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NOVEL SYNTHESIS AND STUDY OF IMPACT OF SUBSTITUTED 1,3-THIAZINE AND ITS NANOPARTICLES ON PHYTOTIC GROWTH OF SOME FLOWERING PLANTS

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ABSTRACT
The synthesis, spectral analysis and biological activities of 4-phenyl-2-hydroxy-chlorosubstituted-2-imino-1,3 thiazines have been carried out. In this case 4-(2'-hydroxy-3',5'-dichlorophenyl)-6-(4"-nitrophenyl)-2-iminophenyl-6H-3N-phenyl-1,3-thiazine (C) has been screened. The compound C was synthesized from 2'-hydroxy-3,5-dichlorophenyl-4-(4"-nitrophenyl)chalcone (a) by the action of diphenylthiourea. The compound (a) was synthesized from 2'-hydroxy-3',5'-dichloroacetophenone by the action of p-nitrobenzaldehyde in ethanol and 40% NaOH. The nanoparticles of the compound C has been prepared by using ultrasonic technique. The titled compound and their nanoparticles were screened for their growth promoting activity on some flowering plants viz.. *Crysanthemum coronarium, Dahalia pinnata, Verbena officinalis, Iberis amara.*

KEYWORDS: Chalcone, thiazine, diphenylthiourea, growth promoting activities.

INTRODUCTION

Thiazine is a six membered ring system, which contains two hetero atoms [N and S] placed in a heterocyclic ring at 1, 3 positions. Many workers have synthesized different 1,3-thiazines. The researchers have reported the synthesis of several thiazines[1-6] and also their potent biological activities such as blood platelet aggregation inhibitors[7], antibacterial[8-9] antiallergic[10], anticholesterenic[11] and antifungal.[12] Moreover thiazine nucleus is a pharmacophore of cephalosporin that occupy a very important place in the field, of antibiotics and drug chemistry. Chalcones and their analogues having α,β-unsaturated carbonyl system are very versatile substrates for the evolution of various reactions and physiologically active compounds. The reaction of thiourea with α, β-unsaturated ketones also results in the formation of 1,3-thiazines.The chlorosubstituted thiazines with amino group at position 2 in the ring exhibit promising biological activities.[13-16]

In the present study, the chlorosubstituted 1,3-thiazine (C) has been prepared along with its nanoparticles and screened them for their growth promoting activity on some flowering plants viz. *Crysanthemum coronarium, Dahalia pinnata, Verbena officinalis, Iberis amara.*

EXPERIMENTAL

All the glassware's used in the present work were of pyrex quality. Melting points were determined in hot paraffin bath and are uncorrected. The purity of compounds was monitored on silica gel coated TLC plate. IR spectra were recorded on Perkin-Elmer spectrophotometer in KBr pelletes, H^1 NMR spectra on spectrophotometer in $CDCl_3$ with TMS as internal standard. UV spectra were recorded in nujol medium. The analytical data of the titled compounds was highly satisfactory. All the chemicals used were of analytical grade. All the solvents used were purified by standard methods. Physical characterisation data of all the compounds is given in Table 1.

Table 1: Characterisation data of newly synthesized compounds.

Compounds	Molecular formula	M.P. in ^{0}C	% of yield	% of element			
				C	H	N	S
	$C_8H_6O_2Cl_2$	54	80	47.90/48	2.95/3		
a	$C_{15}H_9O_4NCl_2$	250	70	53.10/53.25	2.40/2.66	3.98/4.18	
C	$C_{28}H_{19}O_3Cl_2N_3S$	172	70	61.28/61.42	2.98/3.29	7.42/7.68	5.67/5.85

2'-Hydroxy 3',5'-dichloroacetophenone

2'-Hydroxy-5-chloroacetophenone (3g) was dissolved in acetic acid (5 ml), and mixed with sodium acetate (3g). To this reaction mixture chlorine in acetic acid reagent (40 ml; 7.5 w/v) was added dropwise with stirring. The temperature of the reaction mixture was maintained below 20°C. The mixture was allowed to stand for 30 minutes and then poured into water. A pale yellow solid thus obtained was filtered, dried and crystallized from ethanol to yield the compound.

Preparation of 2'-hydroxy-3,5-dichlorophenyl-4-(4"-nitrophenyl)-chalcone (a)

2'-Hydroxy-3',5'-dichloroacetophenone (0.1 mol) was dissolved in ethanol (50 ml) and p-nitrobenzaldehyde (0.1 mol) was added gradually to the solution and the mixture was heated to boiling. Then aquous sodium hydroxide solution [40%; 40 ml] was added dropwise with constant stirring. The mixture was stirred mechanically at room temperature for about half an hour and kept for overnight. It was then acidified by hydrochloric acid (10%) solution. The solid product thus separated, was filtered, and washed with sodium bicarbonate (10%) followed by water. Finally it was crystallized from ethanol acetic acid mixture to get the compound (a).

Preparation of 4-(2'-hydroxy-3',5'-dichlorophenyl)-6-(4"-nitrophenyl)-2- iminophenyl-6H-3N-phenyl-1,3-thiazine (C)

2'-Hydroxy-3,5-dichlorophenyl-4-(4"-nitrophenyl)-chalcone (a) (0.01 mol) and diphenyl thiourea (0.02 mol) were dissolved in ethanol (30 ml). To this aquous KOH solution (0.02 mol) was added. The reaction mixture was refluxed for three hours, cooled, diluted with water and acidified with conc. HCl. The product thus obtained was crystallized from ethanol to get the compound (C).

The newly synthesized compounds were characterised on the basis of elemental analysis, molecular determination, UV, IR, NMR. spectral data.

Compound (C)

UV: Spectrum No. 1

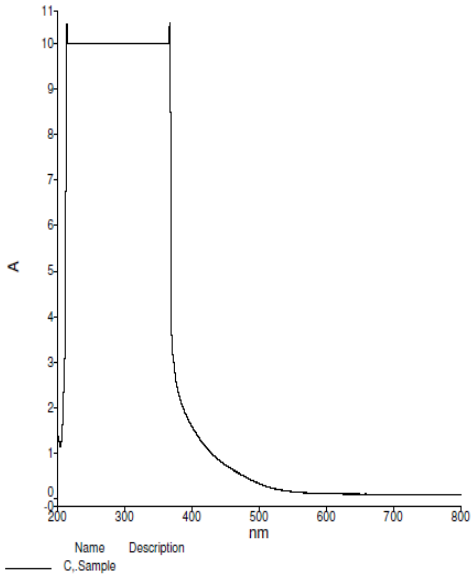
The UV-Vis spectrum of the compound C reported in dioxane showed λ_{max}value385 nm corresponding to $n \rightarrow \pi^*$ transition.

IR KBr: Spectrum No. 2

3464.61 cm^{-1} (-OH phenolic) , 2797.56 cm^{-1} (aliphatic C-H stretching), 3035.27 cm^{-1} (aromatic C-H stretching), 3206.13 cm^{-1} (-NH stretching), 1649.58 cm^{-1} (-C=N stretching), 1344.11 cm^{-1} (-C-N=) (-C-NO_2) stretching, 757.35 cm^{-1} (C-Cl stretching in aliphatic), 1108.54 cm^{-1} (C-Cl stretching in aromatic).

PMR: Spectrum No. 3

∂ 2.51 (d, 1H, -C=C-C-**H**); ∂ 3.3 (d, 1H, C=C-**H**); ∂ 7.09 to 8.07 (m, 17H, Ar-**H**); ∂ 9.6 (s, 1H, O-**H**).



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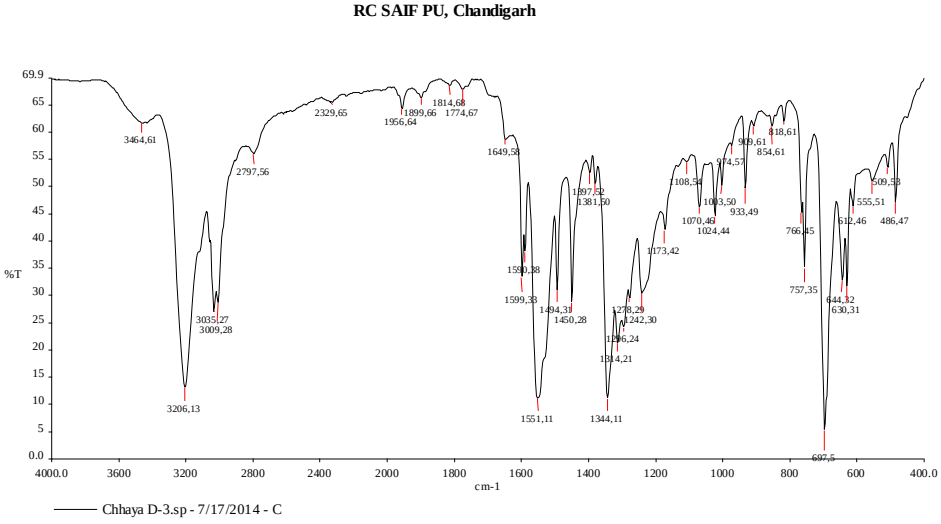

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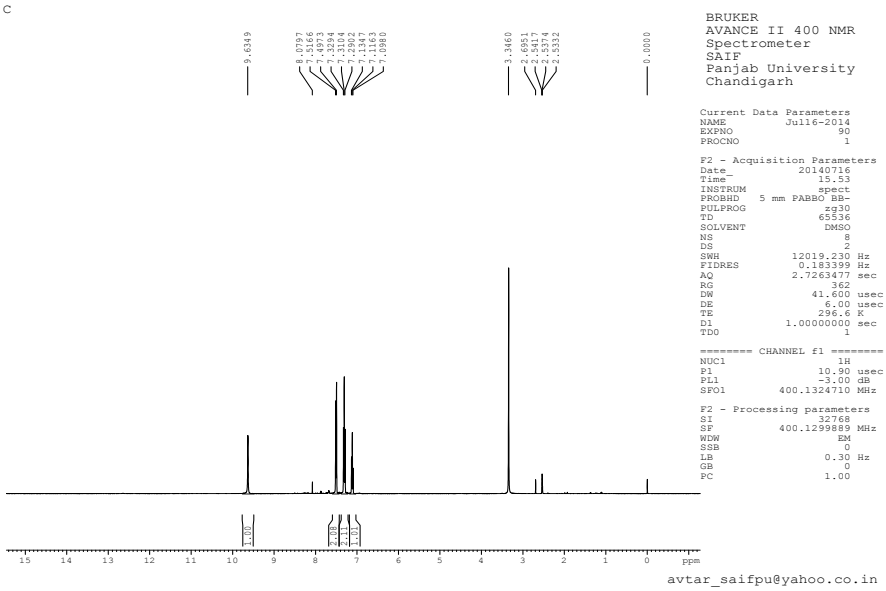

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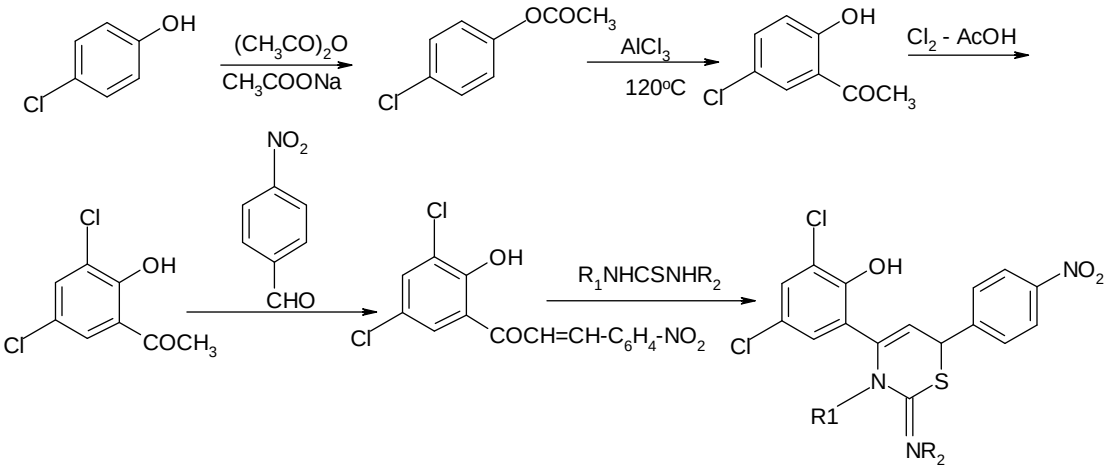


Scheme

Where

1) $R_1 = -C_6H_5$
2) $R_2 = -C_6H_5$

Growth Promoting Effect on some flowering Plants

The experimental set up of the study was devided into two parts:

(i) Seed treatment (ii) Field experiment.

(i) Seed treatment

With a view to safeguard dormant seed's potential from harmful external agencies, the seeds of the test plants were treated by test compounds before sowing.

(ii) Field experiment

Pregerminated quality seeds of *Crysanthemum coronarium, Dahalia pinnata, Verbena officinalis, Iberis amara.*were procured from Department of Horticulture, Dr. PDKV, Akola.

The beds of cotton soil, 2.5 x 2.5 m size were prepared in an open field. The sowing of seeds of all four test flowering plants were done in separate beds and irrigated periodically.

The plants from each bed were devided into two groups i.e. A and B and designated as "Control" and "Treated" group plants respectively.

The plants from group B were sprayed with the solution of test compounds at weekly intervals. The field experiments were conducted to compare the treated plants of group B with untreated plants of controlled group A. In this context, the observations were recorded on 7, 14, 21, 28, 35, 42, 45, 56, 63, 70, 77, 84, 91 days after sowing corresponding to early vegetative, late vegetative, flowering, pod filing and pod maturation, with special reference to number of leaves and height of shoots.

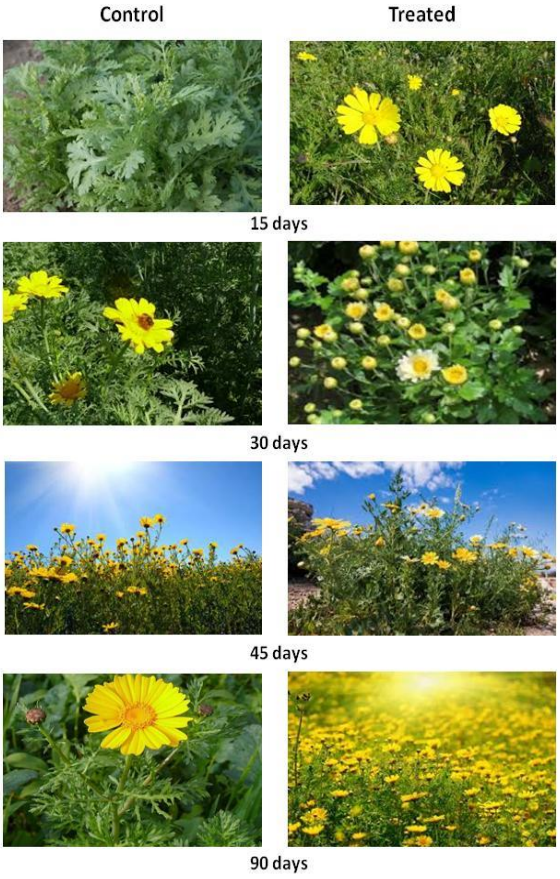
The results of field's experiments are tabulated in the tables 2,3 and 4.

Table 2: Activity of the test compound C:

Table No. (02): 4-(2'-Hydroxy-3',5'-dichlorophenyl)-6-(4"-nitrophenyl)-2-iminophenyl-6H-3-N-phenyl-1,3-thiazine (C)

Periodicity of Observations [in days]	*Crysanthemum coronarium*				*Dahalia pinnata*				*Verbena officinalis*				*Iberis amara*			
	Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves	
	C	T	C	T	C	T	C	T	C	T	C	T	C	T	C	T
7	1.0	1.0	1	1	2.5	1.5	2	2	4.4	4	2	2	2	2	2	3
14	1.2	1.2	2	2	7.5	7	2	2	10	8	2	2	2.1	2.5	2	3
21	1.3	1.4	7	10	8	12	2	4	15	11	3	5	2.3	2.8	3	4
28	1.5	1.6	9	11	9	19	3	6	16	18	4	6	2.5	2.7	4	5
35	1.6	1.8	10	12	11	26	4	7	18	19	5	9	2.8	3.0	5	7
42	1.8	2.0	12	15	17	42	5	8	19	20	7	12	3.0	3.4	6	8
49	2.3	3.5	14	18	25	48	6	8	20	21	8	14	3.5	3.9	8	9
56	3.6	4.0	16	22	28	52	7	9	23	25	10	17	3.8	4.5	10	12
63	5.5	6.7	18	24	31	55	8	10	25	30	12	18	4.2	5.0	12	14
70	7	12	20	28	34	60	9	11	27	32	14	20	4.6	5.4	14	16
77	14	19	22	30	36	63	10	13	28	35	16	23	5.5	7.0	16	18
84	20	24	24	32	38	65	11	15	29	36	18	25	7,2	14	20	24
91	24	30	26	36	40	68	12	17	36	38	20	27	8.2	17	25	29

Impact of the compound 4-(2'-Hydroxy-3',5'-dichlorophenyl)-6-(4"-nitrophenyl)-2-iminophenyl-6H-3-N-phenyl-1,3-thiazine (C) on phytotic growth of *Crysanthemum coronarium*



Impact of the compound 4-(2'-Hydroxy-3',5'-dichlorophenyl)-6-(4"-nitrophenyl)-2-iminophenyl-6H-3-N-phenyl-1,3-thiazine (C) on phytotic growth of *Dahalia pinnata*

RESULT AND DISCUSSION

The titled compounds and their nanoparticles were screened for their growth promoting activity on test flowering plants viz, *Crysanthemum coronarium, Dahalia pinnata, Verbena officinalis, Iberis amara.*

When a comparison of morphological characters was made between those of treated and control group plants, it was interesting to note that all the treated plants exhibited significant shoot growth and considerable increase in the number of leaves as compared to those of untreated ones.

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