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Research Article

SYNTHESIS OF HYDRAZIDE DERAVATIVES FROM 2,4-DICHLOROPHENOXYACETIC ACID: SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC STUDY

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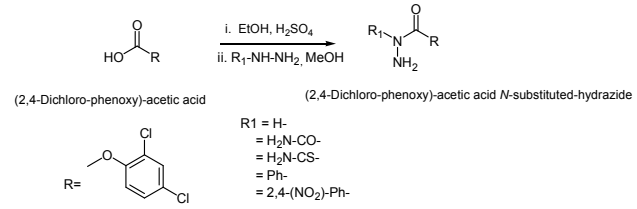
ABSTRACT

The compounds containing H_2N-HN-C(=O)-R hydrazide and H_2N-(R_1)-N-C(=O)-R substituted hydrazide **C-I-a - C-I-e**, were synthesized by reacting and stirring at low temperature 2, 4-dichlorophenoxyacetic acid with hydrazine or substituted phenyl hydrazine. The reaction mixture was tested in process and on completion of reaction by TLC technique. The final products were analysed and characterized by visual viz. nature and colour, physical viz. m.p., analytical viz. TLC, instrumental viz. UV-Vis and IR spectral technique.

INTRODUCTION

2,4-Dichlorophenoxyacetic acid, popularly known as 2,4-D, are the well known plant growth regulating hormones, widely used in agricultural field [1-2]. It is a systemic herbicide which selectively kills most broad-leaf weeds by causing uncontrolled growth in them, but leaves most grasses such as cereals, lawn turf, and grassland relatively unaffected. It is the main or subsidiary ingradient of over 1,500 herbicide formulations. It kills many terrestrial and aquatic broad-leaf weeds, but not grasses. 2,4-D formulation is particularly effective before planting beans, peas, lentils and chickpeas.[3] It control Broad-leaf weeds in pastures, orchards, and cereal crops such as corn, oats, rice and wheat[4] The 2,4-D which is oldest and most widely available herbicides in the world The derivatives of these hormones were also found to have plant growth regulating and other biological activities [1, 5-6]. 2,4-D-degrading bacteria have been isolated and characterized from a variety of environmental habitats. [7-8]

The effect of the 2,4-dichlorophenoxyacetic acid in combination with the maleic anhydride is the subject of various investigation [9-11]. Literature shows very very less reports [12-13] on the synthesis of plain hydrazide of 2,4-dichlorophenoxyacetic acid and there is report[13] available on synthesis of their hydrazones. 2,4-dichlorophenoxyacetic acid reacts with hydrazine, substituted phenyl hydrazine to form hydrazide [H_2N-HN-C(=O)-R] or N-substituted hydrazide, [H_2N-(R_1)-N-C(=O)-R] as depicted in Scheme-I



Scheme-I

The following hydrazide and N-substituted hydrazide derivatives were synthesized from 2,4-Dichloro-phenoxy acetic acid.

C-I-a: (2,4-Dichloro-phenoxy)-acetic acid hydrazide
C-I-b: (2,4-Dichloro-phenoxy)-acetic acid semicarbazide
C-I-c: (2,4-Dichloro-phenoxy)-acetic acid thiosemicarbazide
C-I-d: (2,4-Dichloro-phenoxy)-acetic acid N-phenyl-hydrazide
C-I-e: (2,4-Dichloro-phenoxy)-acetic acid N-(2,4-dinitro-phenyl)- hydrazide

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Experimental

General method of Synthesis of 2, 4-Dichloro-phenoxy-acetic acid hydrazide and N-substituted hydrazide

In a beaker of capacity 150 ml take a mixture 2,4-Dichloro-phenoxy-acetic acid (12 gm, 54.28 mmole), conc. H_2SO_4 (4 ml) and dry methanol (50 ml) was refluxed for about 15 hrs to yield 2,4-Dichloro-phenoxy-acetic ester is separated. In another 150 ml beaker take 2 gm (34.2 mmole) methanolic solution of ester, hydrazine or substituted hydrazine (44.08 mmole) was added slowly and stirred the reaction mixture for 30 min. and the reaction was monitor by TLC to get singal spot of the product, 2, 4-Dichloro-phenoxy-acetic acid N-substituted hydrazide was separated it is washed with methanol. The product is dried and then recrystalised from methanol to obtained 10.71 gm of hydrazide, yield (84%). The other products were also prepared following same method and using substituted hydrazine instead of hydrazine.

The reaction products were analyzed by physical constant (m. p.) determined on Digital melting point Apparatus (EQ-730) of Equiptronics make and are uncorrected. The progress of reaction and purity of hydrazide deravatives were checked by TLC in ethyl acetate: n-hexane (3.6:0.4) using silica gel coated on glass plates. The UV-Vis spectra (700-200 nm) were recorded (using absolute alcohol) on Shimadzu (UV-1800) spectrophotometer. IR spectra were recorded on a IR Spectrophotometer (Shimadzu, 4000-400 cm^{-1}). The chemicals used were of SIGMA-ALDRICH make and were used as supplied without further purification.

RESULTS AND DISCUSSION

The synthesized hydrazide, H_2N-HN-C (=O)-R hydrazide and substituted hydrazide, H_2N-(R_1)-N-C(=O)-R were synthesized from 2,4-dichlorophenoxyacetic acid and hydrazine and substituted phenyl hydrazine respectively by mixing and stirring at low temperature.

The products were designated as C-I-a, C-I-b, C-I-c, C-I-d and C-I-e, respectively as shown in Scheme-1. The above products synthesized were analyzed by TLC (Fig. 1A & 1B), UV-Vis (Fig. 2A & 2B) and IR (Fig. 3A & 3B) techniques. The mobile phase, ethyl acetate: n-hexane (3.6:0.4) was used for TLC as depicted in Fig. 1A and 1B and the obtained R_f values were depicted in the Table-1.

The visual observation i.e colour of product which ranges from cream to orange, physical constant viz. m.p, and the practical % yield ranges from 64 to 92 %. The results of UV-Vis spectra shows two to five bands (in nm), absorbance due to n→π* and π→π*of the aromatic compounds indicated the extent of conjugation of the groups in the molecule. Similarly, the representative IR spectra for the studied series of hydrazides, C-I-a and C-I-b is depicted in Fig. 3 A and B.

The IR spectral results of other new compounds are depicted in Table 2. The IR spectral absorbance for C-I-b, shows 1119, 1232 and 1310 cm^{-1} are assigned for >C-O- stretching, frequency at 1477, 1521 and 1583 cm^{-1} are assigned for >C=C< of aromatic ring, 1684 and 1707 cm^{-1} are assigned for >C=O stretching, 2777 and 2977 cm^{-1} are assigned for >C-H stretching, 3423 cm^{-1} is attributed to -NH_2 stretching vibration, peak at 697 and 720 cm^{-1} are due to bending vibrations of ortho substituent, peak at 837 and 872 cm^{-1} are due to bending vibrations of para substituent and peak at 769,796 and 837 cm^{-1} are due to aromatic >C-Cl stretching vibrations.

All the IR spectra of newly synthesized hydrazide indicated the frequency band in the range 3073-3423 cm^{-1} reveals presence of primary amino group (-NH_2); the frequency band in the range 1684-1739 cm^{-1} indicated presence of >C=O function; frequency band in the range 1477-1625 cm^{-1} indicated presence of >C=C< stretching band of aromatic ring; frequency band in the range 2776-3073 cm^{-1} indicated presence of -C-H stretch. Band function and frequency band in the range 1093-1366 cm^{-1} indicated presence of -C-O stretch. band.

Table 1 Colour, Physical constant, R_f value and percentage yield of N- substituted hydrazides. C-I-a - C-I-e

Sr. No.	Code	-R_1	M.F.	M. Wt. (g/mol)	Colour	m.p.°C	R_f* Value	% Yield
1	**C-I-a**	-H	$C_8H_8O_2Cl_2N_2$	235	Cream	143-145	0.84	84
2	**C-I-b**	NH_2-C(=O)-	$C_9H_9O_3Cl_2N_3$	278	Cream	125-128	0.73	60
3	**C-I-c**	NH_2-C(=S)-	$C_9H_9O_2Cl_2SN_3$	294	White	130-131	0.84	64
4	**C-I-d**	-C_6H_5	$C_{14}H_{12}O_2Cl_2N_2$	311	Choclate brown	201-205	0.70	89
5	**C-I-e**	-2,4-DNP	$C_{14}H_{10}O_6Cl_2N_4$	401	Orange	122-125	0.90	92

* Ethyl Acetate: n-Hexane 3.6:0.4

Fig 1A The representative TLC for **C-I-a.**

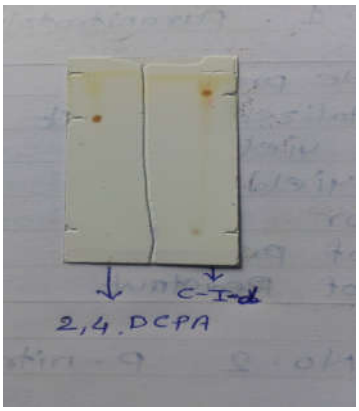


Fig 1B The representative TLC for **C-I-d.**

On combining all the above characterization results one arrives on the following structures for the newly synthesized Hydrazide in the present work, as given in Table 2.

Table 2 Structures of Synthesized hydrazide, C-I-a - C-I-e derived from 2, 4-dichlorophenoxyacetic acid

Compd. ID	UV-Vis Spectra			IR Frequency, cm^{-1}	
	λ_{max}, (nm)	A, $M^{-1}cm^{-1}$	ϵ = A/c $Lgm^{-1}cm^{-1}$		
C-I-a	284, 235	0.512, 3.251	5,120 32,510	1721, 1739 1482,1576,1590 2926,2962,3039 3395 724, 764 806,822,869, 1118,1268,1366 763,822,868	$\nu_{>C=O}$; $\nu_{>C=C<}$ (Ar.); ν_{-C-H} ; ν_{-NH2} ; $\nu_{-ortho\ subst.}$; $\nu_{-para\ subst.}$; ν_{-C-O} ; $\nu_{>C-Cl.}$
C-I-b	575.50, 450.50, 375, 292, 284, 231	0.005, 0.006, 0.007, 0.462, 0.528, 2.246	29.41, 35.29, 41.17, 2,717, 3,105, 13,211	1684, 1707 1477, 1521,1583 2777,2977 3423 697,720 837,872 1119,1232,1310 769,796,837	$\nu_{>C=O}$; $\nu_{>C=C<}$ (Ar.); ν_{-C-H}; ν_{-NH2}; $\nu_{-ortho\ subst.}$; $\nu_{-para\ subst.}$; ν_{-C-O} ; $\nu_{>C-Cl.}$
C-I-c	595 292 284 233.50 217.50	0.004 0.770 0.927 2.758 2.643	23.52 4,529 5,453 16,224 15,547	1734 1478,1585,1625 2776, 2977 3073 696,720 795,851 1104,1232,1310 795, 850 720,1070	$\nu_{>C=O}$; $\nu_{>C=C<}$ (Ar.) ; ν_{-C-H} ; ν_{-NH2} ; $\nu_{-ortho\ subst.}$; $\nu_{-para\ subst.}$; ν_{-C-O} ; $\nu_{>C-Cl}$; $\nu_{>C=S}$
C-I-d	333 228.50	0.456 1.562	2,682 9,188	1695 1495,1592,1616 2923 3373 690,765 820,835,856, 1144,1203,1294 743,765,855	$\nu_{>C=O}$; $\nu_{>C=C<}$ (Ar.) ; ν_{-C-H} ; ν_{-NH2} ; $\nu_{-ortho\ subst.}$; $\nu_{-para\ subst.}$; ν_{-C-O} ; $\nu_{>C-Cl}$
C-I-e	331 292.50 284 234.50	0.412 1.122 1.237 3.159	2,424 6,600 7,276 18,582	1707,1734 1478,1586,1617 2977,3073 3373 696,720 795,821,836 1093,1232,1311 1341,1392,1478 795,821,851	$\nu_{>C=O}$; $\nu_{>C=C<}$ (Ar.) ; ν_{-C-H} ; ν_{-NH2}; $\nu_{-ortho\ subst.}$; $\nu_{-para\ subst.}$; ν_{-C-O} ; ν_{-NO2} ; $\nu_{>C-Cl}$

Except **C-I-a** (1.0 x 10^{-4} gm/L) for all the hydrazides, conc. = **c** = 1.7 x 10^{-4} gm/L.

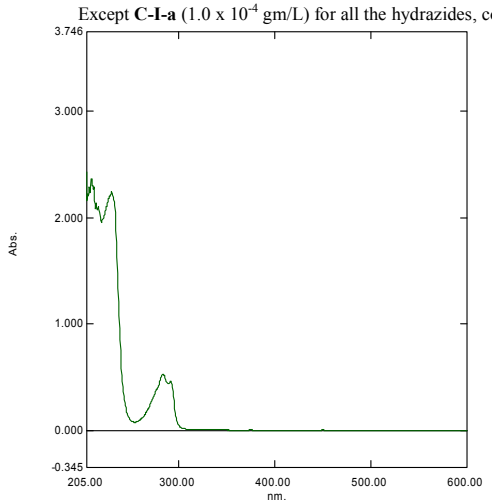


Fig 2A The representative UV-Vis spectra of the Hydrazide, **C-I-b** in ethanol.

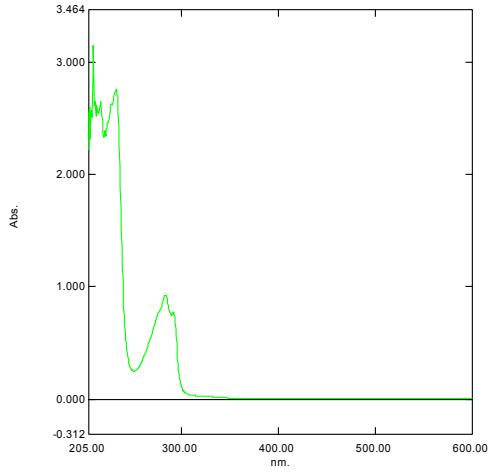


Fig 2B The representative UV-Vis spectra of the Hydrazide, **C-I-c** in ethanol.

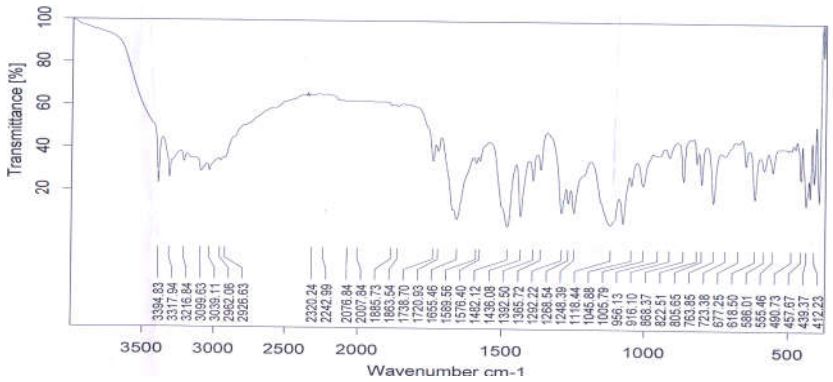


Fig 3A The representative IR spectra for the Hydrazide compound, C-I-a

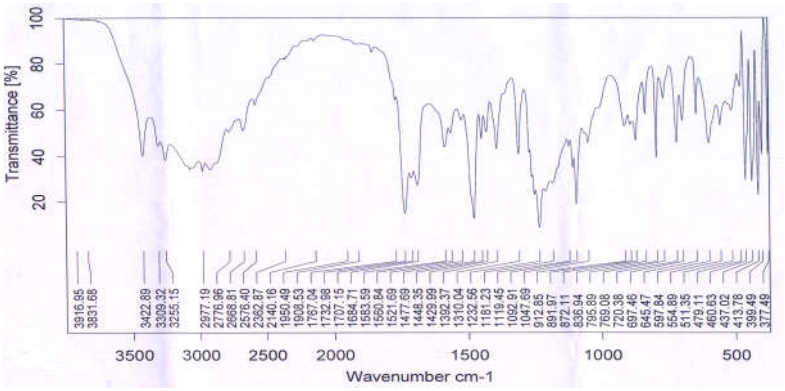
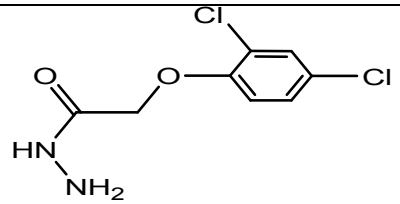
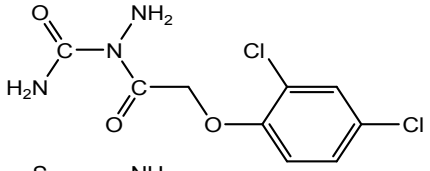
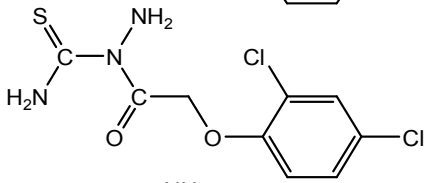
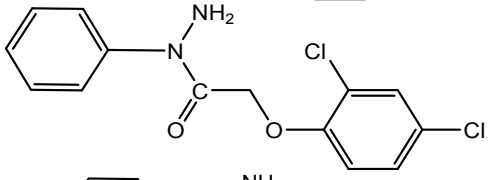
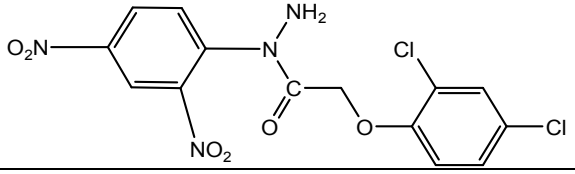


Fig 3B The representative IR spectra for the Hydrazide compound, C-I-b

Table 2 Structures of Synthesized hydrazide, C-I-a to C-I-e derived from 2, 4-dichlorophenoxyacetic acid.

C-I-a		*(2,4-Dichloro-phenoxy)-acetic acid hydrazide*
C-I-b		*(2,4-Dichloro-phenoxy)-acetic acid semicarbazide*
C-I-c		*(2,4-Dichloro-phenoxy)-acetic acid thiosemicarbazide*
C-I-d		*(2,4-Dichloro-phenoxy)-acetic acid N-phenyl-hydrazide*
C-I-e		*(2,4-Dichloro-phenoxy)-acetic acid N-(2,4-dinitro-phenyl)-hydrazide*

CONCLUSION

Novel hydrazide derivative are formed using 2, 4-dichlorophenoxyacetic acid reacting with hydrazine, substituted phenyl hydrazine to form hydrazide [H_2N-HN-C(=O)-R] or Nsubstituted hydrazide, [H2N-(R1)-N-C(=O)-R]. These compounds will be useful for our further, research which is already planned. These compounds will also be useful synthone or building block by organic researchers in the near future.

Scope: There is a future scope for using these compounds for the organic transformations and the data obtained will be useful for the society to study their further studies for Budding Organic and the other Researchers.

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