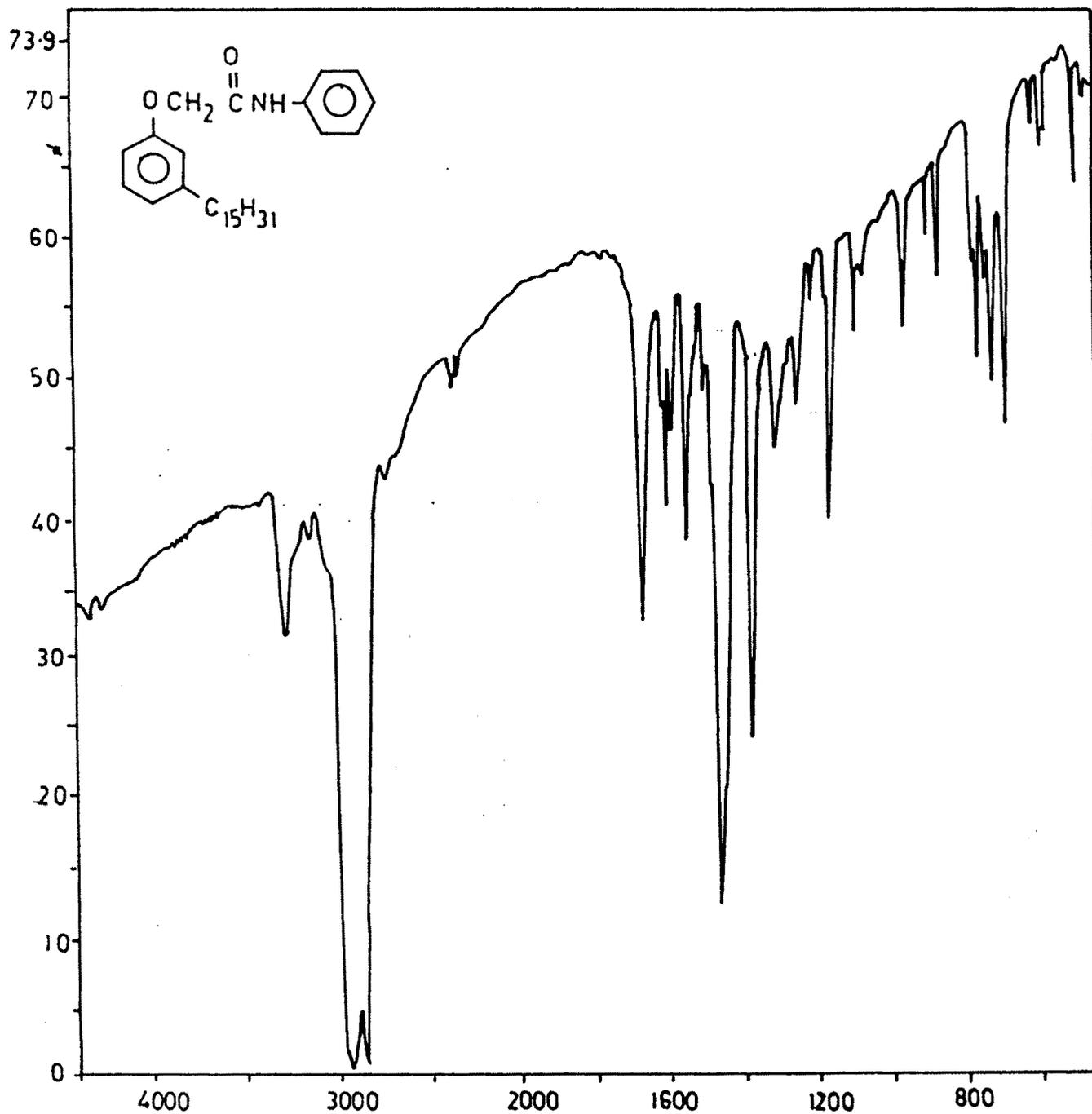
FIG.16: IR SPECTRUM OF (3-PENTADECYL)-PHENOXY (N-PHENYL) ACETAMIDE.

reaction of acid (1) with aromatic amine (aniline) to form amide (3a). Amide II band for secondary amide was observed at 1538-1520 amide III absorption band at 1298 and amide IV at 608 and 592 cm^{-1}.

The IR spectra of 3b additionally showed absorption corresponding to Aryl C-N at 1538-1520 and 1376-1318, whereas amide (3c) showed at 1538-1514 and 1378-1330 cm^{-1}, indicating presence of aryl-Nitro. The characteristic absorption at 504 cm^{-1} for C-Br was observed in the IR spectrum of amide (3d).

Proton NMR spectrum of (3a) shown in fig.17 showed signals at 8.3 δ for NH (s, 1H) and at 4.65 δ for -OCH$_2$- protons (s,2H). Aromatic protons appear at 7.7 to 6.7 δ (m,9h) and individual proton assignment can be done in view of multiplicity and chemical shift. The protons of C$_{15}$H$_{31}$ substituent are at 2.6 δ (t,2H) due to benzylic -CH$_2$- at 1.65 δ (qn,2h) due to CH$_2$ next be benzylic -CH$_2$-, 0.9 δ (t,3H) due to CH$_3$ and all other (CH$_2$)$_{12}$ at 1-3 δ (bs,24H).

C-13 NMR spectrum - H1 decoupled - of (3a) is shown in fig.18. The amide -CO- appeared at 166.43 δ, and ten different types of aromatic carbons at 157.21, 145.15, 137.14, 129.57 129.02, 124.72, 122.55, 120.19, 115.18, 111.87 δ. Three substituted tertiary carbon are at downfield viz 157.21, 145.15, and 137.14 δ. Methylene carbon of -OCH$_2$ showed signal at 67.67 δ.

Signals due to carbons of C$_{15}$H$_{31}$ appeared at 36.03, 32.02, 31.40, 29.79, 29.61, 29.45, 22,77 and 14.20 of which methyl carbon appeared at 14.20 δ.

C-13-DEPT NMR spectrum of (3a) is given in fig.19. The spectrum showed aromatic -CH- signals at 129.57, 129.02, 124.72,
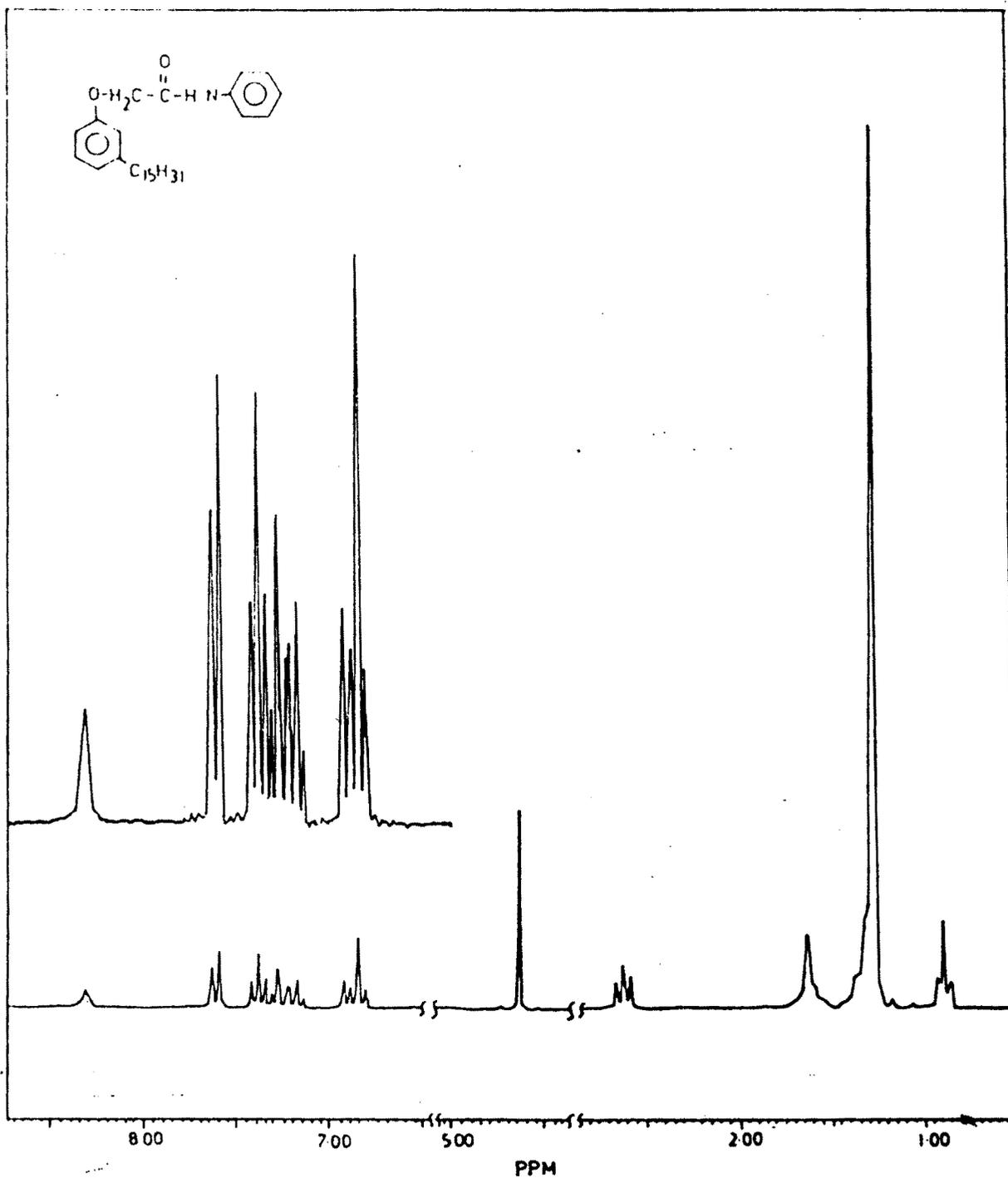
FIG.17: H·1 NMR SPECTRUM OF (3·PENTADECYL)·PHENOXY (N·PHENYL) ACETAMIDE.

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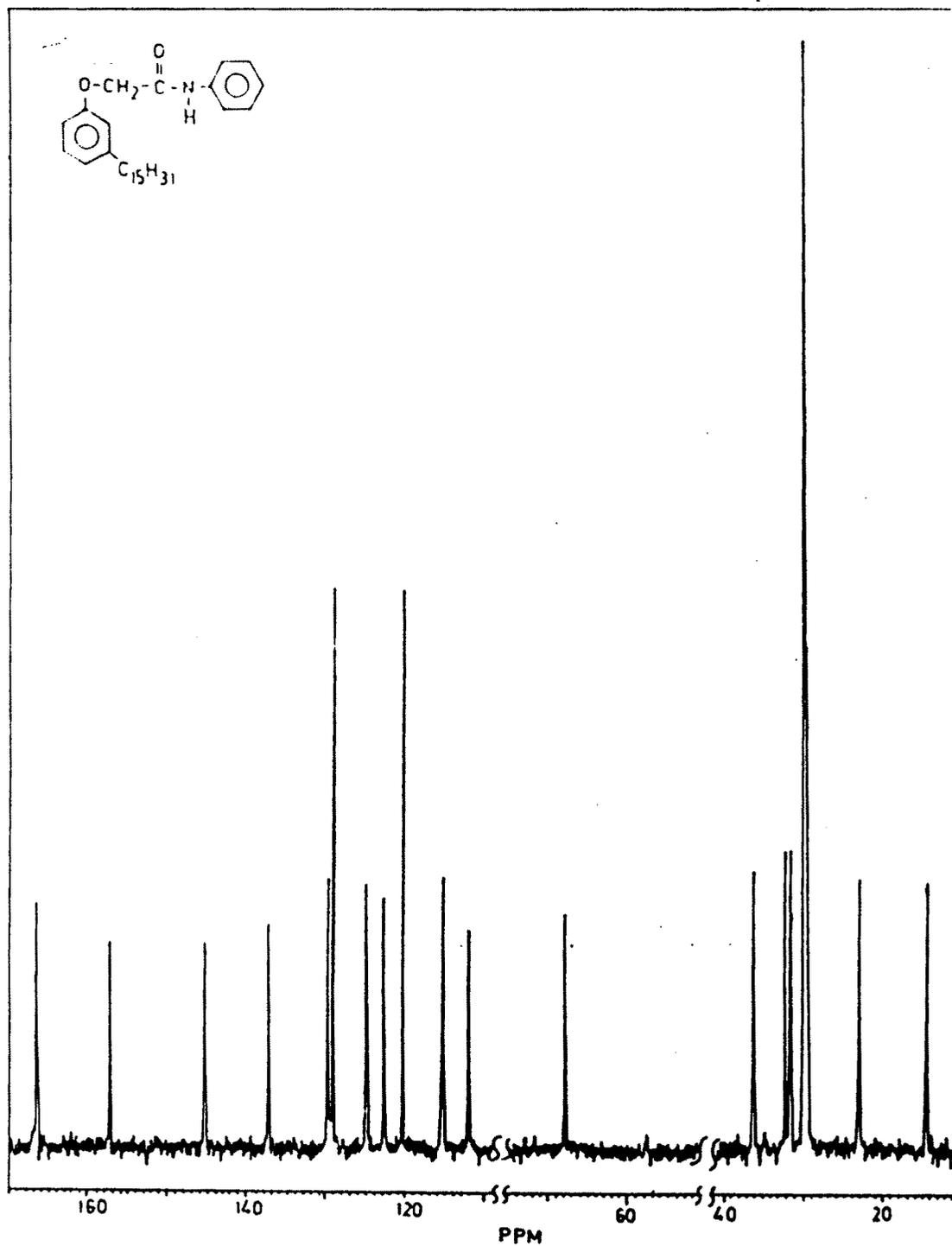
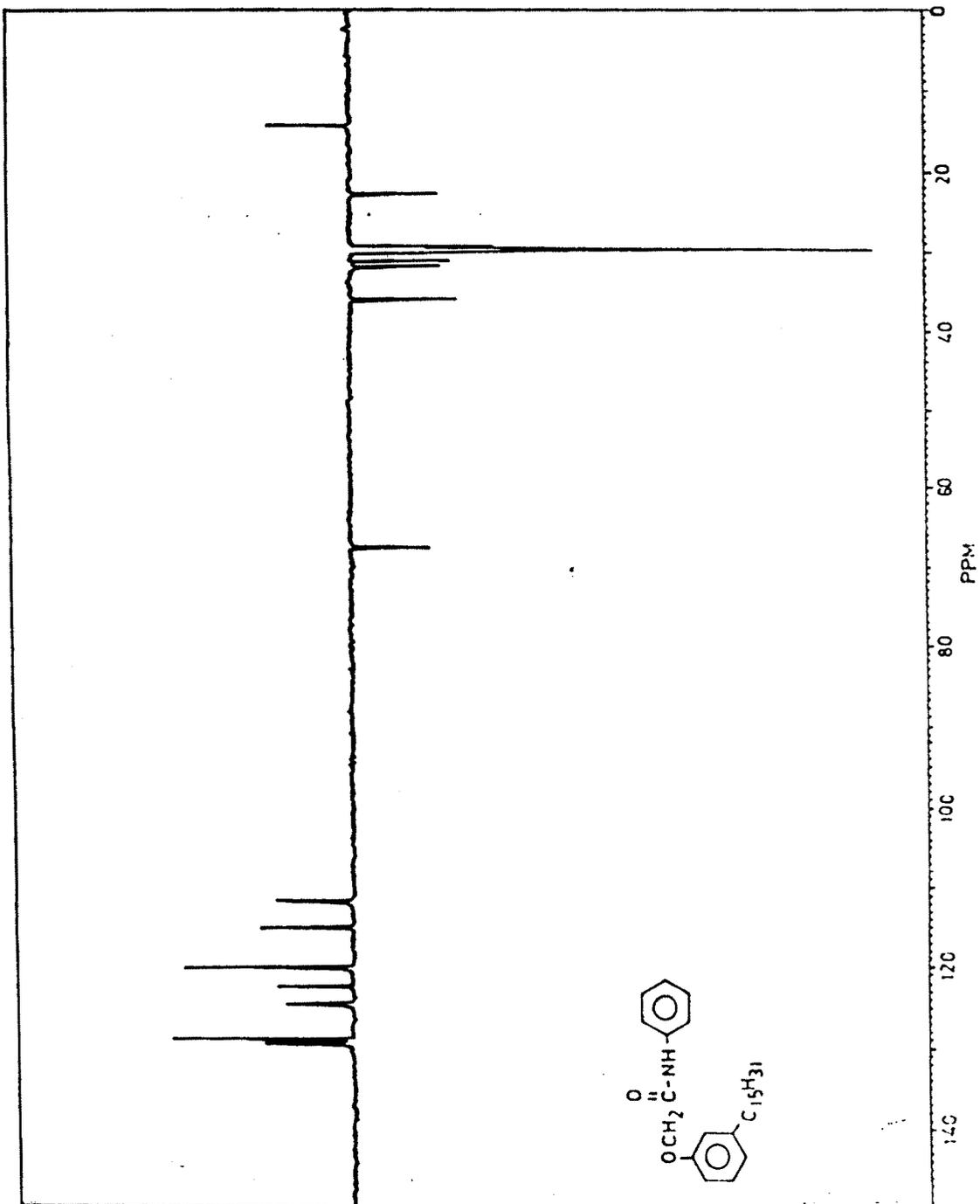FIG.18 : C-13 NMR SPECTRUM -H 1 DECOUPLED-OF (3-PENTADECYL)-PHENOXY (N-PHENYL) ACETAMIDE.

FIG 19 C-13 NMR SPECTRUM-DEPT- OF (3-PENTDECYL) PHENOXY (N-PHENYL) ACETAMIDE.

122.55, 120.19, 115.12, 111.87 δ. The rest three tertiary carbons at 157.21, 145.15 and 137.14 δ are not seen in DEPT. The signal due to -CH$_3$ group appeared at 14.20 δ, whereas the -OCH$_2$- carbon of -OCH$_2$-CO-NH is seen at 67.67 δ Other methylene appeared at 36.03,32.02, 31.40, 29.79, 29.61, 29.45 and 22.77 δ.

The Amide (3b) was prepared by reaction of m-nitroaniline with (3-pentadecyl) phenoxy acetic acid and its PMR spectrum is presented in fig.20 which confirms the structure. NH signal appeared at 8.55 δ (s,1H) and -OCH$_2$ at 4.65 δ (s,2H). C$_{15}$H$_{31}$ unit signals are at 2.6 (t,2H, benzylic CH$_2$), 1.65 (qn, 2H, CH$_2$ next to benzylic CH$_2$) 1.3 (S,24H), 0.9(t,3H, methyl protons). Aromatic protons are in the range 8.5 to 6.7 δ. C-13 NMR spectrum (H1 decouplded) of (3b) shown in fig.21, and DEPT spectrum shown in fig.22 allowed the assignments of various carbons. Thus carbonyl (C=O) appeared at 167.15 δ, whereas the aromatic CH signal at 130.04, 129.80, 125.86, 122.99, 119.46, 115.24, 115.01, 111.92 δ and the aromatic tertiary carbons at 157.05, 148.75, 145.49 and 138.30 δ. The -OCH$_2$ carbon appeared 67.70 δ and CH$_3$ of C$_{15}$H$_{31}$ appeared at 14.27 δ. All other methylenes (CH$_2$)$_{14}$ appeared at 36.13, 32.10, 31.51, 29.86, 29.52 and 22.86 δ.

The reaction product (3c) from (1) and 4-nitroaniline was produced in excellent yields The PMR spectrum of (3c) is given in fig.23. The signal at 8.65 δ is assigned to NH (s,1H) whereas -OCH$_2$- protons appeared at 4.65 δ (s,2H). The signals due to C$_{15}$H$_{31}$ are differentiated benzylic CH$_2$ at 2.65 δ (t,3H) -CH$_2$ next be benzylic at 1.65 δ (qn,2H), CH$_3$ at 0.9 δ (t,3H) and at 1.3 δ for -(CH$_2$)$_{12}$(s,24H).

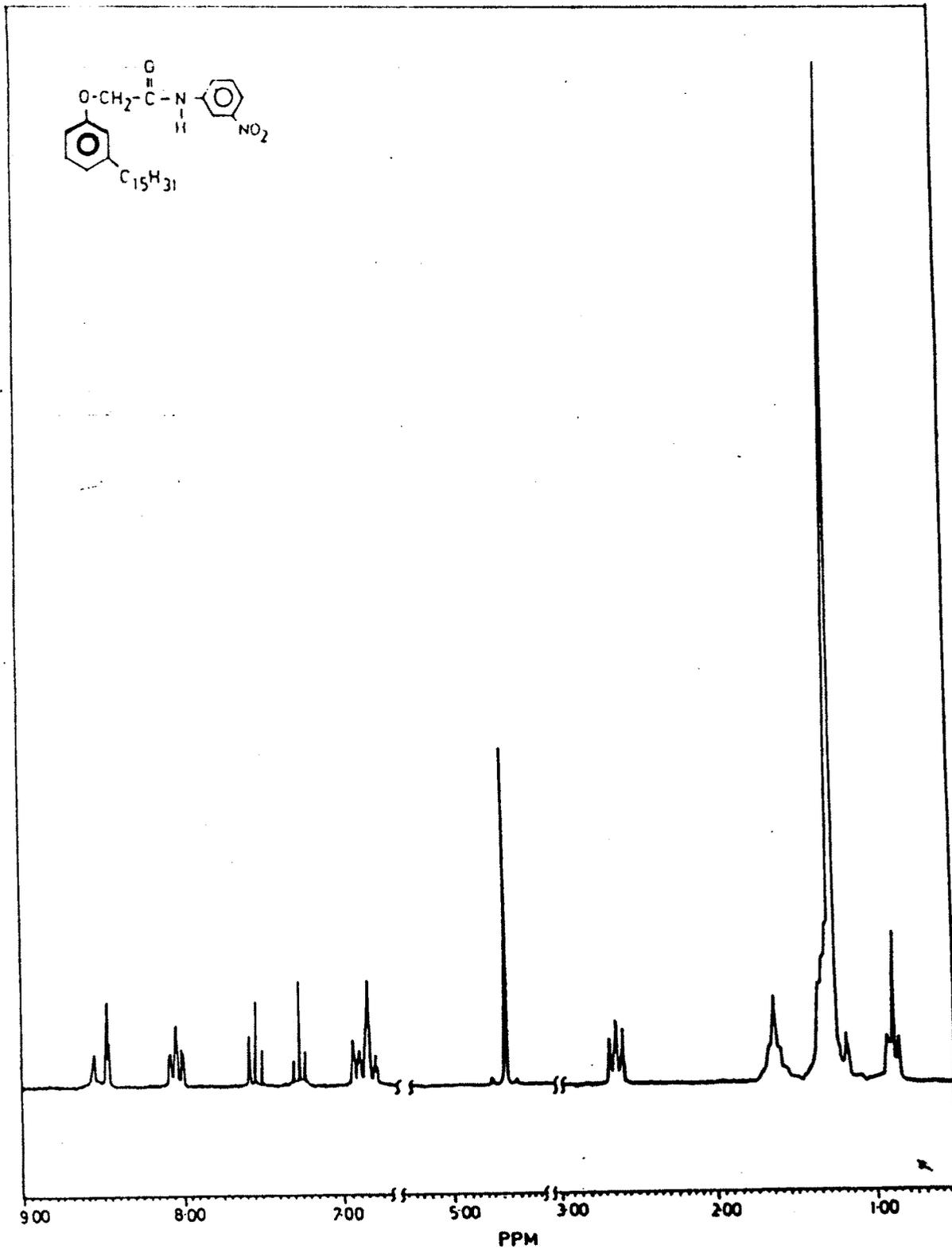Similarly the amide (3d) obtained by reacting 4-bromoaniline

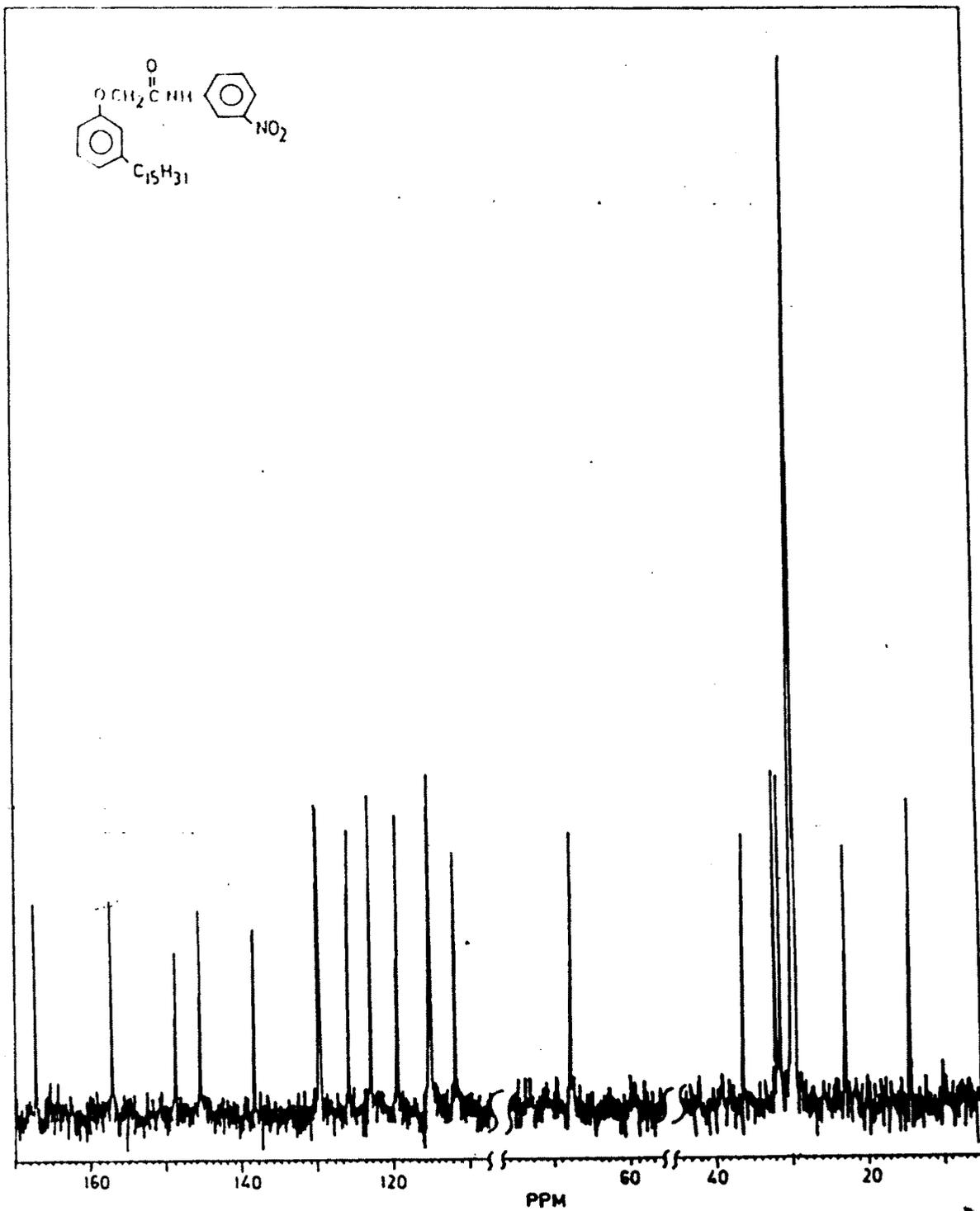FIG. 20: H-1 NMR SPECTRUM OF (3-PENTADECYL) PHENOXY [N-(3-NITROPHENYL)]
ACETAMIDE.

FIG. 21 C-13 NMR SPECTRUM -H1 DECOUPLED- OF (3-PENTADECYL) PHENOXY
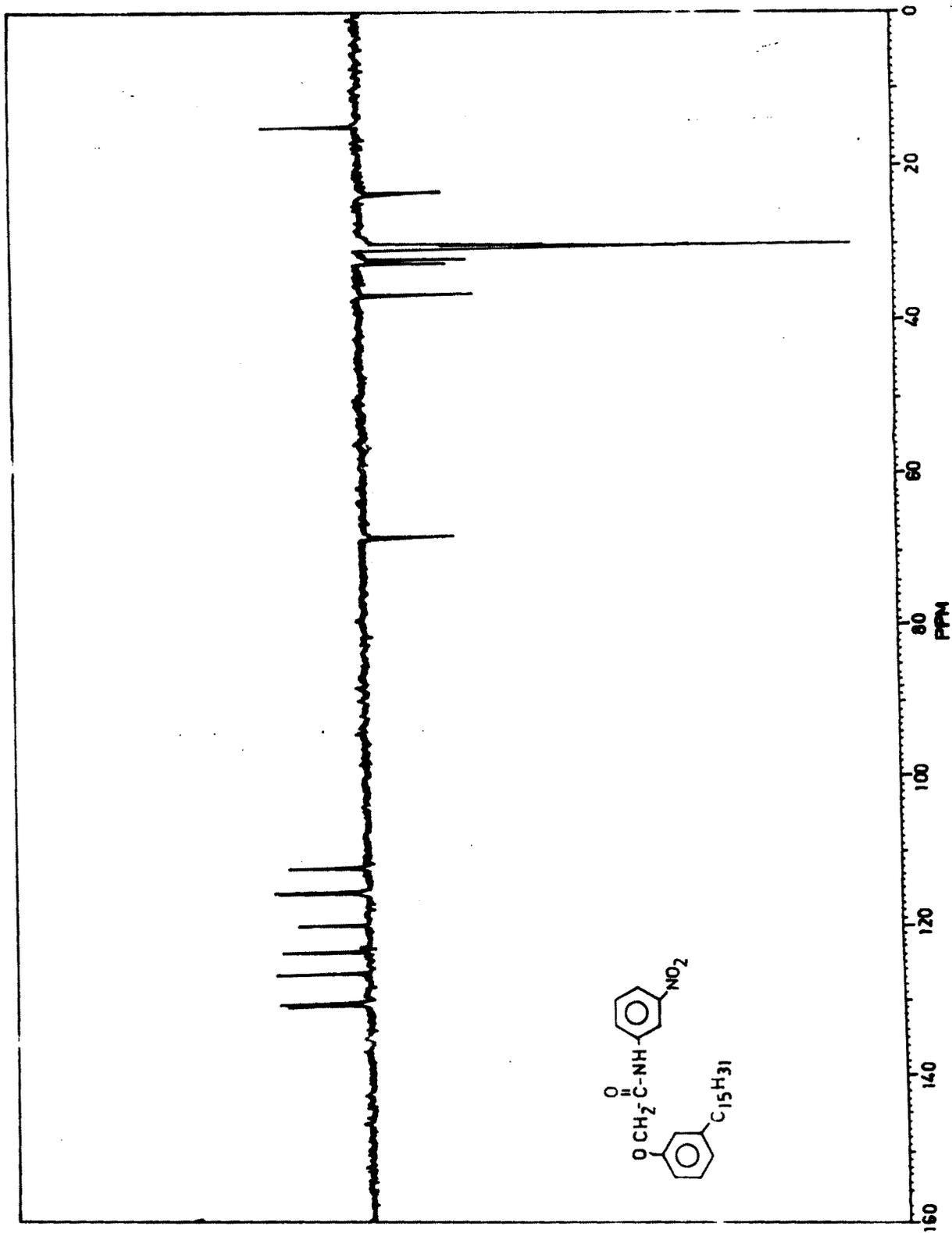[N-(3 NITROPHENYL)] ACETAMIDE.

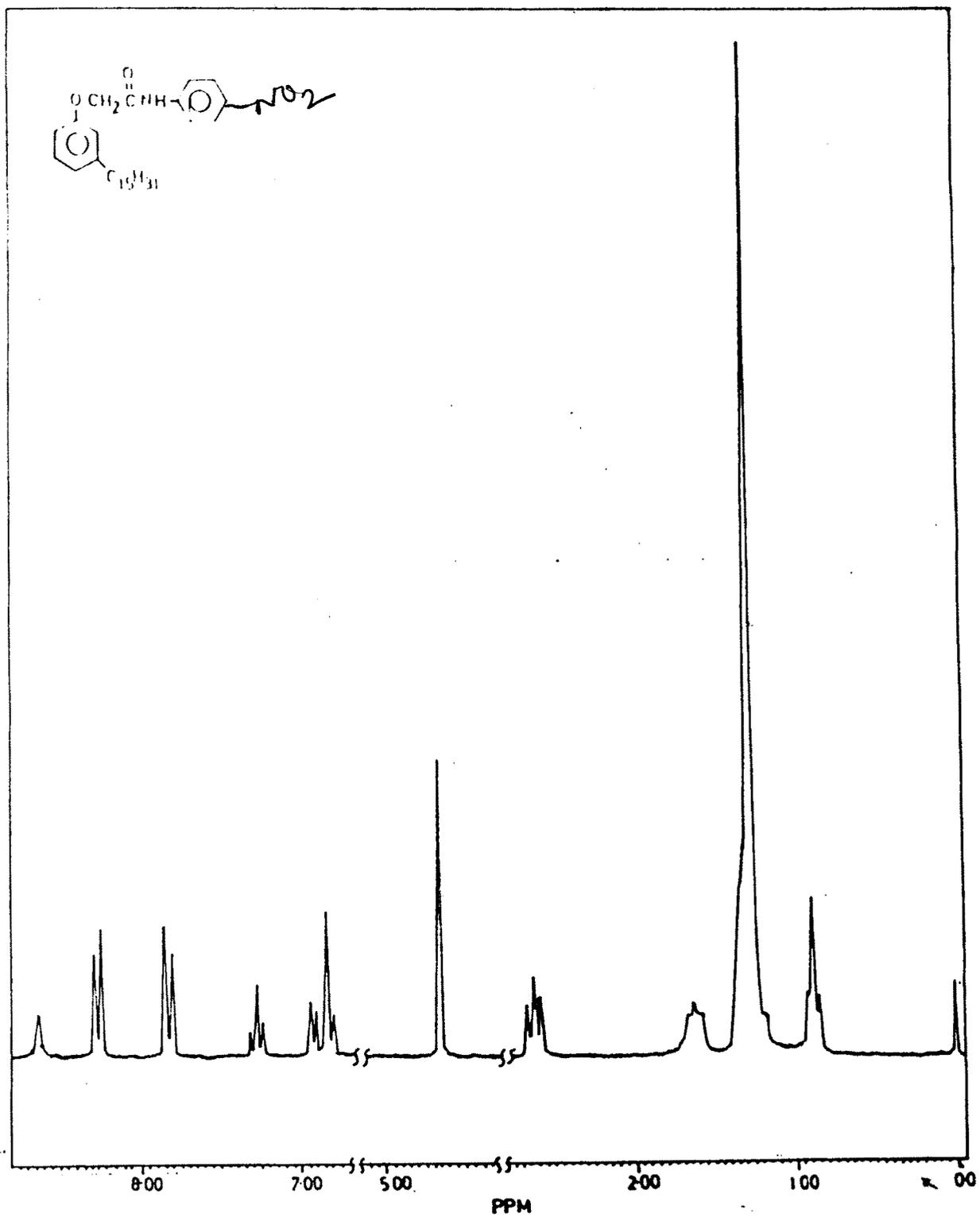FIG. 22 : C-13 NMR SPECTRUM-DEPT- OF (3-PENTADECYL) PHENOXY [N-(3-NITROPHENYL)] ACETAMIDE.

FIG. 23 :H:1 NMR SPECTRUM OF (3-PENTADECYL) PHENOXY [N-(4-NITROPHENYL)]
ACETAMIDE.

with (1) showed desired PMR pattern (fig.24). The signal at 8.55 (s,1H NH), 4.6 (s, 2H, -OCH$_2$), 2.6(t, 2H, benzylic CH$_2$), 1.6(qn, 2H, CH$_2$ next to benzylic CH$_2$), 1.25 (s, 24H (CH$_2$)$_{12}$) and 0.9 δ (t, 3H, CH$_3$) are easily identifiable. Aromatic proton NMR peaks ar seen at 7.5 to 6.7 δ.

Similarly the amides 3e, 3f and 3g were obtained and their spectra investigated to confirm structure. They agree well with the proposed amide moieties.

UV spectra of all amides were recorded and the nm values for the 3a to 3f are given in Table XII and it can be used to quantitatively estimate the product in solutions as and when required.

Table No XII

λ_{max}(nm) values for the various (3-pentadecyl) phenoxy N-aryl acetamides.

S.No.	Amide Code	Name	λ_{max}(nm)
1	3(a)	(3-pentadecyl)phenoxy (N-phenyl)acetamide	280
2	3(b)	(3-pentadecyl)Phenoxy [N-(m-nitrophenyl)]acetamide	290
3	3(c)	(3-pentadecyl)Phenoxy [N-(P-nitrophenyl)]acetamide	300
4	3(d)	(3-pentadecyl)Phenoxy [N-(P-bromophenyl)]acetamide	285
5	3(e)	(3-pentadecyl)Phenoxy [N-(α-naphthyl)]acetamide	305
6	3(f)	(3-pentadecyl)Phenoxy [N(-m-methyl phenyl)]acetamide	285

Thus a series of amides derived from (3-pentadecyl) phenoxy acetic acid was fully characterised.
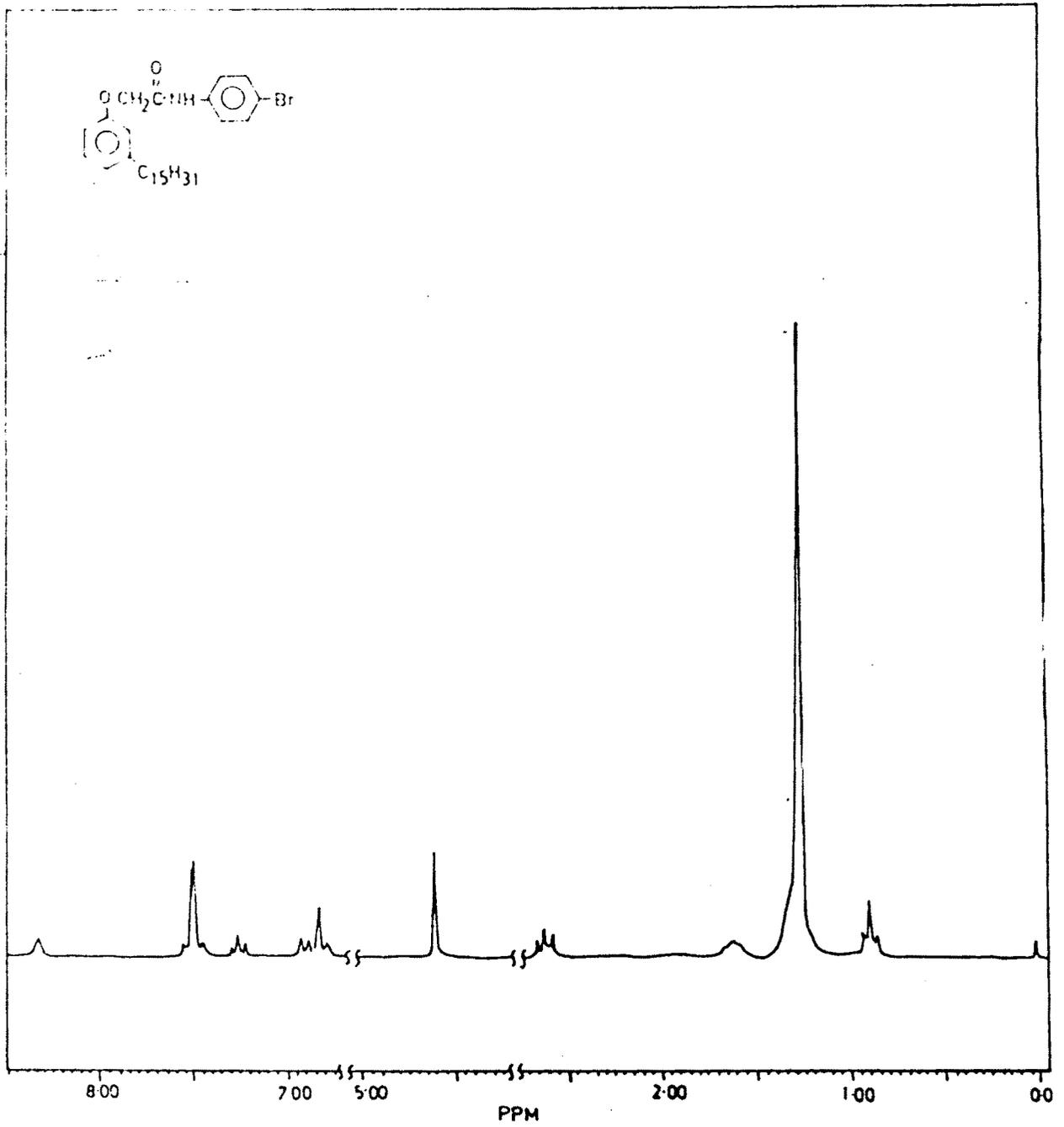
FIG 24 H-1 NMR SPECTRUM OF (3-PENTADECYL) PHENOXY [N-(4-BROMOPHENYL)] ACETAMIDE.