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Preparation, characterization of N: Phenyl B: Nitrobenzo hydroxamic acid and its iron (III) and copper (II) complexes

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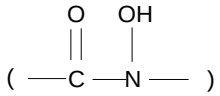
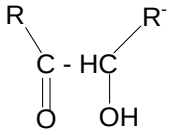
Abstract
N-phenyl b-nitrobenzo hydroxamic acid had been prepared by coupling reaction of the prepared of N-phenyl hydroxylamine and methyl nitro benzoate in alkaline media was characterized by melting point (205-206^{0}C), characters iron and copper color test, FT-IR characteristics spectral bands at 3112cm^{-1} (OH),1693 cm^{-1} (C=O) and 931 cm^{-1} (N-O). The ^{1}H NMR spectrum shows the characteristic attachment of the proton of the hydroxyl group to the nitrogen atom in the region(7.43 – 7.70) ppm, the shift of the resonance signal of hydroxyl proton to lower field to support intermolecular hydrogen bonding, the appearance of protons of aromatic ring in the region (8.06 – 8.35) ppm. The ^{13}C NMR spectra exhibit absorption signal due to carbonyl (C=O) nearly 166.26 ppm. The chemical shifts of aromatic carbons appear in the region (122.49 – 150.45) ppm. Beside these signals, a signal nearly 16 ppm appeared which corresponding to carbon atom of alkyl group.
Iron (III) and copper (II) N-phenyl b-nitrobenzo hydro xamate complexes were prepared by reacting, N-phenyl b-nitro benzo hydroxamic acids with corresponding metal salts at pH= 3. Showing the characteristic colors. They show absorbance at a wavelength of maximum (λ_{max}) 415nm, 425 nm for Fe^{3+},Cu^{2+} complexes respectively indicating that the metal ligand complexes were formed from both.

Keywords: intermolecular N-phenyl b-nitro benzo hydroxamic acid, resonance, chemical shifts, coupling

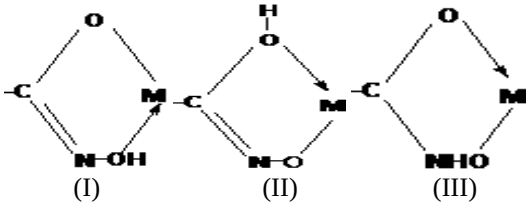
1. Introduction
Hydroxamic acids are known at have the bidentate functional group [1].



Makes complexes with different metal ions and forms a family of chelating agents [12].
They have the general formula:

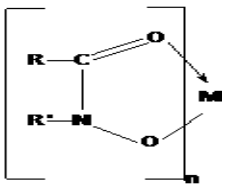


Where R and R` could be hydrogen, alkyl or aryl group. Hydroxamic acids act as bi-dentate ligands. They exist in two tautomeric forms (eno and keto-) of the atoms. The structure of their metal complexes may represent in three different forms as shown below: (I) (II) (III).



(I) (II) (III)

Complexes of mono hydroxamic acids with Fe (III), Co (II) and Cu (II) are shown to co-ordinate via oxygen atoms of the ligand [13].



(n=oxidation state of metal)

Copper (II) forms square planar complexes and vanadium (V) forms oxo-complexes. The best known of these complexes is that, with Fe (III) the beautiful purple color of this compound forms the basis for the sensitive qualitative and quantitative determination of hydroxamic acids and their derivatives [14, 15]. Hydroxamic acids are important chelating agents having complexing ability towards a very great number of metal ions. They have been known for more than a century. They belong to a group of organic compounds, which are derived from hydroxylamine. They are known compounds having the bidentate functional grouping. They form a family of chelating reagents, which are used in colorimetry.
Hydroxamic acids are weak organic acids used as commercial flotation reagents in extractive metallurgical, inhibitors for copper corrosion. Most hydroxamic acids will be hydrogen bonded and exist in the keto- form, bonded to a transition metal through the oxygen atom. They have been classified into three groups: primary hydroxamic acid, secondary hydroxamic acid and cyclic hydroxamic acid.

Hydroxamic acids have particular affinities for 'hard' cations such as Fe (III), Np (IV), and Pu (IV) [2, 3]. Which they form five-membered chelate rings. On acid hydrolysis of free hydroxamic acids, hydroxylamine and the parent carboxylic acid are formed [4]. Metal ions bound to hydro xamates also hydro lyze [5]. The chelating ability of hydroxamic acids has been used to link pharmaceutically useful ions such as radioactive or paramagnetic ions to monoclonal antibodies that direct the ion to a desired target tissue for tumor or tissue imaging or therapy purposes. The use of hydro xamate coordination polymers as molecular magnets [6]. Has also been explored [7]. Owing to all these applications, the coordination chemistry of hydro xamates has evoked much interes [8, 9, 10].

The effect of the phenyl ring on the other phenyl ring increases the electronic density due to the lone pair on the nitrogen leading to increased repulsion between the lone pair electrons and the hydrogen electron clouds at the ortho position of N-phenyl ring. This, in turn, favors the Trans form as the stable configuration.

From these result we conclude that substituents on the N-phenyl ring of nitro benzo hydroxamic acids favor Trans structure and intermolecular hydrogen bonding. The effect of the nitro group, in the case of the nitro group, both the inductive and the resonance effects are believed to result in the with drawal of electronic charge from the ring, thus accounting for its observed deactivation toward electrophiles [16].

The main goal of this study is the synthesis of hydroxamic acid by coupling reaction, its characterization and its application as a ligand for complexation with iron (III) and copper (II) [11].

2. Materials and Methods

2.1 Chemicals

N-phenyl hydroxylamine hydrochloride, methyl nitro benzoate, ethanol (Et OH), methanol (Me OH), ferric chloride hex hydrate, ($FeCl_3.6H_2O$)] and (ammonium meta vandate), sulphuric acid,, sodium hydroxide pellets (Na OH), sodium hydrogen carbonate ($NaHCO_3$), glacial acetic acid, diethyl ether, were obtained from CDH chemical Ltd, Chaina (all chemicals were analytical grade).

2.2 Instruments

Electrical balance, (Aand D Company, Ltd CE Germany). FTIR 300 spectrometer with KBr disc, (Shimatzu. Japan), UV/VIS. spectrophotometer 6505 with printer HP desk jet 640C, (Jenway, England).Melting point electrical, type (Gallenkamp, England), serial No. MFB, 600.100F, APP.NO2CO117, pH meter Model 3030 (Jenway, England).

2.3 Methods

2.3.1 Preparation of the N-phenyl b-nitrobenzo hydroxamic acid

The ligand was prepared in two simple steps, step one the reaction of nitrobenzene with zinc dust with heating and step two by the coupling reaction of N-phenyl hydroxylamine and methyl nitro benzate as shown in Scheme1. 12.2g (0.047 mole) of freshly prepared methyl nitro benzoate were mixed with 135cm^3 of Sodium hydroxide and placed in a 600cm^3 beaker, 5g of N-phenyl hydroxylamine were added. The mixture was cooled in an ice- bath during one day after that diluted sulfuric acid was added until the yield was precipitated. Yield was filtered and recrystallized by using methanol.

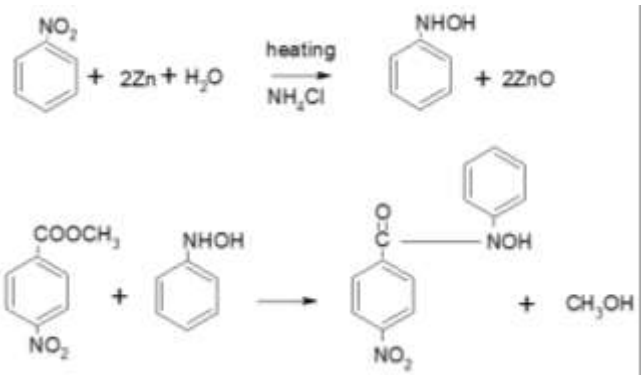


Fig 1: Preparation of the N-phenyl b-nitrobenzo hydroxamic acid

2.3.2 Preparation of Fe (III) and Cu (II) – N-phenyl b-nitrobenzo hydro xamate complexes

In two separate 100cm^3 volumetric flask,0.1g of N-phenyl b-nitrobenzo hydroxamic acid was weighed and dissolved in 50.0 cm^3 ethanol, then transferred to 100cm^3 volumetric flask, 5cm^3 of buffer was added (pH =3), the volume was completed up to the mark with distilled water. In another separate beaker or volumetric flask, 2.90189g of ferric chloride and 2.5119g $CuSO_4.5H_2O$ was weighed and dissolved in distilled water, then transferred to 1000 cm^3 volumetric flask,, then take1cm^3 and dilute to 100cm^3 in volumetric flask, and 5 cm^3 of buffer (pH = 3 iron and copper) was added, the volume was completed up to the mark with distilled water, pH became 3 for iron (III)- N-phenyl b-nitro benzo hydro xamate and 5for copper(II) – N-phenyl b-nitrobenzo hydro xamate complexes. The red color precipitate of iron and green color of copper, the methods of ligand, metals, pH,(5ml of ligand 10ppm add 3ml of metals(Fe, Cu) 10ppm and add 2ml of buffer solution (pH=3 of iron and copper) and complete to the mark with distilled water, and take absorbance at λ_{max} =415 nm(Fe) and 425nm(Cu).

2.3.3 Characterization of N-phenyl b-nitro benzo hydro xamic acids

2.3.3.1 Spot test

Ethanolic solutions of N-phenyl b-nitrobenzo hydroxamic, were added to an aqueous solutions of ferric chloride, copper salt separate. The two solutions of hydroxamic acids were thoroughly mixed and transferred to a watch glass for air dryness.

2.3.3.2 Melting Points of hydroxamic acids

In this technique melting point apparatus with capillary tube was used to determine the melting points of N-phenyl b-nitro benzo hydroxamic acid.

2.3.3.3 Infrared spectrum of hydroxamic acids

The infrared spectroscopy (IR) analysis was carried out for N-phenyl b-nitrobenzo hydroxamic acid by using JENWAY FTIR instrument with KBr disc. The spectrum obtained is shown in figure (1).

2.3.3.4 ^{1}H NMR spectrum of hydroxamic acids

The nuclear magnetic resonance spectroscopy (1H NMR) analysis was carried out for N-phenyl b-nitro benzo hydro xamic acid and Fe (III), Cu (II) – N-pheyl b-nitro benzo hydro xamate complexes by using instrument. The spectrum

obtained is shown in fig (2).

2.3.3.5 ^{13}C NMR spectrum of hydroxamic acids

The nuclear magnetic resonance spectroscopy (^{13}C NMR) analysis was carried out for N-phenyl b-nitro benzo hydro xamic acid and Fe (III)-, Cu (II) – N-phenyl b-nitrobenzo hydro xamate complexes by using instrument. The spectrum obtained is shown in fig (3).

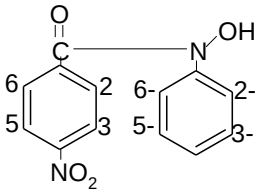
2.3.3.6 Mass spectrum of N-phenyl b-nitrobenzo hydroxamic acid

The mass spectrum of N-phenyl b-nitro benzo hydro xamic acid obtained is shown in figure (4).

3. Results and Discussion

3.1 Characterization of N-phenyl b-nitrobenzo hydro xamic acid

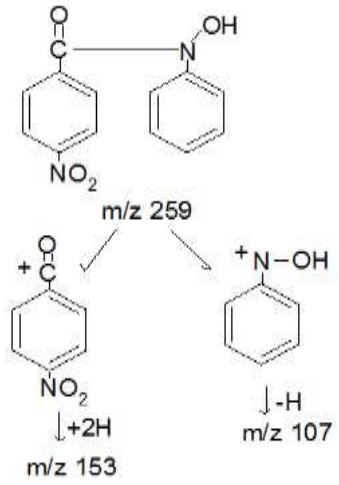
1. N-phenyl b-nitro benzo hydro xamic acid was synthesized by the reaction of methyl nitro benzoate with N-phenyl hydroxylamine.



2. The N-phenyl b-nitro benzo hydro xamic acid was prepared and identified by its melting point (205-206°C) conforming with the literature value and by its colours spot test with iron(III) and copper(II) giving red and green colors respectively.
3. The prepared of ligand Infrared spectral data are shows characteristic absorption bands at 3112 cm^{-1} due to O-H stretching vibration, 1693 cm^{-1} is assigned for the C=O of hydroxamic acid group, A sharp band at 930 cm^{-1} attributed to N-O by stretching vibration(fig.1).
4. The ^{1}H NMR spectrum of N-phenyl b-nitro benzo hydro xamic acid figure (2) revealed a multiplet at (7.43 – 7.70) ppm assigned for C_{3-}, C_{4-}, C_{5-}, C_2, and C_6 protons. Another multiplet appeared at (8.06 – 8.35) ppm. This multiplet accounts for C_3, C_5, C_{2-}, and C_{6-} protons.
5. The ^{13}C NMR spectra figure (3) exhibit absorption signal due to carbonyl (C=O) nearly 166.26 ppm. The chemical shifts of aromatic carbons appear in the region 122.49 – 150.45 ppm. Beside these signals, a signal nearly 16 ppm appeared which corresponding to carbon atom of alkyl group.

Mass spectra

6. The blue structure was supported by the mass spectrum which gave 259 for the molecular ion (M^+).



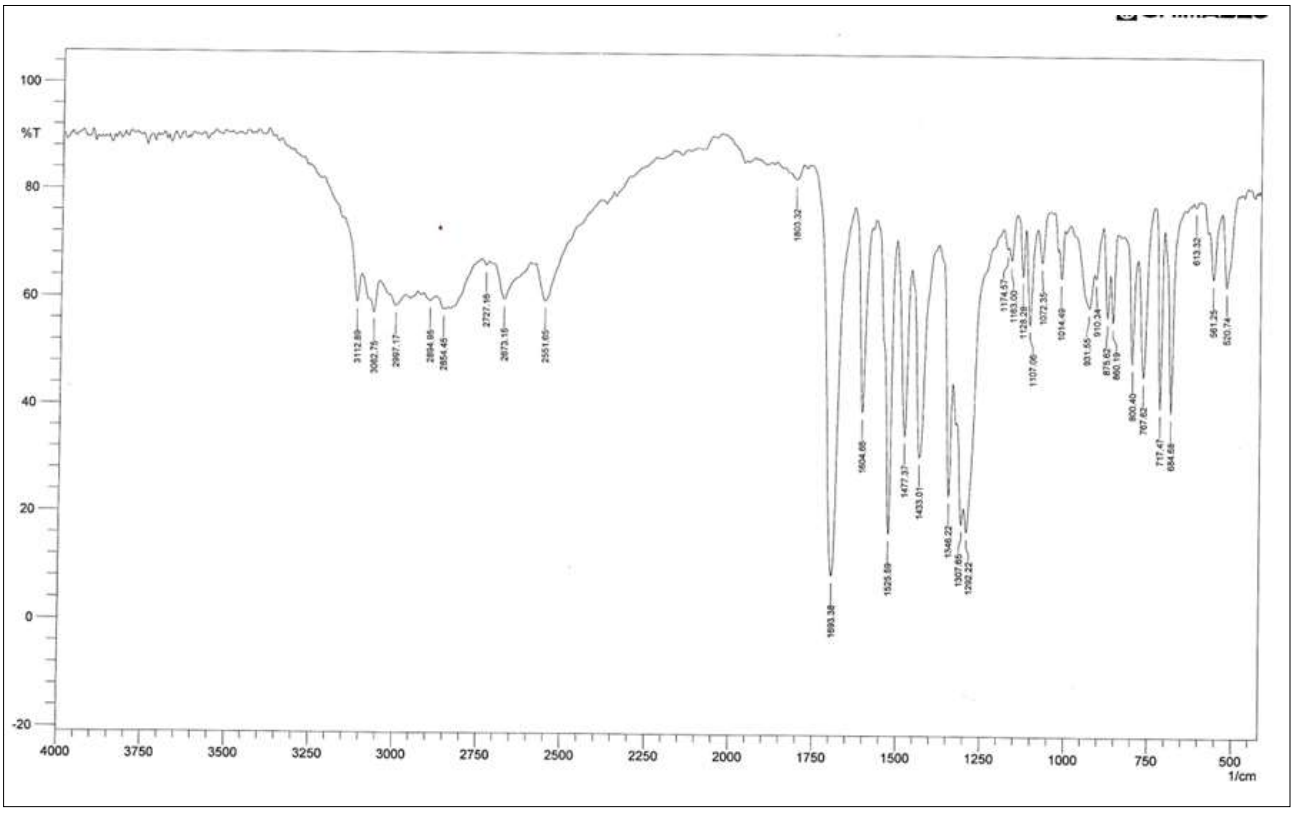


Fig 2: N. phenyl nitro benzo hydro xamic acid

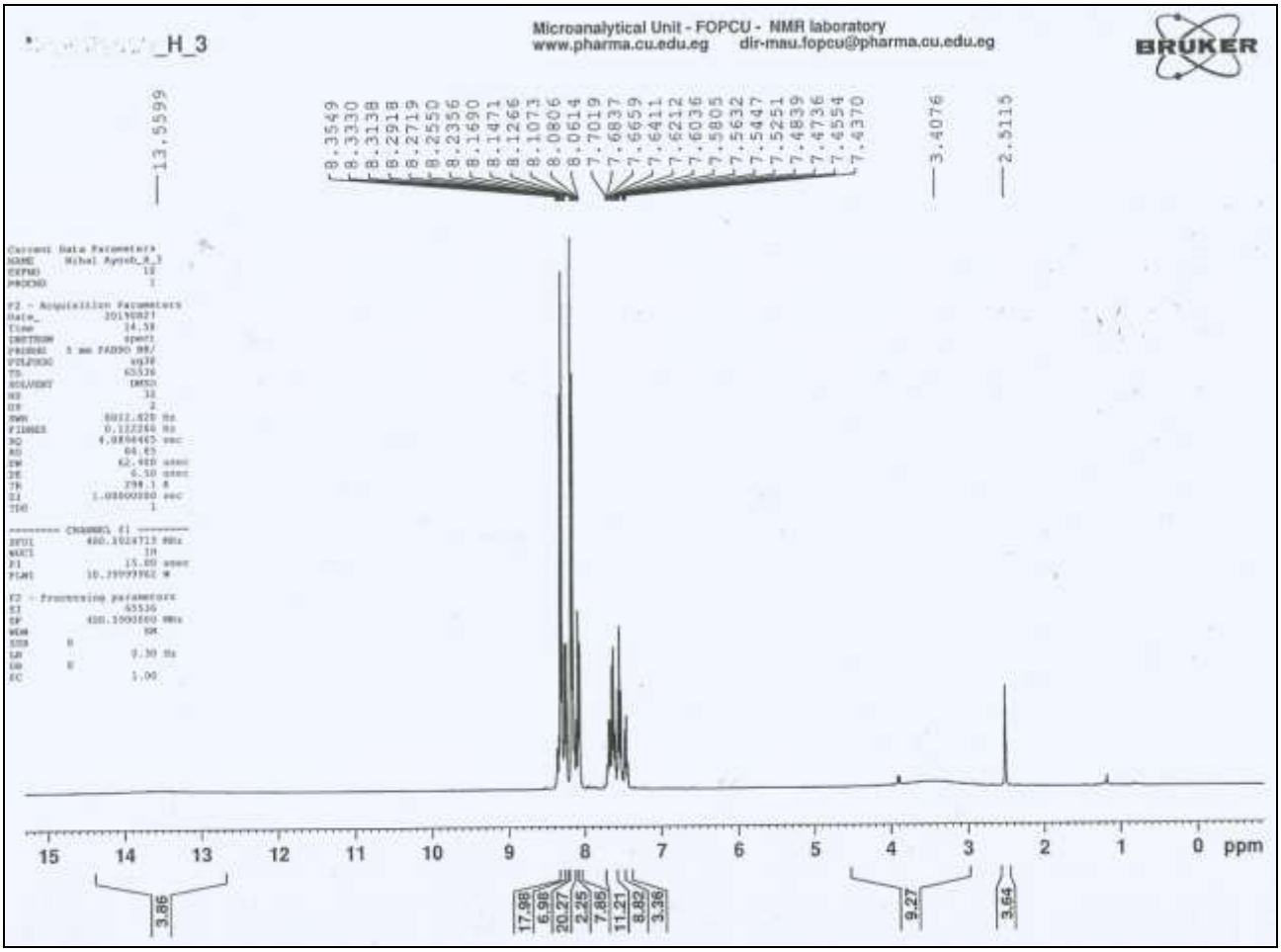


Fig 3: [1]H NMR N. Phenyl nitro benzo hydro xamic acid

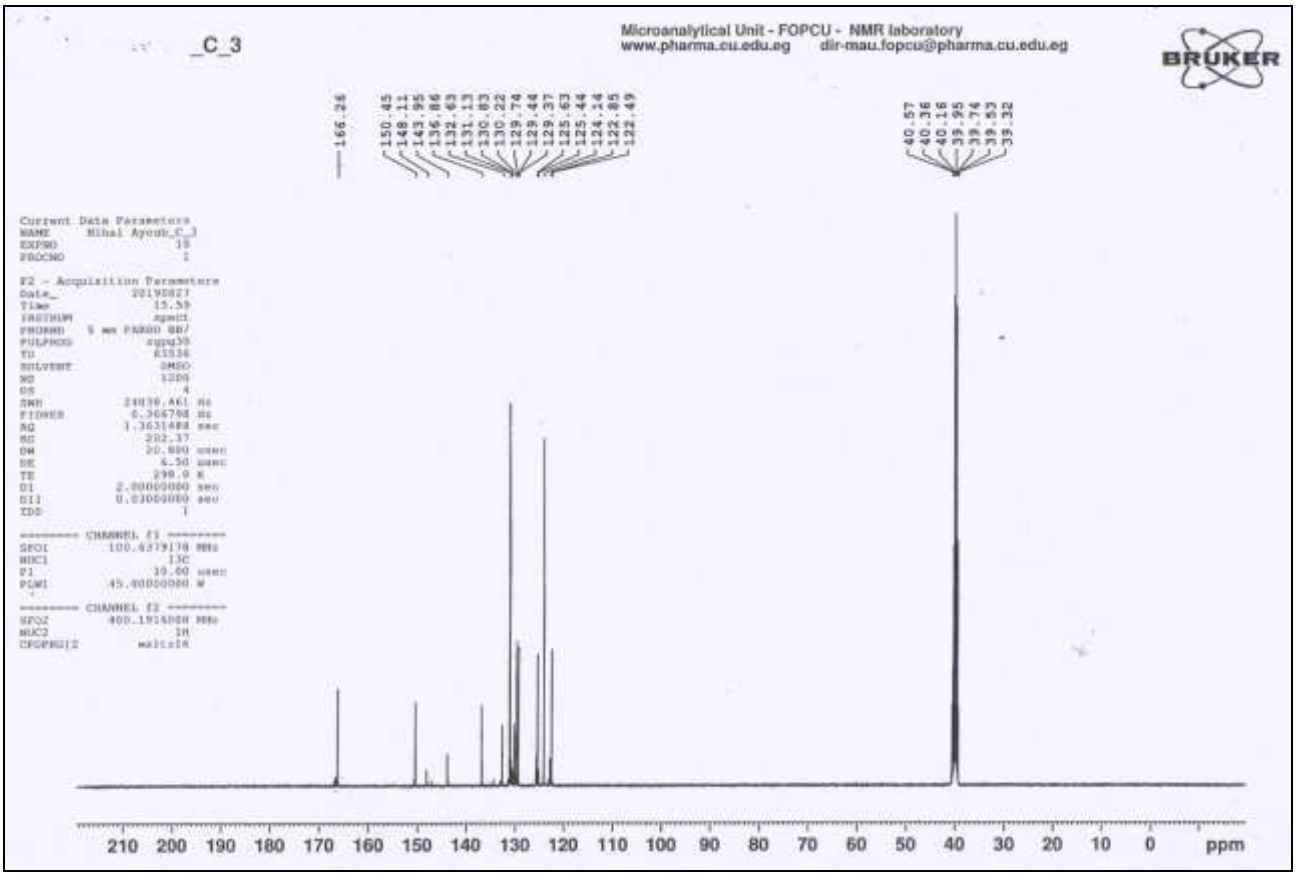


Fig 4: [13]CNMR N. Phenyl nitro benzo hydro xamic acid

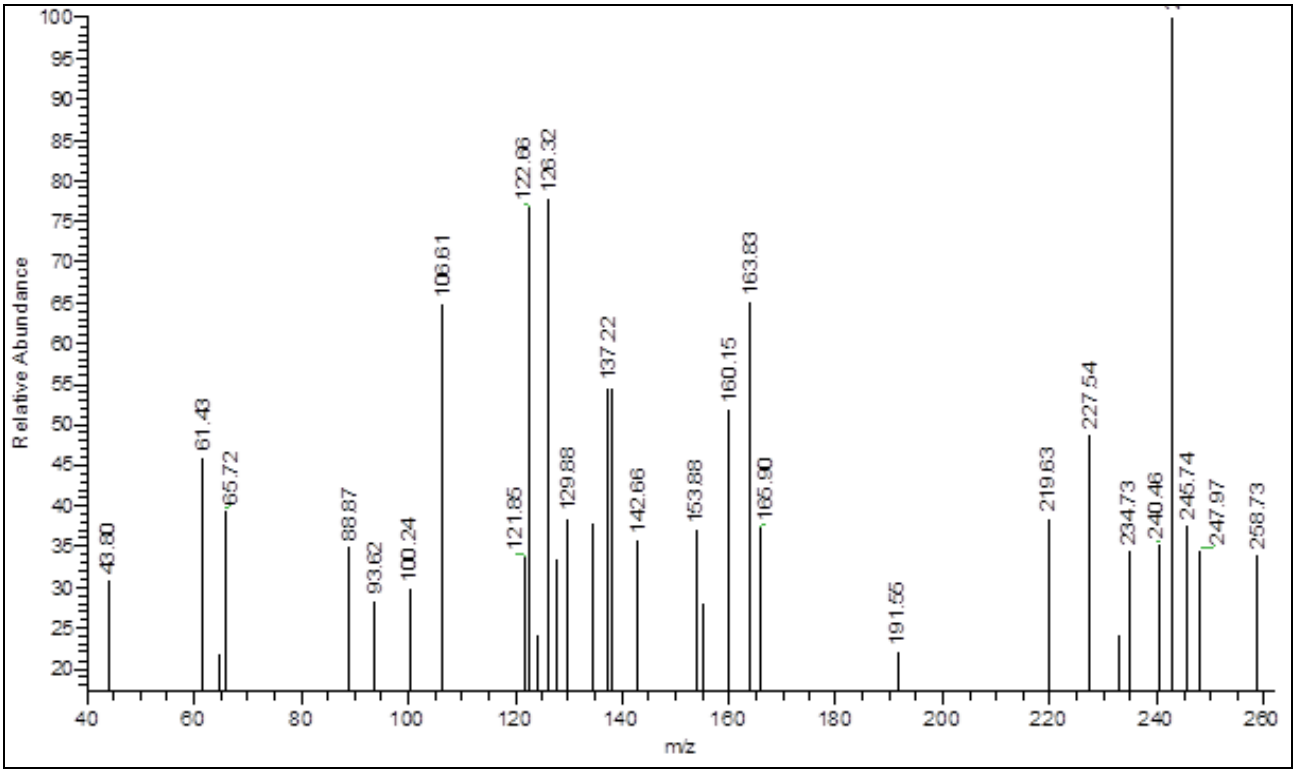


Fig 5: N. phenyl nitro benzo hydro xamic acid

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