

**NOVEL SYNTHESIS AND STUDY OF IMPACT OF CHLOROSUBSTITUTED
4-AROYL/ALKOYL PYRAZOLES AND ITS NANOPARTICLES ON PHYTOTIC
GROWTH OF SOME FLOWERING PLANTS**

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ABSTRACT

Aroyl/alkoylacetophenones (2a-b) undergoes intramolecular claisen condensation to form 1-(2'-hydroxy-3',5'-dichlorophenyl)-3-aryl/alkyl-1,3-propanediones (4a-b) which on treatment with aromatic and aliphatic aldehydes in ethanol containing little piperidine forms 3-aryloyl/alkoylchromanones (5a-b) subsequently 3-aryloyl/alkoylchromones (6a-b). 3-Aroyl/alkoylchromones (6a-b) on treatment with Ph.NH.NH₂.HCl in DMSO containing small amount of piperidine gave 4-aryloyl/alkoylpyrazoles (7a-b). The structures of newly synthesized chlorosubstituted 4-aryloyl/alkoyl-pyrazoles (7a-b) were elucidated on the basis of molecular weight, elemental analysis and their spectral data. The titled compound and its nanoparticles were screened for their growth promoting activity on some flowering plants viz..*Crysanthemum coronarium*, *Dahlia pinnata*, *Verbena officinalis*, *Iberis amara*.

KEYWORDS: Chromanones, Chromones, Pyrazoles, growth promoting activities.

INTRODUCTION

Pyrazoles are well known and important nitrogen containing five membered hetero-cyclic compounds. Various methods have been worked out for their synthesis.^[1-7] Derivatives of pyrazoles have played a crucial role in the history of heterocyclic chemistry and have been extensively instrumental as pharmacophores and synthons in the field of organic chemistry and drug designing. Several pyrazole derivatives have been found to possess significant activities such as antimicrobial,^[8] antibacterial,^[9] 5- α -red-uctase inhibitor,^[10] antiproliferative,^[11] antiparasitic,^[12] herbicides.^[13] A good number of pyrazoles have also been reported to have interesting biological activities like anti-inflammatory,^[14] antimicrobial,^[15] and antiprotozoal,^[16-17] which render them valuable active ingredients of medicine and plant protecting agents.

In the present study, chlorosubstituted 4-aryloyl/alkoyl-pyrazoles has been prepared along with their nanoparticles and screened them for their growth promoting activity on some some flowering plants viz. *Crysanthemum coronarium*, *Dahlia pinnata*, *Verbena officinalis*, *Iberis amara*.

MATERIALS AND METHODS

Synthesis of 2-hydroxy-3, 5-dichloroacetophenone (2b): 2-Hydroxy-5 chloroacetophenone (3g) was dissolved in acetic acid (5ml), sodium acetate (3g) was added to the reaction mixture and chlorine in acetic acid reagent (40ml) was added drop wise with constant stirring. The mixture was allowed to stand for 30 minutes. Then it was poured into cold water. A pale yellow solid product thus separated was filtered and crystallized from ethanol to get the compound (2b).

Synthesis of 2-benzoyloxy-3, 5-dichloroacetophenone (3a): A mixture of 2-hydroxy-3, 5-dichloroacetophenone (0.04 mol) and bezoyl chloride (0.05 mol) was dissolved in NaOH (10%) (30ml). The reaction mixture was shaken for half an hour, the product thus obtained then filtered, washed with NaHCO₃ (10%) and purified by recrystallization with ethanol to get 2-benzoyl-3, 5-dichloroacetophenone (3a).

Synthesis of 1-(2-hydroxy-3, 5-dichlorophenyl)-3-phenyl-1, 3-propanedione (4a): A mixture of 3a 1-(2-hydroxy, 3, 5-dichlorophenyl)-3-phenyl-1, 3-propanedione and dry pyridine was warmed up to 60 OC and pulverized KOH was added slowly with constant stirring and then kept it for overnight. After digestion the

reaction mixture was acidified with cold 1:1 dil. HCl. The product thus obtained was filtered and washed with NaHCO₃ solution. Finally it was crystallized from ethanol.

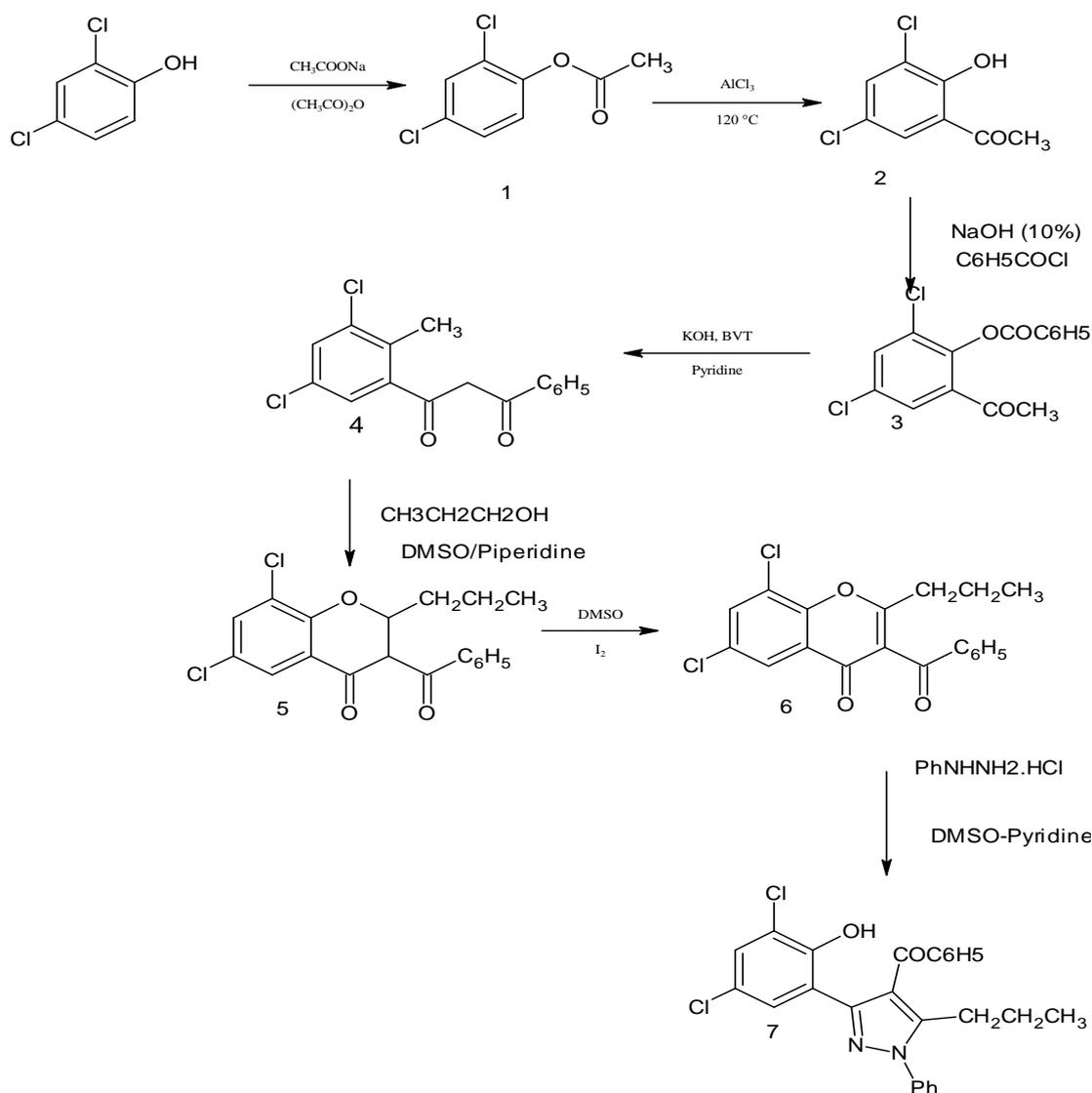
Synthesis of 3-benzoyl-2-(2'-propoyl)-6, 8-dichlorochromanone (5a): A mixture of 1-(2-hydroxy-3, 5-dichlorophenyl)-3-phenyl-1,3-propanedione (4a) (0.01 mol) and propionaldehyde (0.02 mol) was refluxed in DMSO (25 ml) and piperidine (0.5ml) for 15-20 minutes. After cooling the reaction mixture was acidified with dil. HCl (1:1) and the product thus separated was crystallized from ethanol to get the compound 5a.

Synthesis of 3-benzoyl-2-(2'-propoyl)-6, 8-dichlorochromanone (6a): 3-Benzoyl-2-(2'-propoyl)-6,8-dichlorochromanone (5a) (0.01 mol) was refluxed for 10 min. with a crystal of Iodine in DMSO (20ml). After cooling the reaction mixture was diluted with water. The solid product thus separated, filtered, washed with sodium thiosulphate solution and crystallized with ethanol.

Synthesis of 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-propoyl)-1-phenylpyrazole (7a): A mixture of 3-benzoyl-2-(2'-propoyl)-6,8-dichlorochromanone (6a) (0.01 mol) and Ph.NHNH₂HCl (0.02 mol) was refluxed in DMSO (20ml) containing 1 ml piperidine for 1.5 hours. After cooling, the reaction mixture was acidified with dil. HCl. The solid product thus obtained was filtered and washed with sodiumbicarbonate (5%) solution. It was crystallized from ethanol to get the compound 7a.

Synthesis of 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-propoyl)isoxazole (8a): The mixture of 6a (0.01 mol) and NH₂OH.HCl (0.02 mol) was refluxed in DMSO (20ml) containing 0.5ml of piperidine for 1.5 hours. After cooling the reaction mixture was acidified with dil. HCl. The solid product was washed with NaHCO₃ and then crystallized from ethanol to get 8a.

The synthetic route for obtaining the final products is presented in scheme-I.



Physical and analytical data of the newly synthesized compounds are summarized in the following table 1.

Table 1: Physical and analytical data of the newly synthesized compounds.

Compounds	Mol. Formula	Mol Wt.	R	R'	Yield %	M.P. °C	Found (Calcd.%)	
							C	N
2b	C ₈ H ₆ Cl ₂ O ₂	205			75	53		
3a	C ₁₅ H ₁₀ O ₃ Cl ₂	308	-C ₆ H ₅		75	65	58.44	
3b	C ₁₆ H ₁₂ O ₄ Cl ₂	338	-C ₆ H ₅ -OCH ₃		75	113	56.80	
4a	C ₁₅ H ₁₀ O ₃ Cl ₂	308	-C ₆ H ₅		75	113	58.44	
4b	C ₁₆ H ₁₂ O ₄ Cl ₂	338	-C ₆ H ₅ -OCH ₃		60	113	56.80	
5a	C ₁₉ H ₁₆ O ₃ Cl ₂	362	-C ₆ H ₅	-CH ₂ -CH ₂ -CH ₃	70	110	70.00	
5b	C ₂₀ H ₁₈ O ₃ Cl ₂	376	-C ₆ H ₅ -OCH ₃	-CH ₂ -CH ₂ -CH ₃	60	112	61.22	
6a	C ₁₉ H ₁₄ O ₃ Cl ₂	360	-C ₆ H ₅	-CH ₂ -CH ₂ -CH ₃	60	110	63.33	
6b	C ₂₀ H ₁₆ O ₃ Cl ₂	374	-C ₆ H ₅ -OCH ₃	-CH ₂ -CH ₂ -CH ₃	60	90	64.66	
7a	C ₂₅ H ₂₀ O ₂ N ₂ Cl ₂	450	-C ₆ H ₅	-CH ₂ -CH ₂ -CH ₃	60	147	66.66	6.22
7b	C ₂₆ H ₂₂ O ₃ N ₂ Cl ₂	480	-C ₆ H ₅ -OCH ₃	-CH ₂ -CH ₂ -CH ₃	60	210	65.00	5.83
8a	C ₁₉ H ₁₅ O ₃ NCl ₂	375	-C ₆ H ₅	-CH ₂ -CH ₂ -CH ₃	62	180	60.80	3.73
8b	C ₂₀ H ₁₇ O ₄ NCl ₂	406	-C ₆ H ₅ -OCH ₃	-CH ₂ -CH ₂ -CH ₃	60	196	59.11	3.44

Growth Promoting Effect on some Flowering Plants

The experimental set up of the study was divided 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*, *Dahlia 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 vegetable crop plants were done in separate beds and irrigated periodically.

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

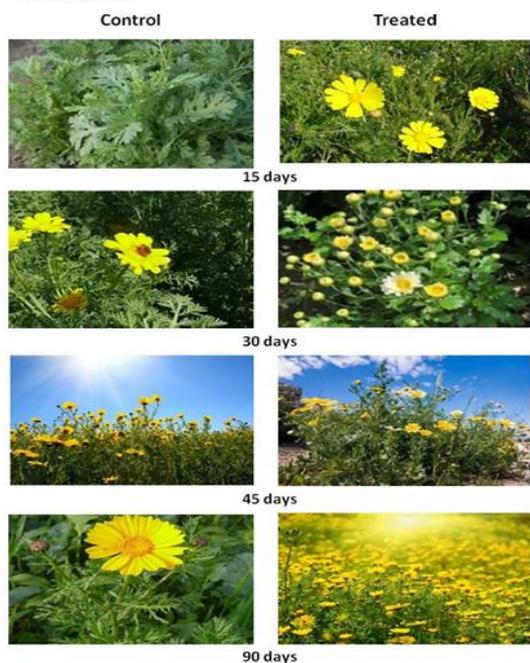
The plants from group B were sprayed with the solution of test compounds at weekly intervals. The field experiments were conducted to compare the treated plants of group B with untreated plants of controlled group A. In this context, the observations were recorded on 7, 14, 21, 28, 35, 42, 45, 56, 63, 70, 77, 84, 91 days after sowing corresponding to early vegetative, late vegetative, flowering, pod filling 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 02.

Table (2): Activity of the test compound (7a).

Table (02): 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-propoyl)-1-phenylpyrazole (7a):																
Periodicity of Observations [in days]	<i>Crysanthemum coronarium</i>				<i>Dahlia pinnata</i>				<i>Verbena officinalis</i>				<i>Iberis amara</i>			
	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 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-propoyl)-1-phenylpyrazole on phytotic growth of *Crysanthemum coronarium*



Impact of the compound 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-propoyl)-1-phenylpyrazole on phytotic growth of *Dahalia pinnata*



Impact of the compound 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-propoyl)-1-phenylpyrazole on phytotic growth of *Verbena officinalis*



Impact of the compound 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-propoyl)-1-phenylpyrazole on phytotic growth of *Iberis amara*



RESULT AND DISCUSSION

The titled compound and its 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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REFERENCES

1. Swarnkar P.K., Kriplani B., Gupta G.N., Oijha K.G., synthesis and antimicrobial activity of some new phenothiazine derivatives, *E.J. Chem.*, 2007; 4(1): 14-20.
2. Kakade B.S., "Synthesis in heterocyclic compounds (Role of DMSO as a solvent," Ph.D. Thesis, Nagpur University, 1981.
3. Chincholkar M.M., and Ramekar M.A. *J. Ind. Chem. Soc.*, 1994; 71(4): 199.
4. S.P. Rathod, A.P. Charjan and P.R. Rajput, *Rasayan J. Chem.*, 2010; 3(2): 363-367.
5. Dabholkar V.V. and F.Y. Ansari, *Indian J. Chem.*, 2008; 47: 1759 – 1761.
6. D.H. Morey and S.N. Patil *ori.*, *J. Chem.*, Mar., 2002.
7. C.Brown and R.N. Davidson, *Adv.Heterocycl. Chem.*, 1985; 38: 135.
8. P. Descacq, A. Nubrich, M. Capdepuy and G. Devanuz, *Eur. J. Med. Chem.*, 1990; 25: 285.
9. M.I. Younes, H.H. Abbas, and S.A.M. Metwally, *Arch. Pharma*, 1987; 230.
10. D.T. Witlar, M.E. Wolff and R.C. Covestri, "In Berger", *S. Medicinal Chemistry*", part III, Edi. Willey, Newyork, 1981; 603.
11. M. Crewzet and F. Helene, *Eurpat App. Ep.*, 121, 489, *Chem. Abstr.*, 102, 1985, 787244, *Chem., Abstr.*, 89, 108943 m, 1978.
12. F.M. Dean, K.A. Thakur and C.H. Gill, "Naturally occurring oxygen ring compounds", *J. Indian Chem. Soc.*, 1983; 60: 668.
13. P. Valenti, A. Bisi, A. Rampa, F. Belluti, S. Gobbi, A. Zampiron, M. Carrara, *Biosy, Med. Chem.*, 2002; 239.
14. Y.Q. Shi, J. Fukai, H Sakagami, W.J. Chang, P.Q. Yang, F.P. Wang, T. Nomura, *J. Nat. Prod.*, 2001; 64: 181.
15. G.J. Reddy, D. Latha, K.S. Rao, *Heterocycl. Commun.*, 2004; 10: 279.
16. T. Ghosh, S. Saba, C. Bandyopadhyaya, *Synthesis*, 2005; 11: 1845.