PART - I

SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF N-ARYL HYDROXAMIC ACIDS

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CHAPTER II

SYNTHESIS OF N-ARYLHYDROXAMIC ACIDS

RESUME

The synthesis and properties of nine new N-aryl-hydroxamic acids derived from substituted α-phenyl-cinnamic acids are described. The syntheses are made by reacting N-arylhydroxylamine with acid chlorides at low temperature in diethyl ether containing aqueous suspensions of sodium bicarbonate.

These acids are characterized by elemental analysis, melting point, ultraviolet, infrared, nuclear magnetic resonance and mass spectra.

The thermal analysis (DTA, TG) and non-aqueous titrations are also performed.

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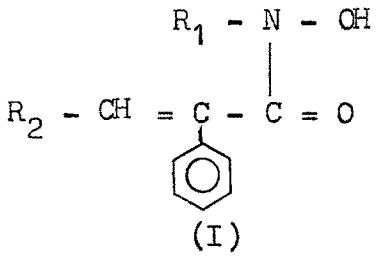
INTRODUCTION

In the present investigation the synthesis of nine new hydroxamic acids represented by the general formula (I), is described.



(I)

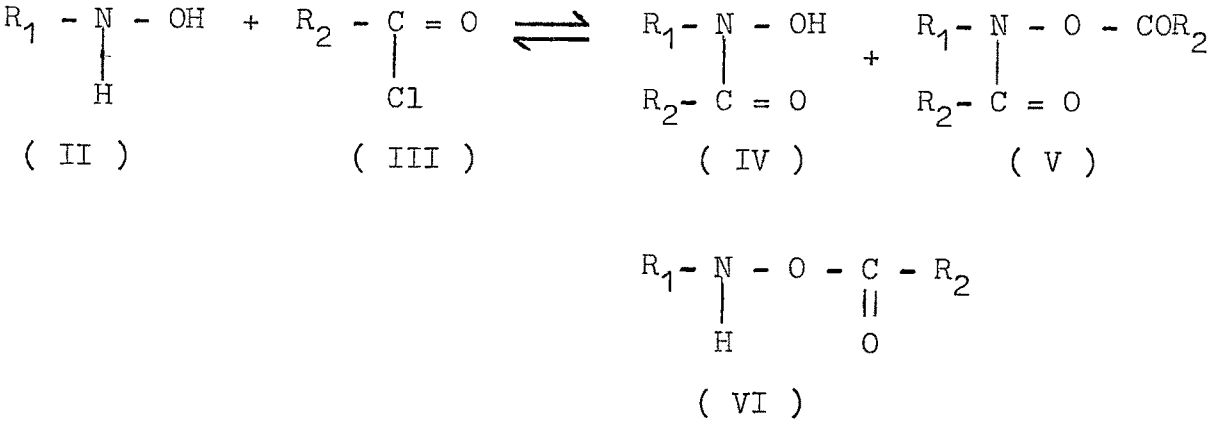
Where R_1= N-phenyl, m-tolyl, p-tolyl or p-chlorophenyl, and

R_2= phenyl, p-methoxyphenyl or 3,4,5 trimethoxyphenyl

SYNTHESIS OF N-ARYLHYDROXAMIC ACIDS

A review on the synthesis of hydroxamic acids is given by Yale (1). The other useful reviews are those by Sandler and Karo, Henecka and Kurtz, Metzger, Mathis, Smith, Coutts and Katritzky (2-8). Generally the syntheses are made by reacting N-arylhydroxylamine with acid chloride at low temperature in diethyl ether solution containing aqueous suspensions of sodium bicarbonate (2). When an N-arylhydroxylamine reacts with acid chloride, both of its hydrogen atoms, attached to the nitrogen and oxygen atoms, are attached thereby

simultaneously producing mono (IV), and di-(V) and O-acyl (VI) substituted derivatives,



(II) (III) (IV) (V)

(VI)

and thus tedious methods of purification, e.g. extraction with ammonia (9,10) becomes necessary. Agrawal, Tandon and coworkers (11-13) have adopted the following conditions for the synthesis of N-arylhydroxamic acids.

(i) N-arylhydroxylamine and acid chloride are used in just equimolar proportions.

(ii) Diethyl ether is used as solvent.

(iii) Finely powdered sodium bicarbonate, suspended in small volume of water, is used in place of pyridine for neutralising hydrochloric acid liberated during the reaction.

(iv) Reaction is carried out at low temperature (0° or lower) while the period of reaction is prolonged to about 75-90 min.

(v) The use of just stoichiometric proportions of N-aryl-hydroxylamine and acid chloride give a pure product in high yield. If the recommended experimental conditions are closely adhered to, the major product is (IV), while (V) and (VI) are produced in negligible amounts. It is thus possible to isolate the desired mono-N-acylated derivative in good yield and analytically pure form by two crystallization from benzene and petroleum ether.

EXPERIMENTAL

CHEMICALS

All the chemicals used were of G.R. or AnalaR grades of E. Merck and BDH, respectively, unless otherwise specified.

SOLVENTS

Ethyl Alcohol

The spectroscopic grade ethyl alcohol was prepared by twice distilling 95% ethyl alcohol over silver nitrate and potassium hydroxide (14).

Methanol

The anhydrous methanol was prepared by the method of Weissberger (14).

Benzene

G.R., Uvasol, E. Merck was used without purification.

Dimethylformamide

Pro Analysis, B.D.H. grade was used without purification.

Tetrabutylammonium hydroxide

Its 0.1 M solution was prepared by the method of Cundiff and Markunas (15).

APPARATUS

Shimadzu UV-VIS 240 double beam recording spectrophotometer, having two 10 mm matched stoppered quartz cells, was used for ultraviolet measurements.

Infrared spectra were recorded in the 2- to 15- μ region on a Perkin-Elmer Model 1420 ratio recording spectrophotometer equipped with sodium chloride optics and calibrated with standard methods. Solids were dried over P_2O_5 finelly powdered in an agate mortar, and examined as KBr pellets or mulls in nujol.

The NMR spectra were recorded on a Varian T-60 spectrophotometer operating at 60 MHz for protons, in $CDCl_3$ with tetramethylsilane as internal standard.

The Mass spectra were recorded on a AEI (UK) mass spectrophotometer Model No. 3074 at 70 ev.

The TG and DTA curves of hydroxamic acids were recorded on a Mettler thermal analyser maintaining the following instrumental factors in all experiments :
TG range - 1 mg full scale sensitivity, DTA range - 50 μv, heating rate 8°/min, air flow rate 100 ml min^{-1}.

The non-aqueous titrations were carried out under nitrogen with ELICO IL 120 pH meter and platinum electrodes.

CINNAMIC ACIDS

These were prepared by the reaction of respective benzaldehydes with phenylacetic acid and acetic anhydride in presence of triethylamine.

A typical preparation of ∝-phenyl-p-methoxycinnamic acid is given below.

In a 500 ml B-19 round bottomed flask fitted with reflux condenser and drying tube, 14.2 g (0.4 mol) p-methoxybenzaldehyde, 13.6 g (0.4 mol) of phenyl acetic acid, 20 ml (0.8 mol) of redistilled aceticanhydride and 10 ml (0.4 mol) of anhydrous triethylamine were placed. The mixture was boiled gently for 5 hrs, steam distilled and the distillate was discarded. The residue was cooled and separated the supernated liquid. The solid mass was dissolved in 150 ml of hot 95% ethanol and mixed with the supernated liquid. The mixture was heated to boiling, filtered and acidified the filtrate with HCl (1:1). The contents were cooled and solid mass separated under vacuum. It was recrystallised from a mixture of ethanol water (60:40). The yield of ∝-phenyl-p-methoxy-cinnamic acid m.p. 188° (reported 188°C (16)) was 61%.

ACID CHLORIDES

The acid chlorides were prepared by the action of thionyl chloride on the corresponding cinnamic acids and were vacuum distilled.

N-Phenylhydroxylamine

This was freshly prepared by the reduction of nitrobenzene with zinc dust and ammonium chloride from aqueous solutions and recrystallized from benzene and petroleum ether. N-phenylhydroxylamine, mp 81°C reported 81-82°C (17) is obtained in 60-65% yield as white needles.

N-p-Tolyl- and N-p-Chlorophenyl hydroxylamine

These are the known compounds but their preparations are briefly described here because optimum conditions for getting maximum yield were established after repetitive work.

Thus, a mixture of 25 g of p-nitrotoluene or p-chloronitrobenzene, 20 ml of ethyl alcohol, 10 ml water and 2 g ammonium chloride was stirred mechanically and treated with 30 g of zinc dust in small lots of 1-1.5 g during the course of 25-30 min. The reaction temperature was maintained between 60 and 65°C throughout, and stirring was continued for another 15 min. While hot, the zinc oxide was filtered and washed with 3 x 10 ml of hot ethyl alcohol. On the addition of about 250 g of ice to the filtrate, the light yellow product was obtained which on crystallization gave a white product. N-p-tolylhydroxylamine 80% yield, mp 93°C reported 93°C (18); N-p-chlorophenylhydroxylamine 75% yield, mp 90°C (reported 90°C (18)).

N-Arylhydroxamic Acids

Generally freshly crystallized N-arylhydroxylamine (0.1 mole) is dissolved in 75 ml diethyl ether and mixed with aqueous suspensions of sodium bicarbonate (0.15-0.2 mole). The mixture is stirred mechanically and cooled externally to keep the temperature 0°C or below. To this a 50 ml ethereal or benzene solution of acid chloride is added dropwise during the course of about 30-40 min. The solid mass is filtered under vacuum and ether layer is separated. The ether is removed under vacuum and solid mass, if any, thus obtained is combined with the bulk and titurated with saturated sodium bicarbonate solution to remove the acidic impurities. The solid product is filtered off, washed with distilled water and recrystallized from the mixture of benzene and petroleum ether.

A typical preparation of an N-arylhydroxamic acid is described here.

N-Phenyl- α-phenyl-3,4,5-trimethoxycinnamohydroxamic Acid

Into a 500-ml, three necked flask, equipped with stirrer, dropping funnel and thermometer, 75 ml of diethyl ether, 10.9 g (0.1 mole) of freshly crystallized N-phenylhydroxylamine and a fine suspensions of 12.6 g (0.15 mole) of sodium bicarbonate in 25-30 ml of distilled water are added. After the mixture is cooled to 0°, 33.3 g (0.1 mole) of α-phenyl-3,4,5-trimethoxycinnamoyl chloride dissolved in 100 ml of

benzene is added dropwise over a period of 50 min. Then the reaction mixture was stirred for an additional 30 min and the temperature kept low to prevent possible side reactions. Some of the products was precipitated as a yellow solid while the benzene-ether layer was separated and the benzene-ether removed under vacuum. The yellow residue was combined with the precipitated yellow product, triturated for about 15 min in a porcelain mortar with a saturated solution of sodium bicarbonate to remove the acid impurities, filtered, washed with cold water. The yield of air dried product, mp 111°C, was 73%. Two crystallizations from a mixture of benzene and petroleum ether without the use of charcoal gave light yellow compound mp 113°C, yield 65%.

RESULTS AND DISCUSSION

SYNTHESIS

The method adopted here for the synthesis of hydroxamic acid is very simple and of general applicability. It gives better yield. The use of stoichiometric proportion of N-arylhydroxylamine and acid chloride was most satisfactory. The excess of acid chloride results in increasing amount of diderivative. Similarly the excess of N-arylhydroxylamine leads to a product which is impure, probably due to the decomposition of the hydroxylamine (18) or due to well known acid catalysed rearrangement of N-arylhydroxylamine and its decomposition to the complex product (17). The synthesised hydroxamic acids are listed in Table 1.

PROPERTIES

The physical properties of N-arylhydroxamic acids are given in Table 1. Percentage yields are reported for twice crystallized products.

ULTRAVIOLET SPECTRA

The ultraviolet spectral data of the newly synthesised N-arylhydroxamic acids in 95% ethyl alcohol are given in Table 2. All the hydroxamic acids examined here possess benzene and carbonyl chromophores in their molecules. The

TABLE 1

Preparation and properties of N-arylhydroxamic acids

Compd No.	Hydroxamic acids	Molecular formula	Molecular weight	Melting point (°C)	Yield (%)	Colour	Elemental Analysis (%)		
							C	H	N
I	N-Phenyl-α-phenyl-p-methoxy cinnamo-	$C_{22}H_{19}NO_3$	345.4	109	60	Light yellow	76.40 (76.50)	5.60 (5.55)	4.04 (4.06)
II	N-p-Tolyl-α-phenyl-p-methoxy cinnamo-	$C_{23}H_{21}NO_3$	359.4	121	72	Light yellow	76.84 (76.86)	5.90 (5.89)	3.85 (3.90)
III	N-m-Tolyl-α-phenyl-p-methoxy cinnamo-	$C_{23}H_{21}NO_3$	359.4	118	62	Light yellow	76.82 (76.86)	5.91 (5.89)	3.88 (3.90)
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy cinnamo-	$C_{22}H_{18}NO_3Cl$	379.8	122	50	Light yellow	69.50 (69.57)	4.75 (4.78)	3.65 (3.69)
V	N-Phenyl-α-phenyl cinnamo-	$C_{21}H_{17}NO_2$	315.4	83	65	Light yellow	79.94 (79.98)	5.42 (5.43)	4.40 (4.44)
VI	N-p-Tolyl-α-phenyl cinnamo-	$C_{22}H_{19}NO_2$	329.4	113	70	Light yellow	80.23 (80.22)	5.80 (5.81)	4.23 (4.25)
VII	N-m-Tolyl-α-phenyl cinnamo-	$C_{22}H_{19}NO_2$	329.4	62	55	Light yellow	80.21 (80.22)	5.82 (5.81)	4.27 (4.25)
VIII	N-p-Chlorophenyl-α-phenyl cinnamo-	$C_{21}H_{16}NO_2Cl$	349.8	143	65	Light yellow	72.08 (72.10)	4.62 (4.61)	4.01 (4.0)
IX	N-phenyl-α-phenyl-3,4,5 trimethoxy cinnamo-	$C_{24}H_{23}NO_5$	405.4	114	65	Light yellow	71.07 (71.10)	5.70 (5.72)	3.46 (3.45)
X *	N-Phenylbenzo-	$C_{13}H_{11}NO_2$	213.2	121	70	White	73.22 (73.15)	5.18 (5.20)	6.50 (6.50)

The theoretical values are given in parenthesis.

* Agrawal, Y.K., D.Sc. Thesis, A.P.S. University Rewa, Rewa (1979).

TABLE 2

Ultraviolet spectral characteristics of hydroxamic acids in ethanol

Compd No.	Hydroxamic acid	λ_{max} (nm)	$\epsilon \times 10^{-4}$ l mol cm^{-1}	$\frac{\lambda_{II}}{\lambda_{I}}$
I	N-Phenyl-α-phenyl-p-methoxy cinnamo-	299 (205)	1.8 (3.4)	1.46
II	N-p-Tolyl-α-phenyl-p-methoxy cinnamo-	299 (206)	1.7 (3.2)	1.45
III	N-m-Tolyl-α-phenyl-p-methoxy cinnamo-	299 (206)	1.8 (3.8)	1.45
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy cinnamo-	298 (205)	1.9 (3.2)	1.44
V	N-Phenyl-α-phenyl-cinnamo-	279 (205)	1.6 (3.4)	1.36
VI	N-p-Tolyl-α-phenyl-cinnamo-	279 (206)	1.7 (3.6)	1.35
VII	N-m-Tolyl-α-phenyl-cinnamo-	277 (206)	1.7 (3.6)	1.34
VIII	N-p-Chlorophenyl-α-phenyl-cinnamo-	277 (206)	1.8 (3.4)	1.34
IX	N-Phenyl-α-phenyl-3,4,5 trimethoxy cinnamo-	300 (206)	1.6 (3.7)	1.45
X *	N-Phenylbenzo-	268	0.9	-

* Agrawal, Y.K. and Tandon, S.G., Spectroscopy Lett., 49, 911 (1972).

absorption bands due to the carbonyl chromophore are usually very weak and are here eclipsed by the strong bands of benzene.

The commonly accessible ultraviolet absorption spectra of benzene consists of three well-defined main absorption bands, all due to $\pi - \pi^*$ transitions (19,20). These bands are designated as bands I, II and III (19,21).

	Band I	Band II	Band III
nm	183	203.5	225
ϵ	50,000	7,400	200

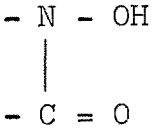
Substitution in benzene ring does not usually produce great changes or new bands in the spectra, but only modifies the spectrum of the parent compound. On the basis of the extensive and now classic studies of Doub and Vandenbelt (22) it is generally possible to correlate the spectra of substituted benzenes. The bands are discriminated by their position, magnitude of intensity, and the ratio of wavelengths of bands λ_{II}/λ_{I}.

In the present investigation the hydroxamic acids derived from α-phenylcinnamohydroxamic acid two strong bands at 206 and around 300-(280) nm are observed. These are the characteristic benzene bands I and II, respectively. These bands show bathochromic shift. Thus in α-phenyl methoxy substituted

cinnamohydroxamic acids the band II undergoes bathochromic shift by about 95 nm relative to benzene (Compd II-VI) while in simple substituted ∝-phenylcinnamohydroxamic acids (Compd VII-IX) the bathochromic shift by about 75 nm, which is similar to N-phenylbenzohydroxamic acid where the shift is 65 nm relative to the benzene.Substitution of methoxy group in the benzene ring displaces the band II generally to higher shift compared to halogen, methyl group etc. (23). In all the hydroxamic acids the shift in benzene band I is by 23 nm. The ratio of λ_{II}/λ_{I} in substituted ∝-phenylcinnamohydroxamic acids is around 1.4,is in agreement with reported earlier (24,25).

INFRARED SPECTRA

The frequencies of the absorption bands of the synthesised ∝-phenyl-cinnamohydroxamic acids examined here are given in Table 3. Those bands which are associated with the hydroxamic acid functional group



are due to (O-H) and (C=O) stretching vibrations are assigned unambiguously. The (N-O), (C-N) and (C-Cl) stretching vibrations are assigned with less confirmity because of the overlapping with several other modes of vibrations and also the non-availability of systematic data on the assignment of

TABLE 3

Infrared spectral characteristics of hydroxamic acids

Compd.No.	Hydroxamic acid	ν_{O-H}	$\nu_{C=O}$	ν_{N-O}	ν_{C-N}	ν_{C-Cl}
I	N-phenyl-α-phenyl-p-methoxy cinnamo-	3270	1625	940	1370	-
II	N-p-Tolyl-α-phenyl-p-methoxy cinnamo-	3140	1600	940	1360	-
III	N-m-Tolyl-α-phenyl-p-methoxy cinnamo-	3100	1635	940	1350	-
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy cinnamo-	3280	1625	910	1370	750
V	N-Phenyl-α-phenyl cinnamo-	3160	1640	935	1370	-
VI	N-p-Tolyl-α-phenyl cinnamo-	3180	1630	935	1350	-
VII	N-m-Tolyl-α-phenyl cinnamo-	3170	1630	938	1350	-
VIII	N-p-Chlorophenyl-α-phenyl cinnamo-	3140	1640	935	1340	780
IX	N-phenyl-α-phenyl-3,4,5-trimethoxy cinnamo-	3160	1600	910	1370	-
X	*N-Phenylbenzo-	3175	1635	909	1370	-

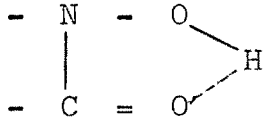
* Agrawal, Y.K. and Tandon, S.G., Spectroscopy Lett., 6, 547 (1973).

the bands in infrared spectra of these hydroxamic acids. The assignment of various bands is briefly discussed.

(O-H) Stretching Vibrations

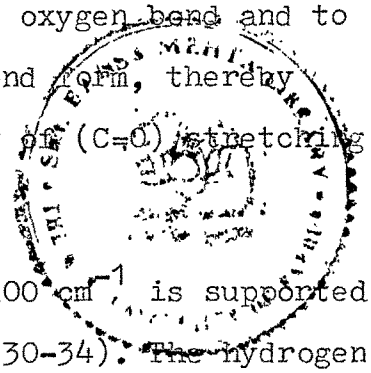
In the ∝-phenyl substituted cinnamohydroxamic acids examined here the band due to (O-H) stretching vibrations has been assigned in the region between 3280 cm^{-1} and 3100 cm^{-1} (Table 3). It is well known that the absorption bands due to (O-H) stretching vibrations, when free, appear around 3600 cm^{-1}; hydrogen bonding shifts these bands to lower frequencies (26-29), Thus it implies that these hydroxamic acids are involved in strong hydrogen bonding.

Most of the changes in the (O-H) stretching vibrations are mainly due to the ability of acidic hydrogen of hydroxyl group to form "hydrogen bonds" with electron rich atoms. In hydroxamic acids, the acidic (O-H) group is placed in a very close proximity of the polar carbonyl group, $= C^{\delta+} = O^{\delta-}$. This situation is highly favourable of strong intramolecular hydrogen bonding of the type given below.



The formation of strong hydrogen bond causes a large shift in the absorption band to lower frequencies, of the order of 500 cm^{-1} and may be ascribed to the resonance stabilization.

A consequence of this resonance stabilization should be to lower the force constant of the carbon oxygen bond and to increase the contribution of single bond form, thereby causing a lower shift in the frequency of (C=O) stretching vibrations.



The assignment of bands around 3200 cm^{-1} is supported by the work of Hadzi (30) and others (30-34). The hydrogen bonding is of intramolecular type and is confirmed by solution studies made by other workers (31-35).

(C=O) Stretching Vibrations

In the α-phenylcinnamohydroxamic acids examined here the (C=O) stretching vibrations are assigned in the region 1640-1600 cm^{-1}. The assignment is made with reference to the spectra of amide, anilides and unsubstituted hydroxamic acids. It is well observed that the amide I band is primarily due to C=O (36,37). In substituted amides, $RCONH_2$, this band is located between 1690 and 1650 cm^{-1}, while in substituted amides, RCONHR, it is observed between 1680 and 1650 cm^{-1}(37). In unsubstituted hydroxamic acids like benzohydroxamic acid it is assigned at 1667 cm^{-1} by Faraha (32), and 1661 cm^{-1} by Usova (38). Oriville-Thomas assigned this band at 1647 cm^{-1} in formohydroxamic acid (39). Mathis (5) assigned this band in benzo-, propiono-, cinnamo- and p-methoxybenzohydroxamic acids at 1640 ± 30 cm^{-1}.

The position of (C=O) stretching band is much influenced by molecular structure and generally shifted to lower frequencies (40, 41). Thus the hydrogen bonding lower (C=O) by 10-45 cm^{-1} (40,41). Conjugation of the carbonyl group with C=C lowers the absorption band by about 30 cm^{-1} for first conjugation. When an aromatic ring is directly attached to the carbon atom of the carbonyl group, the frequency shift of the carbonyl group is generally less than that occuring with a full double bond in conjugation. The substituents in the aromatic ring and the ring strain also lower the carbonyl absorption frequency (40). Thus stretching vibrations are assigned in the range of 1640-1600 cm^{-1} for α-phenyl-cinnamohydroxamic acids which is in fair agreement with the above referred empirical rules.

(N-O) Stretching Vibrations

In the N-arylhydroxylamines the ν(N-O) appears around 915 cm^{-1} (42,43). In aromatic hydroxamic acids such as PBHA it appears at 900 cm^{-1}(5 ,44). In several oximes this band appears at around 950 cm^{-1} (31,39,45). It therefore, appears reasonable to look for this band in the region 950 to 900 cm^{-1}. A reference sharp band at 920$\pm$20 cm^{-1} may be attributed to (N-O) stretching mode. The band is rather conspicuous in all the spectra examined here. This assignment is supported by the work of Pilipenko (34) who assigned this band in the

spectra of PBHA and N-phenyl-2-furohydroxamic acid at 915 and 912 cm^{-1}, respectively. Earlier Hadzi (30) assigned this band at 890 cm^{-1} in PBHA.

It may be noted that this portion of infrared spectrum contains several aromatic and other bands and hence caution must be exercised in assigning (N-O) band.

(C-N) Stretching Vibrations

The assignment of the bands due to the vibrations of the (C-N) groups required more careful attention. In the present study, the weak to medium absorption band at 1355±15 cm^{-1} have been assigned to these vibrations. The spectra of α-phenylcinnamohydroxamic acids can be compared with the spectra of tertiary aromatic amines for (C-N) stretching vibrations. The (C-N) band in aromatic tertiary amine too, appears in the same region, e.g. 1360-1310 cm^{-1} (27,29,45).

(C-Cl) Stretching Vibrations

The (C-Cl) stretching vibrations for the compounds containing chlorine atom attached directly to benzene ring had been assigned between 750-700 cm^{-1} (26,27,29). The band observed in the spectrum of α-phenylcinnamohydroxamic acid reported here, corresponds to the N-phenyl chlorine atom.

NMR AND MASS SPECTRA

The nmr and mass spectra of the nine newly synthesised α-phenylcinnamohydroxamic acids have been discussed here. The PMR spectra were recorded (Tables 4-12). in the range of 0-10δ with off set in $CDCl_3$ containing TMS as an internal reference. Chemical shifts are expressed in δ-scale. The mass spectra were recorded are given in Tables 4-12.

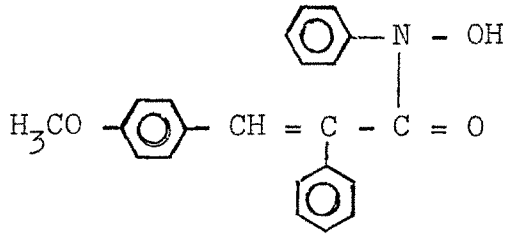
The PMR spectra of the compounds I-IX show the signals at 10.6, 10.5, 10.7, 10.8, 10.9, 10.6, 10.7, 10.5 and 10.8 respectively, which disappears on deuterium exchange and correspond to one proton due to (O-H) group.

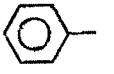
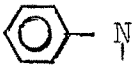
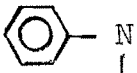
The PMR spectra of N-phenyl-α-phenyl-p-methoxycinnamohydroxamic acid (I) is having the chemical shifts at 1.05, 3.6, 7.1 δ. The shift at 1.05 δ is illdefined for (1H) and due to -CH=C-. The doublet 3.6 δ is for (3H) of the methoxy group ($-OCH_3$). A multiplet between 6.42 and 7.1 δ is due to the (14H) which are originated from the aromatic rings.

The spectrum of p-tolyl-α-phenyl p-methoxycinnamohydroxamic acid (II) showed the signals at 1.05, 2.0, 3.6, 7.2 δ. A shift at 1.05 δ is of (1H) due to -CH=C-. The triplet observed at 2.1 δ is due to (3H) of the ($-CH_3$). The doublet 3.6 δ is for (3H) of the methoxy group ($-OCH_3$). A multiplet between 6.43 and 7.2 δ is due to the (13H) which are originated from the aromatic rings.

TABLE 4

Mass spectral data of compound I

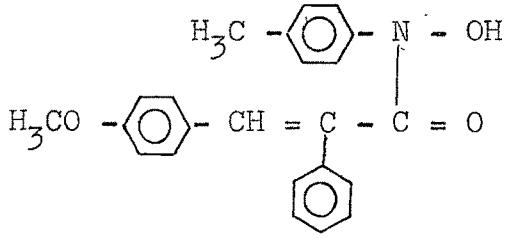
Structural formula	Molecular formula	Molecular weight
	$C_{22}H_{19}NO_3$	345.4

M/E	Relative abundance	Assignment
345	25.6	M
343	12.8	M - (2H)
330	15.4	M - (NH)
329	62.8	M - (O)
254	41.0	M - ()
237	92.3	M - ( - OH)
209*	100	M - ( - OH) - C = O

* Base peak

TABLE 5

Mass spectral data of compound II

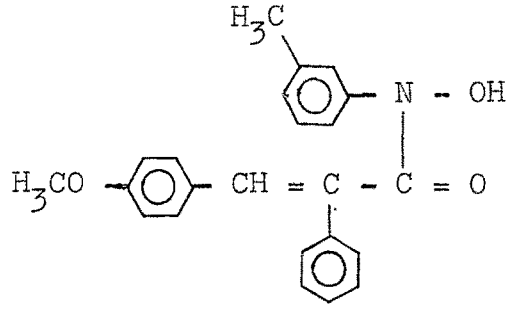
Structural formula	Molecular formula	Molecular weight
	$C_{23}H_{21}NO_3$	359.43

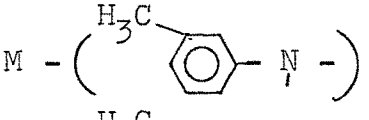
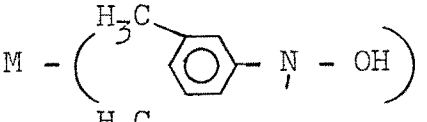
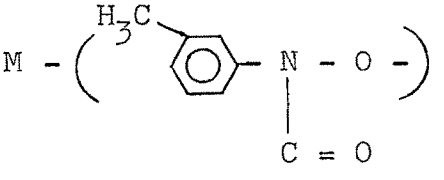
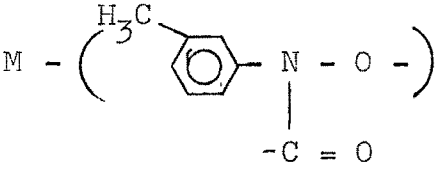
M/E	Relative abundance	Assignment
360	6.0	M^+
359	23.8	M
357	9.5	M - (2H)
344	14.3	M - (NH)
343	52.4	M - (O)
254	16.7	M - (CH_3-C$_6$H$_4$-N-)
237*	100	M - (H_3C-C$_6$H$_4$-N-OH)
209	86.9	M - (H_3C-C$_6$H$_4$-N(-C=O)-OH)

* Base peak

TABLE 6

Mass spectral data of compound III

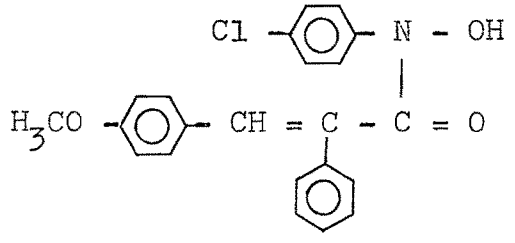
Structural formula	Molecular formula	Molecular weight
	$C_{23}H_{21}NO_3$	359.43

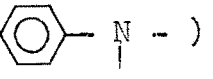
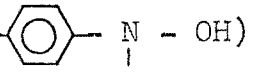
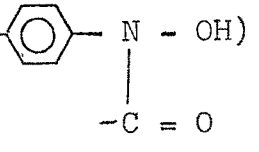
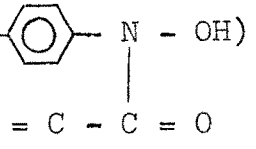
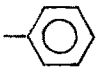
M/E	Relative abundance	Assignment
360	9.0	M^+
359	14.1	M
357	17.9	M - (2H)
344	15.4	M - (NH)
343	66.7	M - (O)
254	16.7	
237	96.1	
210	14.1	
209*	100.	

* Base peak

TABLE 7

Mass spectral data of compound IV

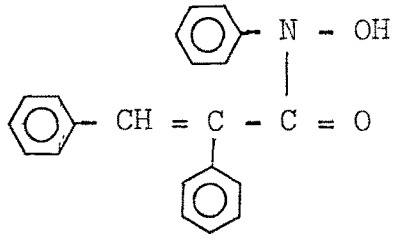
Structural formula	Molecular formula	Molecular weight
	$C_{22}H_{18}NO_3Cl$	379.84

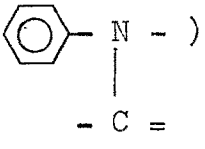
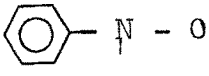
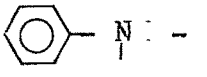
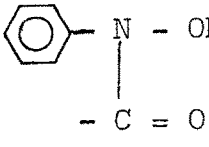
M/E	Relative abundance	Assignment
379	14.1	M^+
377	15.4	M - (2H)
364	12.8	M - (NH)
363	60.0	M - (O)
254	20.5	M - (Cl  N -)
237	69.2	M - (Cl  N - OH)
209*	100	M - (Cl  N - OH) -C = O
194	21.8	Presence of (Cl  N - OH) - C = C - C = O
77	7.7	Presence of 

* Base peak

TABLE 8

Mass spectral data of compound V

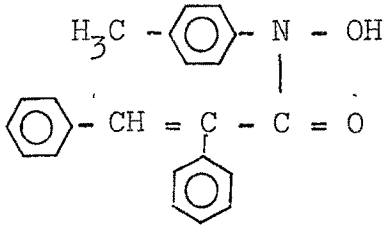
Structural formula	Molecular formula	Molecular weight
	$C_{21}H_{17}NO_2$	315.37

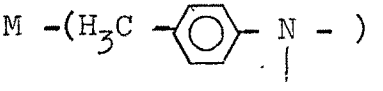
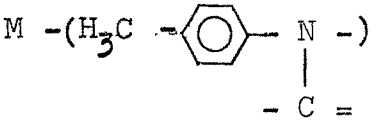
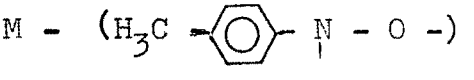
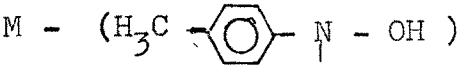
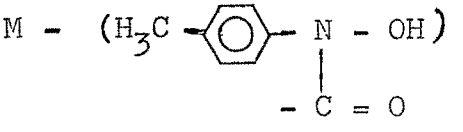
M/E	Relative Abundance	Assignment
316	23.8	M^+
315	88.1	M
300	20.2	M - (NH)
299	85.7	M - (O)
212	35.7	M - ()
208	11.9	M - ()
207	73.8	M - ()
179*	100	M - ()

* Base peak

TABLE 9

Mass spectral data of compound VI

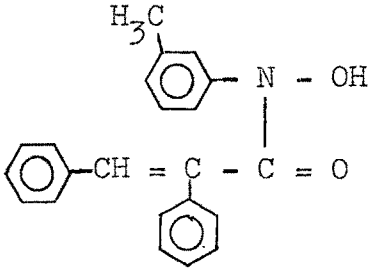
Structural formula	Molecular formula	Molecular weight
	$C_{22}H_{19}NO_2$	329.4

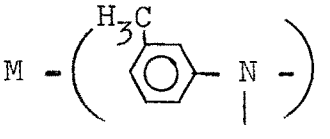
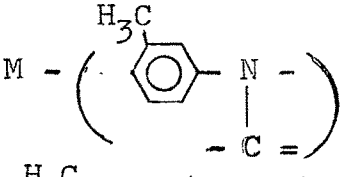
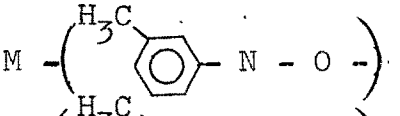
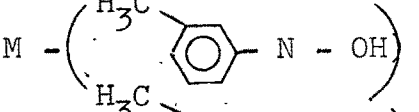
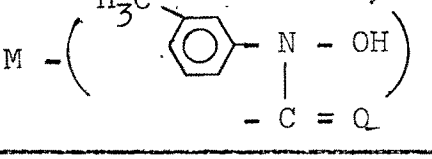
M/E	Relative Abundance	Assignment
330	30.6	M^+
329	99.8	M
314	16.5	M - (NH)
313	63.5	M(O)
301	11.9	M (- C = O)
224	16.5	
212	21.2	
208	14.1	
207	89.4	
179*	100	

* Base peak

TABLE 10

Mass spectral data of compound VII

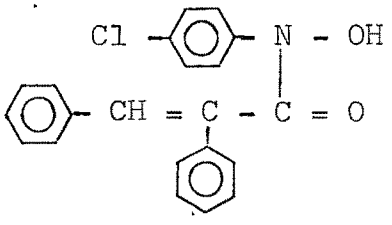
Structural formula	Molecular formula	Molecular weight
	$C_{22}H_{19}NO_2$	329.40

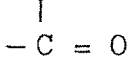
M/E	Relative abundance	Assignment
330	18.8	M^+
329	65.5	M
314	9.4	M- (NH)
313	34.5	M- (O)
312	7.1	M - (OH)
224	16.6	
212	11.9	
208	16.6	
207*	100	
179	88.1	

* Base peak

TABLE 11

Mass spectral data of compound VIII

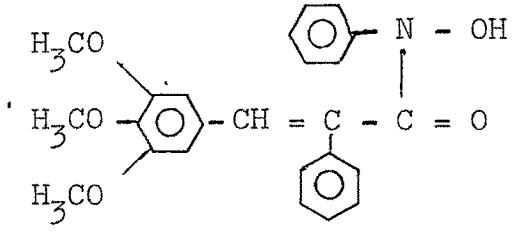
Structural formula	Molecular formula	Molecular weight
	$C_{21}H_{16}NO_2Cl$	349.82

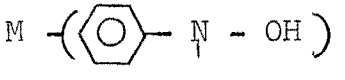
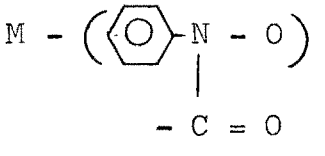
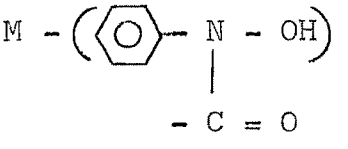
M/E	Relative abundance	Assignment
349	19.0	M
334	20.2	M - (NH)
333	55.9	M - (O)
224	22.6	M - (Cl  N -)
208	11.9	M - (Cl  N - O)
207	71.4	M - (Cl  N - OH)
179*	100	M - (Cl  N - OH) 

* Base peak

TABLE 12

Mass spectral data of compound IX

Structural formula	Molecular formula	Molecular weight
	$C_{24}H_{23}NO_5$	405.45

M/E	Relative abundance	Assignment
405	1.3	M
389	7.7	M - (O)
297	92.3	
270	12.8	
269	62.8	
78*	100	Presence of 

* Base peak

The spectrum of N-m-tolyl-α-phenyl p-methoxycinnamohydroxamic acid (III) have the signals at 1.05, 2.1, 3.6, 7.0 δ. These are assigned similar to compound II, viz. 1.05 δ due to -CH=C-, triplet at 2.0 δ of (3H) of the ($-CH_3$) group, the doublet at 3.6 is of (3H) of ($-OCH_3$) and 6.4-7.0 δ of multiplet (13H) of aromatic rings.

The spectrum of N-p-chlorophenyl-α-phenyl-p-methoxy cinnamohydroxamic acids (IV) showed the signals 1.04 δ, (1H) of -CH=C-; doublet at 3.58 δ, (3H) of ($-OCH_3$) and multiplet between 6.40 and 7.0 δ of (13H) aromatic rings.

The spectrum of N-phenyl-α-phenylcinnamohydroxamic acid (V) showed the signals 1.06 δ, (1H) of -CH=C- and the multiplet between 6.42 and 7.3 δ of (15H) of aromatic rings.

The spectra of N-p-tolyl-α-phenylcinnamohydroxamic acid (VI), N-m-tolyl-α-phenylcinnamohydroxamic acid (VII) and N-p-chlorophenyl α-phenylcinnamohydroxamic acid (VIII) showed the signals at 1.05, 1.04 and 1.06 δ, respectively, due to (1H) of -CH=C-. The triplet 1.9 and 2.0 δ is observed (Compd VI and VII, respectively) due to (3H) of the ($-CH_3$). The multiplets between 6.4 to 7.2 observed are due to (14H), of the aromatic rings (Compd VI, VII and VIII).

The spectrum of N-phenyl-α-phenyl-3,4,5 trimethoxy cinnamohydroxamic acid (IX) showed the signals at 1.05, 3.6

multiplets 6.1-7.13 δ. The shift at 1.05 δ is (1H) of -CH=C-. The shift at 3.6 δ is doublet for (9H) and is due to the three methoxy group ($-OCH_3$). A multiplet between 6.1 and 7.13 δ is due to (12H) which are originated from the aromatic rings.

DTA

The data on the DTA curves of substituted α-phenyl cinnamohydroxamic acids are given in Table 13.

Generally the DTA curves show two peaks, one endothermic and another exothermic. The endothermic peak is very sharp around 110±33°C and the exothermic peak is around 300±40°C with weight loss.

The major products of hydroxamic acids were characterised by UV, IR and X-ray analysis to be corresponding cinnamic acids, benzinlides and finally tars. At about 105±45°C the hydroxamic acids melt (endothermic peak) and then decompose (exothermic peak) in the corresponding cinnamic acids, benzanilides with contineous weight loss. Further at about 300±40°C the organic matter decomposed into tars (exothermic) with heavy weight loss.

TABLE 13

Thermal analysis (DTA) of substituted ∝-phenyl-cinnamohydroxamic acids

Compd No.	Hydroxamic acids	mp °C	DTA Endothermic °C	DTA Exothermic °C	TG Wt. loss °C
I	N-Phenyl-∝-phenyl-p-methoxy cinnamo-	109	111	315	250-480
II	N-p-Tolyl-∝-phenyl-p-methoxy cinnamo-	121	123	325	300-500
III	N-m-Tolyl-∝-phenyl-p-methoxy cinnamo-	118	120	320	295-550
IV	N-p-Chlorophenyl-∝-phenyl-p-methoxy-	122	125	330	305-560
V	N-Phenyl-∝-phenyl-cinnamo-	83	85	300	280-510
VI	N-p-Tolyl-∝-phenyl-cinnamo-	113	115	318	290-500
VII	N-m-Tolyl-∝-phenyl-cinnamo-	62	65	260	240-400
VIII.	N-p-Chlorophenyl-∝-phenyl-cinnamo-	143	145	340	320-600
IX	N-Phenyl-∝-phenyl-3,4,5 trimethoxy-	114	115	320	305-590

NON-AQUEOUS TITRATIONS

The substituted α-phenylcinnamohydroxamic acids are weak acids and can be titrated in aqueous or mixed aqueous media with phenolphthalein as the indicator, however, no sharp neutral point is obtained; which leads to unsatisfactory results. In the present work the substituted α-phenylcinnamohydroxamic acids are titrated in non-aqueous medium with thymol blue as the indicator. These are also titrated potentiometrically.

The data on the visual titration of substituted α-phenylcinnamohydroxamic acids are given in Table 14.

The indicator thymol blue colour changes in dimethylformamide from acid to base, yellow-red green, for compounds I, II, III, IV and IX and yellow-orange green for compounds V, VI, VII and VIII. The same colour change was observed in methanol.

The non-aqueous titrations are also performed in dimethyl formamide and methanol potentiometrically using platinum and calomel (saturated KCl in methanol) electrodes. The results given in Table 15 show that potentiometric titration technique is more accurate as compared to visual titrations. Mostly in the potentiometric determinations of these acids a sharp end point is obtained. The results thus, obtained, Tables 13-16, are in agreement with the theoretical values.

TABLE 14

Non-Aqueous (visual) titration results in the determination of substituted α-phenyl cinnamohydroxamic acids

Compd No.	Hydroxamic acids	Molecular Wt. (Theoretical)	Visible colour change	Molecular Wt.found (Visual)	Standard Deviation
I	N-Phenyl-α-phenyl-p-methoxy cinnamo-	345.5	Y-RG	346	±1.0
II	N-p-Tolyl-α-phenyl-p-methoxy cinnamo-	359.4	Y-RG	361	±2.0
III	N-m-Tolyl-α-phenyl-p-methoxy cinnamo-	359.4	Y-RG	358	±1.5
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy cinnamo-	379.8	Y-RG	381	±1.8
V	N-Phenyl-α-phenyl-cinnamo-	315.4	Y-OG	316	±1.0
VI	N-p-Tolyl-α-phenyl-cinnamo-	329.4	Y-OG	330	±1.0
VII	N-m-Tolyl-α-phenyl-cinnamo-	329.4	Y-OG	328	±2.0
VIII	N-p-Chlorophenyl-α-phenyl cinnamo-	349.8	Y-OG	350	±0.8
IX	N-Phenyl-α-phenyl 3,4,5 trimethoxy-	405.4	Y-OG	406	±1.0

Y = Yellow; RG = Reddish Green; OG = Orange Green brown.

TABLE 15

Effect of carbon dioxide on apparent molarity of the titrant final solution in DMF, 0.1 M tetrabutylammonium hydroxide and 0.025 M in carbonate

N-phenyl-α-phenyl-cinnamohydroxamic acid M	Apparent molarity	Molarity change
0.01	0.089	0.011
0.02	0.087	0.013
0.05	0.085	0.015
0.25	0.079	0.021
0.50	0.072	0.028

TABLE 16

Non-Aqueous potentiometric titration results in the determination of substituted ∝-phenylcinnamohydroxamic acids

Compd No.	Hydroxamic acids	Molecular weight (Theoretical)	Molecular weight found (Potentiometrically)	Standard deviation
I	N-Phenyl-∝-phenyl-p-methoxy cinnamo-	345.5	345.8	±0.50
II	N-p-Tolyl-∝-phenyl-p-methoxy cinnamo	359.4	359.2	±0.80
III.	N-m-Tolyl-∝-phenyl-p-methoxy cinnamo-	359.4	359.7	±0.85
IV	N-p-Chlorophenyl-∝-phenyl-p-methoxy cinnamo-	379.8	379.9	±0.30
V	N-Phenyl-∝-phenyl-cinnamo-	315.4	315.8	±0.90
VI	N-p-Tolyl-∝-phenyl-cinnamo-	329.4	329.1	±0.75
VII	N-m-Tolyl-∝-phenyl-cinnamo-	329.4	329.7	±0.90
VIII	N-p-Chlorophenyl-∝-phenyl-cinnamo	349.8	350.1	±0.60
IX	N-Phenyl-∝-phenyl-3,4,5 trimethoxy cinnamo-	405.4	405.3	±0.55

The carbon dioxide decreases the apparent molarity of the titrant indicate the formation of carbonate (46-48), Table 16. It also becomes apparent that the change in molarity of the titrant was dependent on the amount of acid titrated and solvent used (49). The error due to carbon dioxide was eliminated by carrying out the titrations in an atmosphere of nitrogen and ensuring that the titrants and solvents both are free from carbon dioxide.

REFERENCES

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