Chapter 5

Structure Elucidation and Identification of Pesticides Using Various Spectroscopic Instruments

CONTENTS

1. Introduction

The identification of active ingredients and impurities using an appropriate procedure is very important prior to any physico-chemical analysis. There must be proper procedures to confirm the pesticide identity in sample. Several chromatographic and spectroscopic techniques have been published in CIPAC Handbook[1], FAO[2] and WHO[3] for identification of pesticides in commercial samples. Majority of the procedures employed the identification of pesticides by analyzing both sample and standard under similar analytical conditions using one or more techniques and matching their characteristic informations obtained from different instruments viz., R_f values in TLC[4]; retention time and elution pattern in GLC[5] and HPLC[4] analysis; fragmentation pattern and mass of specific ions in GC/MS or MS[5] analysis; specific bands in IR[6] analysis; chemical shift values and splitting patterns in NMR[7] analysis or λ_{max} values in UV-Visible[8] analysis. In case of identification of an unknown sample or in absence of standard, the sample was analysed by one or more spectroscopic techniques and data was interpreted independently to illustrate the structure of sample with literature.

In the present chapter, attempt has been made to elucidate the structure of three selected pesticides viz., metalaxyl, tebuconazole and napropamide using various analytical instruments viz., gas chromatograph coupled with mass spectrometer (GC/MS), IR spectrometer, NMR spectrometer, UV-visible spectrophotometer, and differential scanning calorimeter (DSC). The instrumental data obtained from different instrumental analysis was interpreted independently based on the structural informations to confirm the structure of the compound. Various instrumental informations about the structure of the compound were compared to find most suitable method for structure elucidation and identity confirmation of an unknown compound.

2. Experimental Procedure

2.1 Instruments and Equipments

Sr. No.	Instruments	Model	Manufacturer
1	Weighing Balance (Least Count 0.01 mg)	Model: CP 225 D	Sartorius, Germany
2	Gas Chromatograph with Mass Selective Detector (GC/MS)	6890/5973	Hewlett Packard, USA
3	GC Column [30 m x 0.25 mm (i.d.) x 0.25 µm film thickness]	HP-5 MS	Hewlett Packard, USA
4	Fourier Transform Infrared Spectrometer (FT-IR)	Spectrum RX 1	Perkin Elmer, UK
5	Ultra Violet-Visible Spectrophotometer (UV-Visible)	UV-160A	Shimadzu, Japan
6	Proton Nuclear Magnetic Resonance Spectrometer (^{1}H-NMR)	Av 400 (400 MHz)	Bruker, Switzerland
7	Differential Scanning Calorimeter (DSC) with Purity Software	Pyris 6 DSC	Perkin Elmer, UK

2.2 Solvents and Chemicals

Sr. No.	Solvents/Reagents	Grade	Supplier
1	Dichloromethane	ExcelaR	Qualigens, India
2	Methanol	HPLC & Spectroscopic	s.d.fine-chem Ltd., India

2.3 Pesticide Samples

Sr. No.	Pesticides	Group	Purity	Source
1	Napropamide	Herbicide	99.85%	Chem Service, USA
5	Tebuconazole	Fungicide	99.50%	Chem Service, USA
6	Metalaxyl	Fungicide	99.60%	Chem Service, USA

3. Methodology

3.1 Identification of Pesticides by Gas Chromatography/Mass Spectrometry

The pesticide sample solutions were injected onto gas chromatograph coupled with mass spectrometer (GC/MS) and identification of main peak (active ingredient) was performed through its mass spectra on the basis of the mass of molecular ion (molecular weight), base ion and fragmentation pattern.

3.1.1 Preparation of Sample Solutions

A known quantity of each pesticide sample (10 mg approx.) was weighed into separate volumetric flasks of 10 mL capacity, contents were dissolved in 5 mL dichloromethane and volume was made upto the mark with dichloromethane.

3.1.2 GC/MS Analytical Parameters

The above sample solutions were injected onto GC/MS using following parameters:

Instrument	:	GC/MS (Hewlett Packard-6890/5973), HP ChemStation
Column	:	HP-5 MS; [30 m x 0.25 mm (i.d.) x 0.25 µm film thickness]
Carrier gas	:	Helium
Carrier gas flow	:	1.0 mL/min
Injection volume	:	1 µl
Injection mode	:	Split (Split ratio 20:1)
Temperatures (Metalaxyl)		
Oven	:	40 °C (hold for 3.0 min) to 280 °C @ 15 °C/min (hold for 5.0 min)
Injector	:	250 °C
Transfer line	:	280 °C
Temperature (Tebuconazole)		
Oven	:	60 °C (hold for 1.0 min) to 260 °C @ 8 °C/min (hold for 2.0 min)
Injector	:	250 °C
Transfer line	:	280 °C
Temperatures (Napropamide)		
Oven	:	50 °C (hold for 3.0 min) to 300 °C @ 10 °C/min (hold for 2.0 min)
Injector	:	250 °C
Transfer line	:	300 °C
Detector	:	Mass selective detector (MSD)
Mass range	:	30 to 450 m/z
Filament delay	:	4.0 min.
Quadrupole temp	:	150 °C
Retention time (approx.)	:	Metalaxyl 15.4 min Tebuconazole 11.5 min Napropamide 19.9 min

3.2 Identification of Pesticide Samples by FT-IR Spectrometer

On scanning a pesticide on IR spectrometer the various functional groups present in the molecule absorb IR radiations of specific wave numbers due to change in its vibrational energy, which appears as sharp bands at different wave numbers in IR Spectrum. The structure of a pesticide was determined by identifying various functional groups based on their specific wave numbers.

3.2.1 Preparation of Sample Pellets

The KBr pellets of pesticide samples were prepared by mixing 1 mg of sample with 150 mg potassium bromide (KBr) using a pestle and mortar and applying a pressure of 7 ton/in^2 using a hydraulic press. A blank pellet of pure KBr was also prepared similarly for background analysis. The pesticide pellets were analysed by Perkin Elmer, Spectrum RX-1 FT-IR Spectrometer between 4400 - 440 cm^{-1} wave number range at 4 cm^{-1} resolutions.

3.3 Identification of Pesticide Samples by UV-Visible Spectrophotometer

Pesticide sample were analysed on a double beam UV-visible spectrophotometer at full wavelength range to find the λ_{max} value at which maximum absorbance takes place for each pesticide, separately. The λ_{max} value was specific for each pesticide and used for identification.

3.3.1 Preparation of Sample for UV Analysis

The pesticide sample solutions were prepared by weighing a known quantity of each pesticide sample (100 mg approx.) into a volumetric flask of 250 mL capacity, dissolving the contents in 25 mL methanol and making the volume upto the mark with methanol. The pesticide solutions were diluted and analysed onto a double beam UV-Visible spectrophotometer of Shimadzu at wavelength range of 800 to 200 nm and absorbance range of 0.0 to 205 units using the matched pair quartz sample cells of 1 cm path length.

3.4 Identification of Pesticide Samples by ^{1}H-NMR Spectrometer

Pesticide samples were analysed on a proton NMR Spectrometer using tetramethylsilane as internal standard. The spectrum was interpreted for number of hydrogen atoms present in various organic groups by the integration and chemical shift values and splitting pattern of the peaks to identify the compound.

3.4.1 Preparation of Sample for NMR Analysis

A 10% solution of each pesticide was prepared by dissolving 1 mg sample in 10 mL deuterochloroform ($CDCl_3$) containing tetramethylsilane as internal standard. The solution was analysed on 400 MHz Bruker AV400, ^{1}H-NMR spectrometer.

3.5 Identification of Pesticide Samples by Differential Scanning Calorimeter

In a heat-flux differential scanning calorimeter (DSC), sample was heated at a specified rate and the difference in the heat flow between the sample and the reference is measured as a function of temperature. The heat transition in the sample during its melting was observed as an endotherm in DSC scan, whose onset determine the exact melting point of the compound. The melting temperature value of pesticide was matched with theoretical value to confirm its identity.

3.5.1 Preparation of Sample Capsule for DSC Scanning

A small quantity (1 to 2 mg) of desired sample (finely powdered and homogenized) was transferred into an aluminum pan/sample holder and encaped using a sample pan crimper press. Both, sample capsule and an empty capsule of same material were placed carefully at the sample and reference positions within the DSC cell. A nitrogen gas purge was applied and samples were scanned using a Perkin Elmer, Pyris 6 differential scanning calorimeter (DSC) using following parameters:

Temperature Range

Metalaxyl	:	50 °C to 86 °C
Tebuconazole	:	90 °C to 124 °C
Napropamide	:	30 °C to 56 °C
Heating rate	:	2 °C/min
Purge gas	:	Nitrogen
Purge gas flow	:	40 mL/min

4. Results and Discussion

The various spectroscopic techniques provide valuable information about the structure of the compound, which helps to confirm the identity of an unknown compound. In the present study, three typical pesticides viz., metalaxyl, tebuconazole and napropamide were analysed using various spectroscopic instruments and data was interpreted independently to confirm their identity. The structural informations obtained by different instruments were compared.

The infrared spectra of pesticides confirmed the presence of various functional groups in pesticide, therefore provided valuable contribution in structure elucidation. The IR spectra of metalaxyl, tebuconazole and napropamide (**Fig. 1.1, 2.1 and 3.1**) showed characteristic bands at specific wave numbers corresponding to various functional groups of compound. In **Section 4.1.1,** the structure of metalaxyl with FTIR has been elucidated by identifying the various characteristic functional groups in metalaxyl sample by correlating the wave numbers of specific bands in IR spectrum with their theoretical values (**Table 1.1**) available in the litrature[6,9]. Similarly characterization of tebuconazole and napropamide has also been performed by FTIR in **section 4.1.2, 4.2.3** by determining the presence of functional groups corresponding to specific bands of their IR spectrum and correlating them with their structure (**Table 1.2 & 1.3**).

4.1 Identification by Infrared Spectroscopy

4.1.1 Characterization of Metalaxyl by FTIR

The interpretation of IR spectrum of metalaxyl, confirmed the presence of following Functional groups in metalaxyl sample by comparing the wave numbers of its specific bands with their theoretical values:

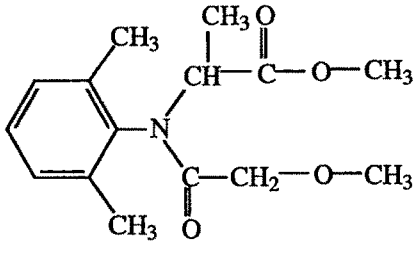

Table 1.1: Interpretation of various bands obtained in IR spectrum of metalaxyl.

Sr. No.	Wave Numbers of IR Peaks (cm^{-1})	Vibration Motions of Functional Groups
1.	2997.6 & 2954.6	C-H stretch. of CH_3 groups
2.	2816.9	C-H stretch. of CH_2 group
3.	1759.3	C=O stretch. of saturated acyclic ester group
4.	1671.4	C=O stretch. of tertiary amide group
5.	1298.5	C-N stretch. of tertiary aromatic amine group
6.	1199.0	C-O stretch. of propanate ester group
7.	1174.2 & 1131.5	C-O stretch. of dialkyl ether group
8.	784.5	C-H bending out-of-plane of 3 adjacent H atom of benzene ring

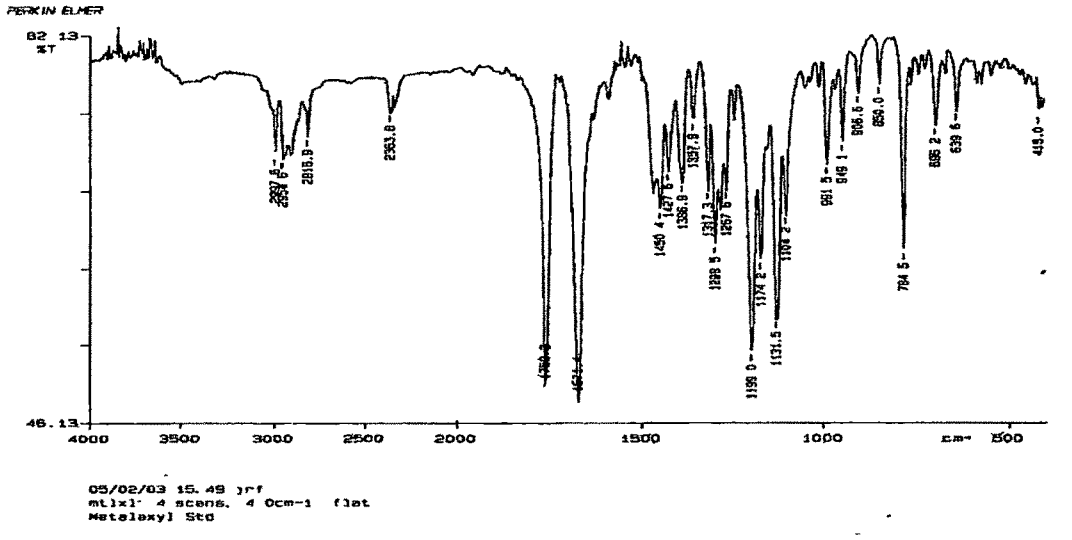

Fig. 1.1: IR spectrum of metalaxyl.

4.1.2 Characterization of Tebuconazole by FTIR

The interpretation of IR spectrum of tebuconazole, confirmed the presence of following functional groups in tebuconazole sample:

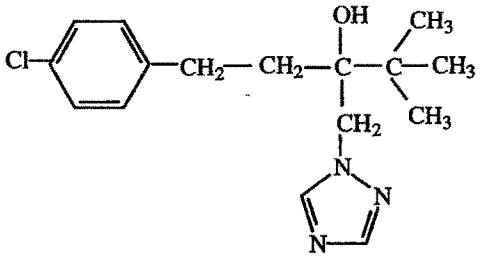

Table 1.2: Interpretation of various bands obtained in IR spectrum of tebuconazole.

Sr. No.	Wave Numbers of IR Peaks (cm^{-1})	Vibration Motions of Functional Groups
1.	3299.4	O-H stretch. due to intermolecular association of alcohol group
2.	2972.3	C-H stretch. of CH_3 groups
3.	1511.7 & 1490.4	N-N and C=N stretch. of triazide group
4.	1408.1	C-O stretch. of C-OH group
5.	1367.0	C-H bend. of C-(CH_3)group
6.	1272.2 & 1205.5	Skeleton of C-(CH_3)group
7.	1134.8	O-H bend. of tertiary alcohol group
8.	1092.9	C-N stretch. of aliphatic amine group
9.	851.0 & 811.1	C-H bend. of p-disubstituted benzene ring
10.	680.0	C-Cl stretch. of p-aryl chloride group

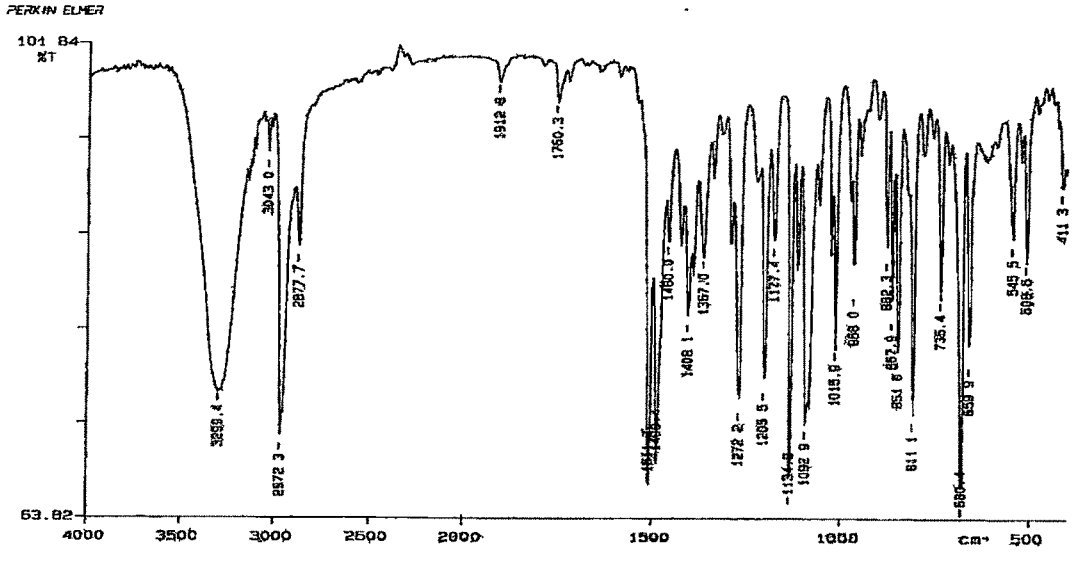

Fig. 1.2: IR spectrum of tebuconazole.

4.1.3 Characterization of Napropamide by FTIR

The interpretation of IR spectrum of napropamide, confirmed the presence of following functional groups in napropamide sample:

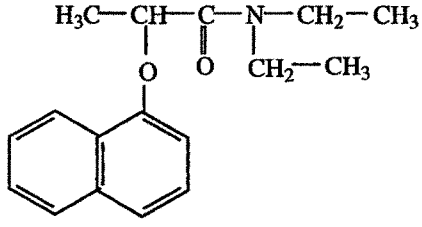

Table 1.3: Interpretation of various bands obtained in IR spectrum of napropamide.

Sr. No.	Wave Numbers of IR Peaks (cm^{-1})	Vibration Motions of Functional Groups
1.	2981.1 & 2937.4	C-H stretch. of CH_2CH_3 groups
2.	1629.5	C=O stretch. of tertiary amide group
3.	1597.2, 1578.9 & 1463.7	C-C skeletal vib. Of aromatic ring
4.	1441.4	C-H bend. of N-CH_2 group
5.	1398.0	C-H bend. of CH-CO group
6.	1269.8, 1241.9 & 1101.8	C-O stretch. of aryl alkyl ether group
7.	1179.9	C-N stretch. of aliphatic amine group
8.	787.5 & 799.2	C-H bend. of 5 adjacent H atom of naphthalene ring

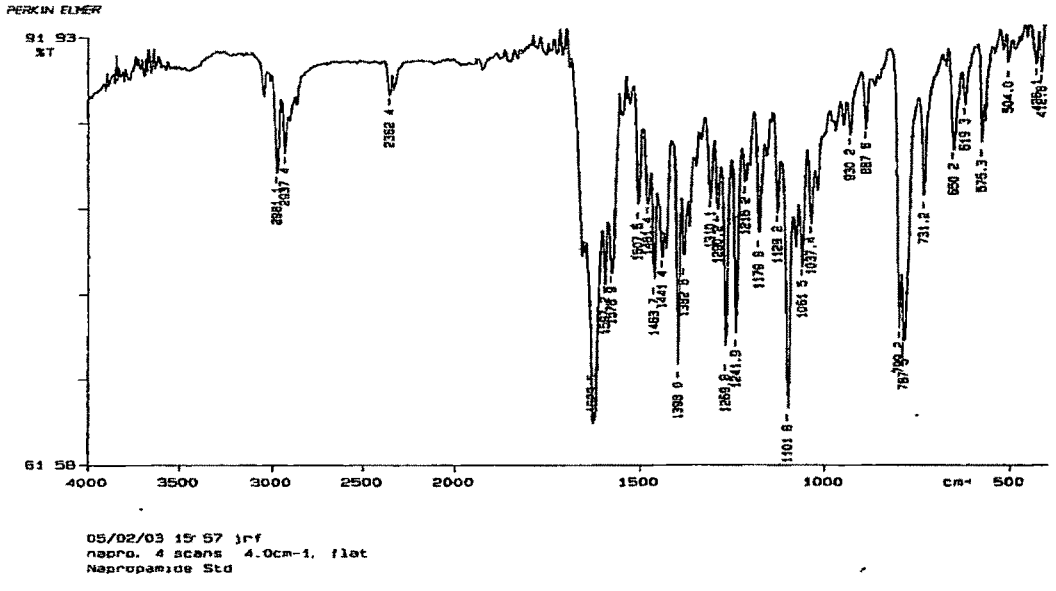

Fig. 1.3: IR spectrum of napropamide.

The molecular structures of pesticides were determined with the help of nuclear magnetic resonance spectrum (^{1}H-NMR) by finding the numbers of hydrogen atoms in various groups of the molecule and their chemical and structural environment (**Section 4.2.1, 4.2.2, 4.2.3**). The NMR spectra of metalaxyl, tebuconazole and napropamide (**Fig. 2.1, 2.2, 2.3**) were interpreted to determine the number of hydrogen atoms present in various groups and their neighboring groups on the basis of the integration values, chemical shifting and splitting pattern of various peaks in NMR spectrum of the compound (**Table 2.1, 2.2, 2.3**).

The mass spectra of pesticides provided the valuable information about its molecular weight and structure (**Section 4.3.1, 4.3.2, 4.3.3**). The mass spectrum of metalaxyl, tebuconazole and napropamide (**Fig. 1.2, 2.2 and 3.2**) showed the molecular ion peak, highest stable base peak and the fragmentation pattern of pesticides, obtained due to bombardment of its molecules with high-energy electrons. The relative abundances of various fragments/free radicals represents its stability while the m/z values represents the mass of the fragments, which helped a lot to determine the structures of the fragments and corresponding structure of molecule for the identification of the compound (**Table 3.1, 3.2, 3.3**).

4.2 Identification by NMR Spectroscopy

4.2.1 Characterization of Metalaxyl by ^{1}H-NMR

The interpretation of ^{1}H NMR spectrum of metalaxyl provided the following structural information regarding the protons and their chemical environment to confirm the structure of metalaxyl:

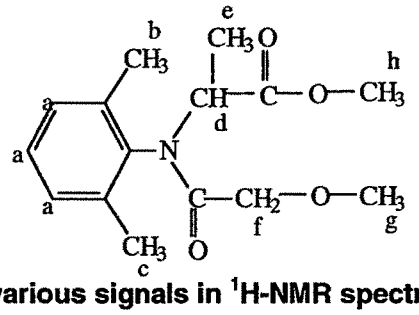

Table 2.1: Interpretation of various signals in ^{1}H-NMR spectrum of metalaxyl.

Sr. No.	Chemical Shifts (δ), ppm	Integration	No. of protons	Splitting	Identity in Structure	Interpretation
1.	7.085-7.202	2.9998	3	Multiplet	a	3 aromatic protons in benzene ring
2.	2.137	2.9775	3	Singlet	b	Aromatic methyl group at 2 position
3.	2.453	2.9546	3	Singlet	c	Aromatic methyl group at 6 position
4.	4.488-4.506	1.0000	1	Quartet	d	-CH groups attached to N
5.	0.975-0.994	3.0360	3	Doublet	e	-CH_3 group attached to –CH group
6.	3.441-3.611	2.0849	2	Quartet	f	-CH_2 group attached to –OCH_3 group
7.	3.316	2.9443	3	Singlet	g	-OCH_3 group attached to –CH_2 group
8.	3.779	2.9432	3	Singlet	h	-OCH_3 group attached to –C=O group

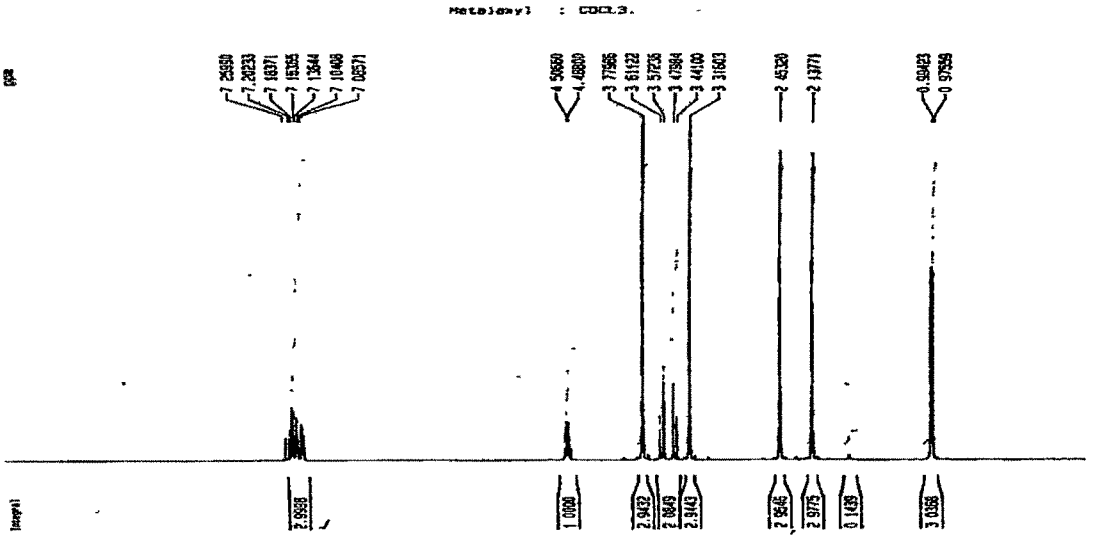

Fig. 2.1: ^{1}H-NMR spectrum of metalaxyl.

4.2.2 Characterization of Tebuconazole by ^{1}H NMR

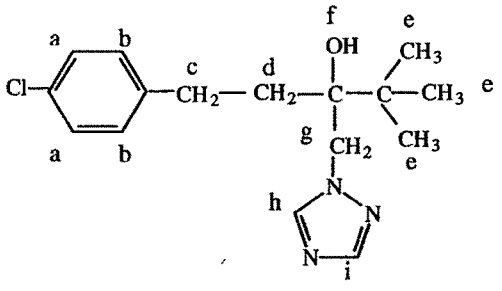

Table 2.2: Interpretation of various signals in ^{1}H NMR spectrum of tebuconazole.

Sr. No.	Chemical Shifts (δ), ppm	Integration	No. of protons	Splitting	Identity in Structure	Interpretation
1.	7.165-7.186	2.0116	2	Multiplet	a	Aromatic protons next to Chlorine atom
2.	6.92-6.95 & 6.927-6.948	2.0395	2	Multiplet	b	Aromatic protons near to aliphatic chain
3.	2.429-2.439	1.0507	4	Multiplet	c,d	2 –CH_2 groups in side chain
	1.675-1.821	3.1397				
4.	1.015	9.0157	9	Singlet	e	9 protons from 3 –CH_3 groups in t-butyl group
5.	3.249	0.9934	1	Singlet	f	Hydroxyl group proton, D_2O exchangeable
6.	4.336	2.0381	2	Singlet	g	-CH_2 group attached to triazole ring
7.	8.204	1.0000	1	Singlet	h	Aromatic protons in triazole ring at 5 position
8.	7.987	0 9870	1	Singlet	ı	Aromatic protons in triazole ring at position

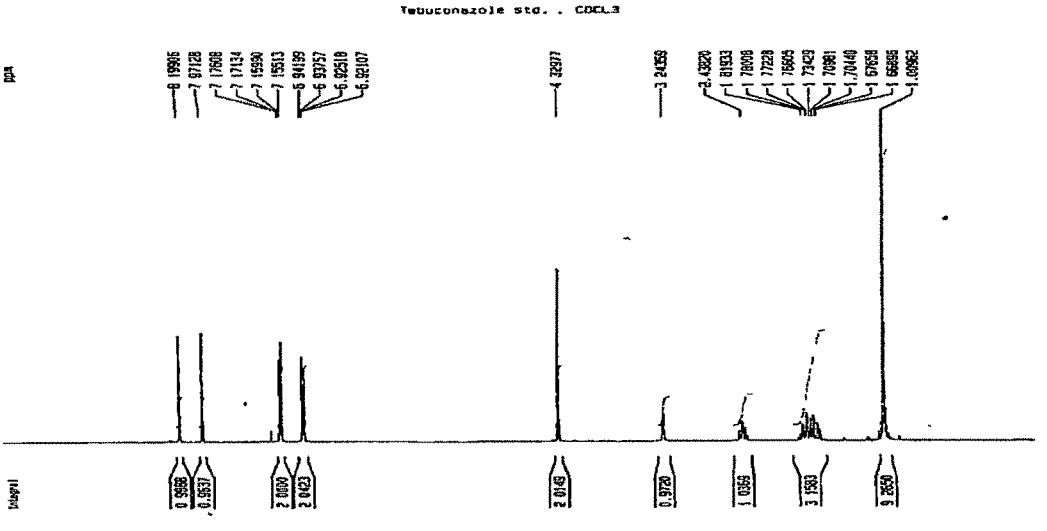

Fig. 2.2: ^{1}H-NMR spectrum of tebuconazole.

4.2.3 Characterization of Napropamide by ^{1}H NMR

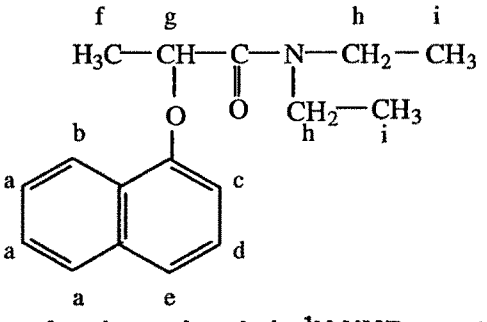

Table 2.3: Interpretation of various signals in ^{1}H NMR spectrum of napropamide.

Sr. No.	Chemical Shifts (δ), ppm	Integration	No. of protons	Splitting	Identity in Structure	Interpretation
1.	7.432-7.497	3.0401	3	Multiplet	a	Aromatic protons on position 5,6,7
2.	7.781-7.805	1.0092	1	Multiplet	b	Aromatic protons on position 8
3.	8.293-8.317	1.0000	1	Triplet	c	Aromatic protons on position 2
4.	7.316-7.355	1.0186	1	Triplet	d	Aromatic protons on position 3
5.	6.817-6.836	1.0178	1	Doublet	e	Aromatic protons on position 4
6.	1.721-1.738	3.0700	3	Doublet	f	-CH_3 proton attached to –CH group
7.	5.112-5.145	1.0218	1	Triplet	g	-CH proton attached to O atom
8.	3.353-3.439 & 3.538-3.592	3.0890 1.0510	3 1	Multiplet	h	-CH proton attached to N atom
9.	0.974-1.010	3.1040	3	Triplet	i	-CH_3 proton attached to –CH_2 group
	1.091-1.127	3.1030	3	Triplet		

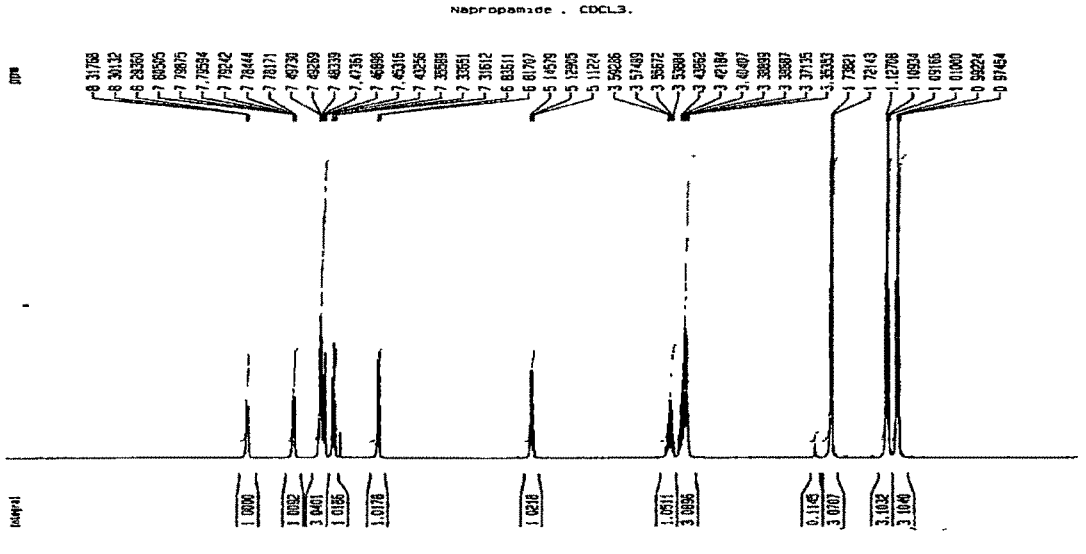

Fig. 2.3: ^{1}H-NMR spectrum of napropamide.

4.3 Identification by Mass Spectrometry

4.3.1 Characterization of Metalaxyl by Mass Spectrometer

The interpretation of mass spectrum of metalaxyl provided valuable information about the molecular weight and structure of pesticide based on mass and relative abundances of various fragments obtained due to bombardment of molecule with high-energy electrons.

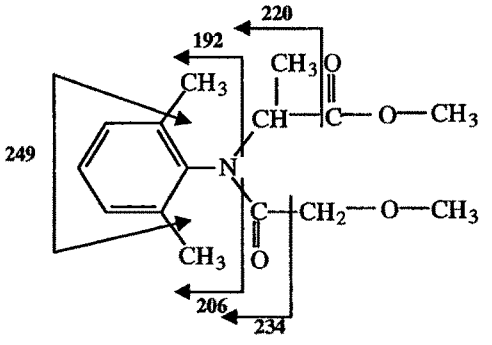

Table 3.1: Fragmentation pattern of metalaxyl by mass spectrometric analysis.

Sr. No.	Remark	Mass of Fragments	Molecular Formula of Fragments
1.	Molecular Ion Peak	**279**	$C_{15}H_{21}NO_4$
2.	279 - $(CH_3)_2$	249	$C_{13}H_{15}NO_4$
3.	279 - $[CH_2\text{-}O\text{-}CH_3]$	234	$C_{13}H_{16}NO_3$
4.	279 - $[CO\text{-}O\text{-}CH_3]$	220	$C_{13}H_{18}NO_2$
5.	234 - C=O	206	$C_{12}H_{16}NO_2$
6.	220 - $[CH\text{-}CH_3]$	192	$C_{11}H_{14}NO_2$
7.	279 - $[C_6H_4\text{-}(CH_3)_2]$	174	$C_7H_{12}NO_4$

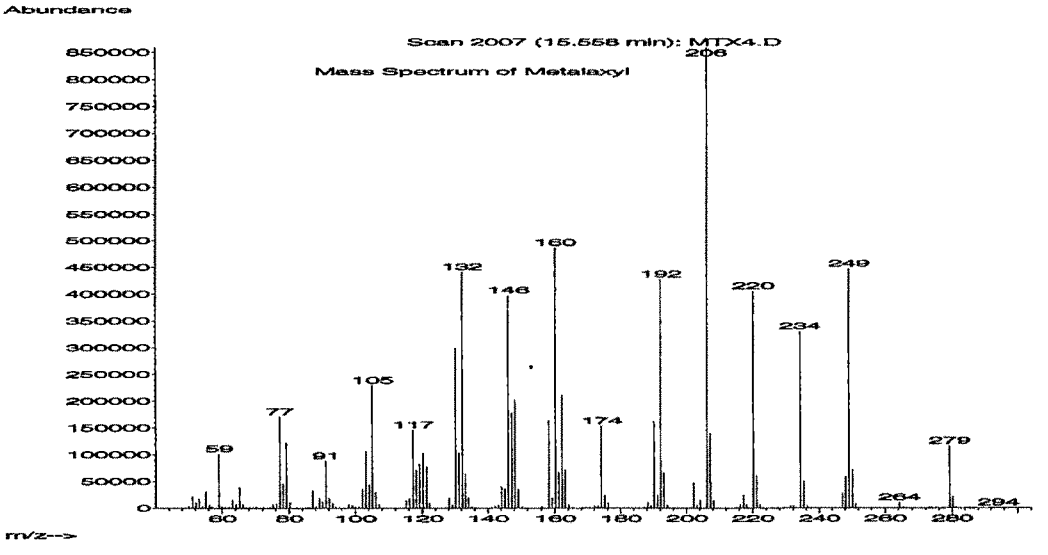

Fig. 3.1: Mass spectrum of metalaxyl.

4.3.2 Characterization of Tebuconazole by Mass Spectrometer

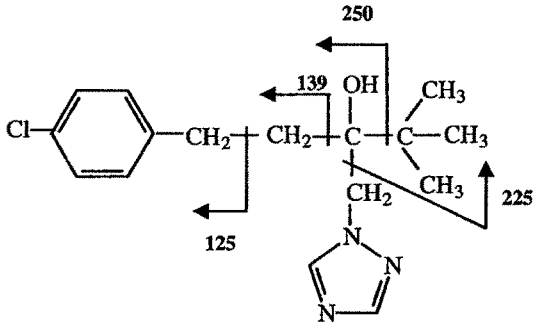

Table 3.2: Fragmentation pattern of tebuconazole by mass spectrometric analysis.

Sr. No.	Remark	Mass of Fragments	Molecular Formula of Fragments
1.	Molecular Ion Peak	**307**	$C_{16}H_{22}ClN_3O$
2.	307 - CH_3	292	$C_{15}H_{19}ClN_3O$
3.	292 - OH	274	$C_{15}H_{17}ClN_3$
4.	307 - [C.$(CH_3)_3$]	250	$C_{12}H_{13}ClN_3O$
5.	307 - [CH_2- $N_3C_2H_2$]	225	$C_{13}H_{18}ClO$
6.	225 - OH	207	$C_{13}H_{16}Cl$
7.	207 - $(CH_3)_3$	163	$C_{10}H_8Cl$
8.	250 - [HO.C.CH_2-$N_3C_2H_2$]	139	C_8H_8Cl
9.	139 - CH_2	125	C_7H_6Cl

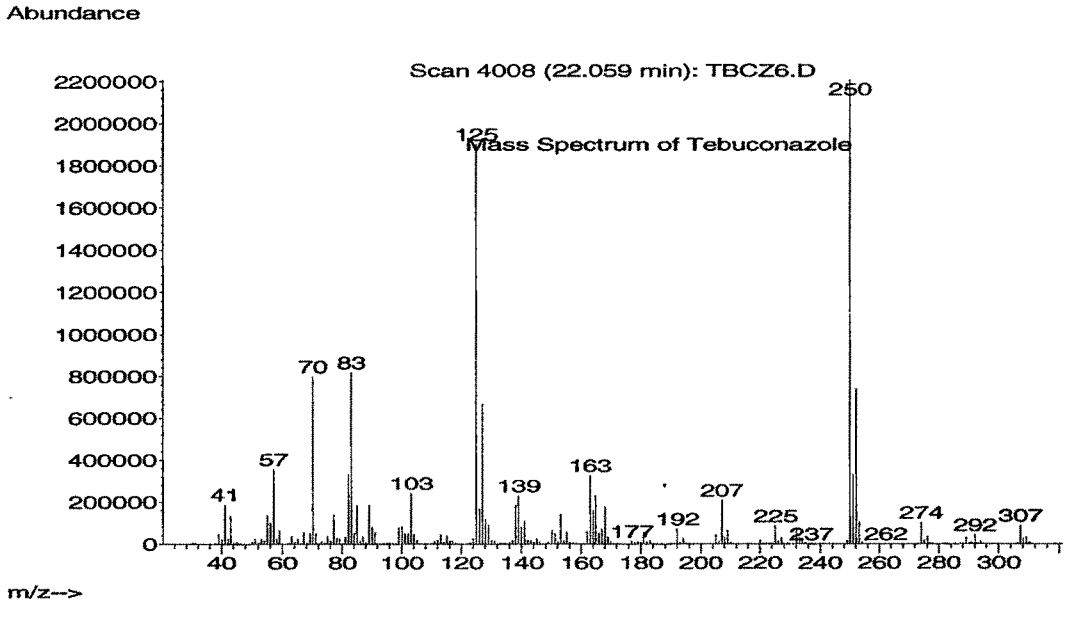

Fig. 3.2: Mass spectrum of tebuconazole.

4.3.3 Characterization of Napropamide by Mass Spectrometer

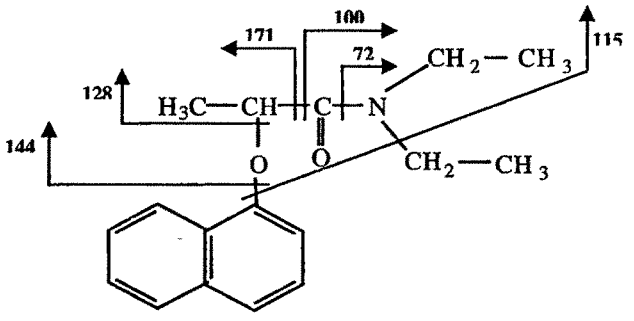

Table 3.3: Fragmentation pattern of napropamide by mass spectrometric analysis.

Sr. No.	Remark	Mass of Fragments	Molecular Formula of Fragments
1.	Molecular Ion Peak	**271**	$C_{17}H_{21}NO_2$
2.	271 - [CO.N(CH_2CH_3)$_2$]	171	$C_{12}H_{11}O_2$
3.	271 - [$C_{10}H_8$]	144	$C_7H_{14}NO_2$
4.	144 - [O]	128	$C_7H_{14}NO$
5.	128 - [CH_3CH]	100	$C_5H_{10}NO$
6.	100 - [C=O]	72	$C_4H_{10}N$
7.	72 - [CH_3]	57	C_3H_7N
8.	144 - [CH_2CH_3]	115	$C_5H_9NO_2$

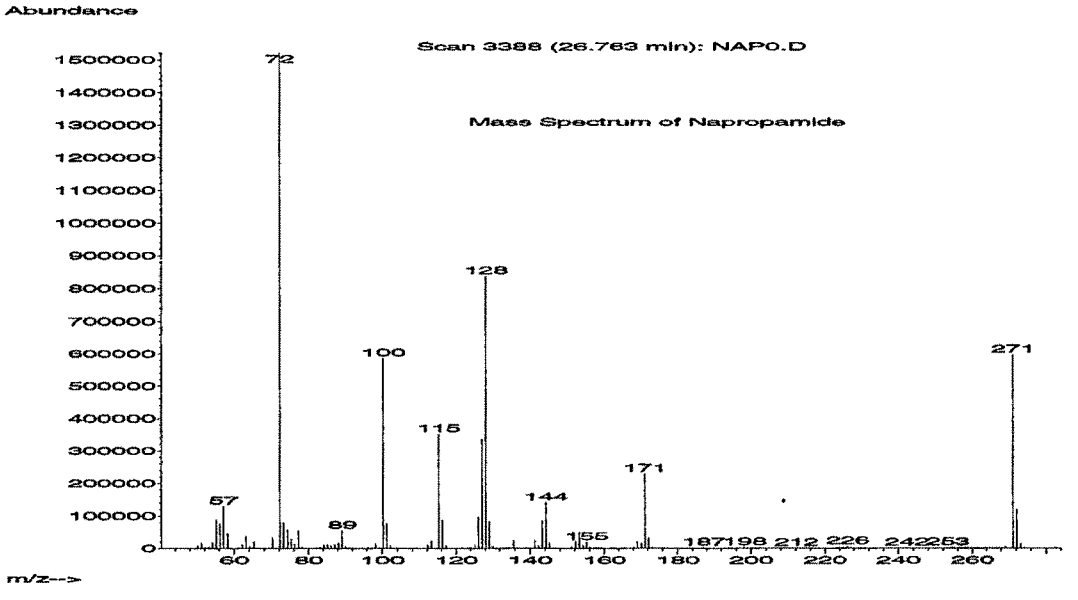

Fig. 3.3: Mass spectrum of napropamide.

4.4 Identification by UV-Visible Spectrophotometer

The UV-visible spectrum of pesticides (**Fig. 4**) identified the compound on the basis of the specific wavelength (λ_{max}) values of pesticides at which maximum absorption is obtained viz., 217 for metalaxyl, 226 for napropamide and 220 for tebuconazole.

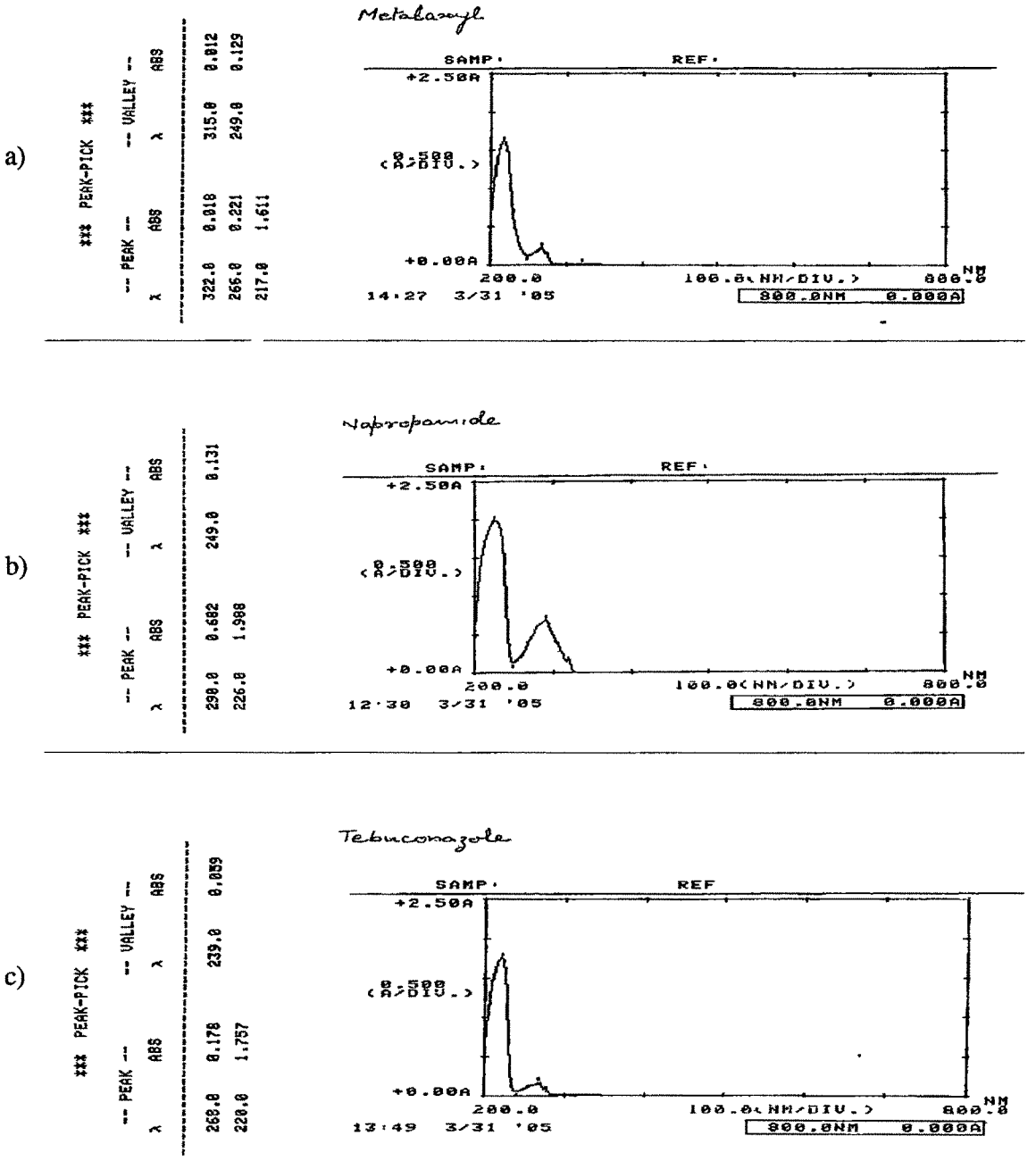

Fig. 4: UV/Vis spectrum of a) metalaxyl, b) napropamode, and c) tebuconazole.

4.5 Identification by Differential Scanning Calorimeter

The differential scanning calorimeter (DSC) heated the compound at a fixed rate and recorded the change in heat flow through it, therefore a sharp endothermic curve was obtained at melting temperature of the compound (**Fig. 5**). The melting point values of pesticides obtained by DSC, helped in identification by matching with theoretical melting point values[10].

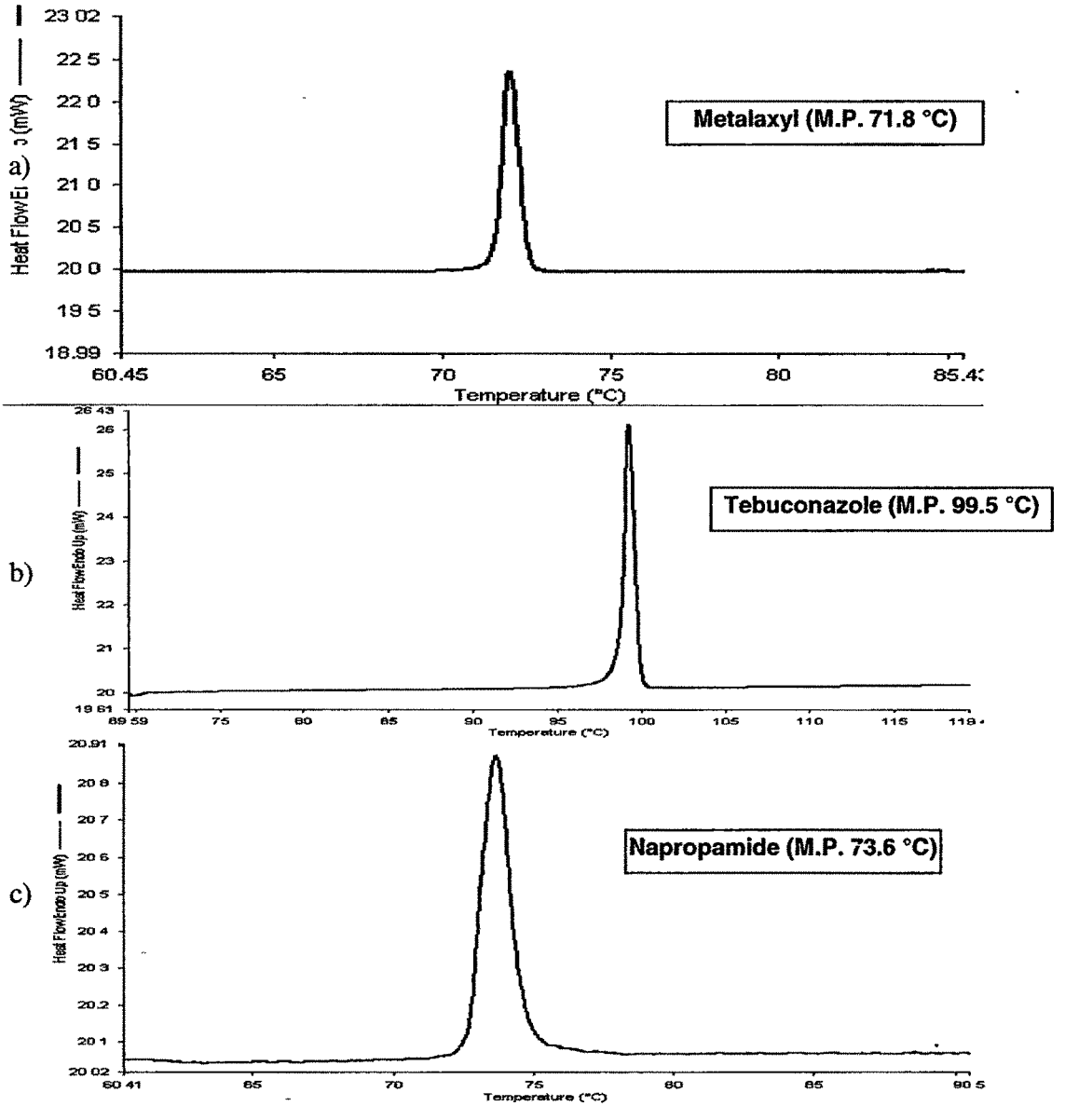

Fig. 5: DSC endotherms of a) metalaxyl, b) napropamode, and c) tebuconazole.

Table 4: Structural informations obtained from various instruments for the identification of metalaxyl.

S. N°	Instrument	Characteristics	Structural Information
1.	DSC	Melting Point	71.8 °C
2.	UV-Vis	λ_{max} Value	217 cm
3.	FTIR	Functional Groups	$-CH_3$, $-CH_2$, -COOH, $-CONH_2$, $-CH_2OCH_3$, aromatic amine
4.	MS	Fragments	279, 249, 234, 220, 206, 192, 174
5.	H^1-NMR	Protons of various groups	Ar-H, Ar-CH_3, -CH-N, CH_3-CH, -OCH_3-CH_2, -OCH_3-CO, $-CH_2$

5. Conclusion

On comparing the structural associated informations data, obtained from various analytical instruments (**Table 4**) it was observed that these instruments are supplementary to each other and provide significant informations for structure elucidation and identification of the pesticides. The spectral informations and analytical data obtained by the instruments provide specific information about the structure of a pesticide but no single method was sufficient to provide complete structural information for confirmation. Therefore, the identity of the active ingredient of a pesticide should be established by comparing the data with an equivalent standard using at least three instrumental techniques, at least one of which should be spectroscopic. In case of absence of suitable standard, or for identification of an unknown pesticide at least two spectroscopic techniques must be used. The data may be interpreted independently [interpretated in this chapter] to characterize the typical pesticides viz., metalaxyl, napropamide and tebuconazole based on the structural informations obtained with various instruments to confirm the structure.

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