



SYNTHESIS OF 4-AROYLISOXAZOLES AND EFFECTS OF CHLOROSUBSTITUTED 4 AROYLISOXAZOLES ON SOME HORTICULTURAL CROP PLANTS

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ABSTRACT

The synthesis, spectral analysis and effect on some crop plants by some 4-Aroylisoxazoles with 3- aroylflavone on treatment with NH₂OH.HCl. We got two series while carried out in different aromatic acids. In series, we got 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(3-nitro phenyl) isoxazole and 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(3'-nitrophenyl) isoxazole. It has been revealed that, the use of piperidine in DMSO as the solvent in the above reaction influences the rate of the reaction and also the yield of the products.. All these compounds have been analyzed by UV, IR and NMR for structure. The newly synthesized chlorosubstituted isoxazoles were studied.

Keywords: isoxazole, horticultural crops, 3- aroylflavone .

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INTRODUCTION

Isoxazole is a five membered heterocyclic compound containing both oxygen and nitrogen atoms in the 1,3 positions placed in the heterocyclic ring. Many workers have synthesized different Isoxazole¹⁻⁷. Heterocyclic compounds are very useful units in the fields of medicinal and pharmaceutical chemistry and have been reported to exhibit a variety of biological activities⁸⁻¹³. 3-aroyleflavone on treatment with NH₂OH.HCl. It has been revealed that, the use of piperidine in DMSO as the solvent in the above reaction influences the rate of the reaction and also the yield of the products. 3-aroyleflavone on treatment with NH₂OH.HCl to gives final product. It has been well focused that, the presence of chlorosubstituted moieties is an important structural feature also, the present work deals with the study of vegetative growth promoting effects of some newly synthesized chlorosubstituted 1,3-Isoxazoles with special reference to horticulture crop.

EXPERIMENTAL

All the glassware's used in the present work were of Pyrex quality. Melting points were determined in open capillary and are uncorrected. Purity of compounds was monitored on silica gel coated TLC plate. The IR spectra were recorded on `Perkin-Elmer 202` Infra red spectrophotometer 1310. The UV-VIS spectra were recorded on Systronics 119 spectrophotometer. The PMR spectra were recorded on Varian Mercury YH - 300 spectrometer in CDCl₃.. The analytical data of compounds were highly satisfactory. All the chemicals used were of analytical grade. All the solvents used were purified by standard methods. Physical characterization data of all the compounds are given in Table 1.

RESULT AND DISCUSSION

The synthetic methods used in present work are given below along with their UV, IR and NMR data.

2-Hydroxyacetophenones (2)

2-Hydroxy-5-chloroacetophenone (2a) , m.p.56°C and 2-hydroxy-3, 5-dichloroacetophenone, (2b), m.p. 53°C were used as starting materials. The former was prepared by known method while the later was prepared by a new method invented by Rajput et al.

Preparation 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 then chlorine in acetic acid reagent (20ml) (7.5 w/v) was added drop wise with stirring. The temperature of the reaction mixture was maintained below 20°C. The mixture was allowed to stand for about 30 minutes. Finally it was poured into water with stirring. The pale yellow solid product thus separated was filtered and crystallized from ethanol, m.p. 53°C yield 1.5g.

IR (KBr): 3040 (-OH phenolic stretching); 1660 (>C=O stretching); 1345 (-OH bending in phenol); 650 (C-Cl stretching); NMR: δ 2.60 (s, 3H, -ArOCH₃); δ 7 to 8 (s, 2H, -ArH); δ 12.11 (s, 1H, Ar-OH); UV: 346nm.

Preparation of 2-benzoyloxy -3, 5-dichloroacetophenone (3a)

2-Hydroxy-3,5-dichloroacetophenone (0.04 mol) and benzoyl- chloride (0.05mol) were dissolved in NaOH (10%) (30ml). The reaction mixture was shaken for about half an hour. The product thus separated was filtered, washed with water followed by sodium bicarbonate (10%) washing and then again with water. The solid product was crystallized from ethanol to obtain 2-benzoyloxy-3,5-dichloroacetophenone (3a), m.p.66°C, yield 76%.

IR (KBr): 3040 (-OH phenolic stretching); 1660 (>C=O stretching); 1345 (-OH bending in phenol); 650 (C-Cl stretching).PMR: δ 2.60 (s, 3H, -ArOCH₃); δ 6.8 to 7.64 (m, 2H, -ArH); δ 12.7 (s, 1H, Ar-OH).UV: 346 nm.

Preparation of 1-(2-hydroxy-3,5-dichlorophenyl)-3-phenyl-1,3-propane-dione (4a)

2-Benzoyloxy-3,5-dichloroacetophenone (3a) (0.05 mol) was dissolved in dry pyridine (40ml). The solution was warmed up to 60°C and pulverized KOH (15g) was added slowly with constant stirring. After 4 hours of heating the reaction mixture was acidified by adding ice cold dil. HCl (1:1). The brownish yellow solid product thus separated was filtered, washed with sodium bicarbonate solution (10%) and finally again with water. It was then crystallized from ethanol acetic acid mixture to get 1-(2-hydroxy-3-dichloro-phenyl)-3-phenyl-1,3-propanedione(4a),m.p.110°C yield 75%.

IR (KBr):3030 (-OH phenolic stretching); 1600 (>C=O stretching); 1170 (-OH bending in phenol); 790 (C-Cl stretching).PMR: δ 3.60 (s, 3H, -ArOCH₃); δ 4.56 (s, 2H -due to dione) δ 6.6 (s, 6H, -ArH); δ 12.75 (s, 1H, Ar-OH);UV:359 nm

Preparation of 3-anisoyl-2-(3'-nitrophenyl)-6,8-dichloroflavanone(5a)

A mixture of 1-(2-hydroxy-3,5-dichlorophenyl)-3-phenyl-1,3 -propanedione (4a) (0.01mol) and 3-nitrobenzaldehyde (0.012 mol) was refluxed in ethanol (25ml) and piperidine (0.5 mol) for 15-20 min. After cooling, the reaction mixture was acidified with dil HCl (1:1) and the product thus separated, was crystallized from ethanol-acetic acid mixture to get the compound (5a), m.p.187°C yield 80%.

IR (KBr):3070 (-OH phenolic stretching); 1650 (>C=O stretching); 1550 (-NO₂ stretching); 758 (C-Cl stretching); PMR: δ 3.08 (s, 3H, -ArOCH₃); δ 5.3 (d, 1H -CH_A-CH); δ 5.9 (d, 1H -CH-CH_A); δ 6.76 to 8.08 (m, 10H, -ArH); UV:262 nm.

Formation of 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(3-nitro- phenyl)- isoxazole (6a)

A mixture of 3-anisoyl-2-(3-nitrophenyl)-6,8-dichloroflavone (5a), (0.01 mol) and NH₂OH.HCl (0.02 mol) was refluxed in DMSO (20ml) containing a few drops of piperidine (0.5 ml) for about 1.5 hrs. After cooling, the reaction mixture was acidified with dil. HCl (1.1). The product thus separated was filtered, washed first with sodium bicarbonate solution (10%) and then with water. Finally it was crystallized from ethanol-acetic acid mixture to get the compound(6a), m.p. 190°C, yield 65%.

IR (KBr):3076 (-OH phenolic stretching); 1608 (>C=O stretching); 1365 (>C=N stretching); 810 (C-Cl stretching); PMR: δ 3.08 (s, 3H, -ArOCH₃); δ 6.66 to 8.08 (m, 11H, -ArH); δ 10.68 (s, 1H, -ArOH);UV: 323.2 nm

Preparation of 2-anisoyloxy-3, 5-dichloroacetophenone (3b)

2-Hydroxy-3,5-dichloroacetophenone (2b) (0.04mol) and anisic acid (0.05mol) were suspended in dry pyridine (30ml) and to this POCl₃ (3ml) was added drop wise with constant stirring and cooling. The reaction mixture was kept for overnight and then worked up by dilution and acidification with ice cold HCl (50%) to neutralize pyridine. The solid product thus obtained was filtered washed with water

followed by sodium carbonate (10%) washing and finally again with water. It was crystallized from ethanol to obtain 2-anisoyloxy-3,5-dichloroacetophenone (3b), m.p. 111°C and yield 74%.

IR (KBr): 3045 (-OH phenolic stretching); 1680 (>C=O stretching); 1365 (-OH bending in phenol); 670 (C-Cl stretching); PMR: δ 2.65 (s, 3H, -ArOCH₃); δ 6 to 7.64 (m, 2H, -ArH); δ 12.5 (s, 1H, Ar-OH)

Preparation of 1-(2-hydroxy-3,5-dichlorophenyl)-3-(4'-methoxyphenyl)-1,3-propanedione (4b)

2-Anisoyloxy-3,5-dichloroacetophenone (3b) (0.05 mol) was dissolved in dry pyridine (40 ml). The solution was warmed at about 60°C and pulverized KOH (0.15 mol) was added slowly with constant stirring. After 4 hours the reaction mixture was acidified with ice cold dil. HCl (1:1) and processed as described in (4a) to get the compound, 1-(2-hydroxy-3,5-dichlorophenyl)-3-(4'-methoxyphenyl)-1,3-propanedione (4b), m.p. 114°C, yield 75%.

IR (KBr): 3045 (-OH phenolic stretching); 1650 (>C=O stretching); 1160 (-OH bending in phenol); 760 (C-Cl stretching); PMR: δ 3.50 (s, 3H, -ArOCH₃); δ 4.35 (s, 2H -due to dione) δ 6.3 (s, 6H, -ArH); δ 12.6 (s, 1H, Ar-OH); UV:348 nm

Preparation of 3-benzoyl-2-(3'-nitrophenyl)-6,8-dichloroflavanone(5b)

A mixture of 1-(2-hydroxy-3,5-dichlorophenyl)-3-(4'-methoxy-phenyl)-1,3-propanedione (4b) (0.01mol) and 3-nitrobenzaldehyde (0.012mol) was refluxed in ethanol(25ml) and piperidine (0.5 ml) for 15-20 min. After cooling, the reaction mixture was acidified with dil HCl (1:1) and the product thus separated, was crystallized from ethanol-acetic acid mixture to get the compound (5b) m.p.175°C yield 78%.

IR (KBr): 3065 (-OH phenolic stretching); 1645 (>C=O stretching); 1535 (-NO₂ stretching); 748 (C-Cl stretching); PMR: δ 3.06 (s, 3H, -ArOCH₃); δ 5.8 (d, 1H -CH_A-CH); δ 5.6 (d, 1H -CH-CH_A); δ 6.66 to 8.10 (m, 10H, -ArH).

3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(3'-nitrophenyl)-isoxazole(6b)

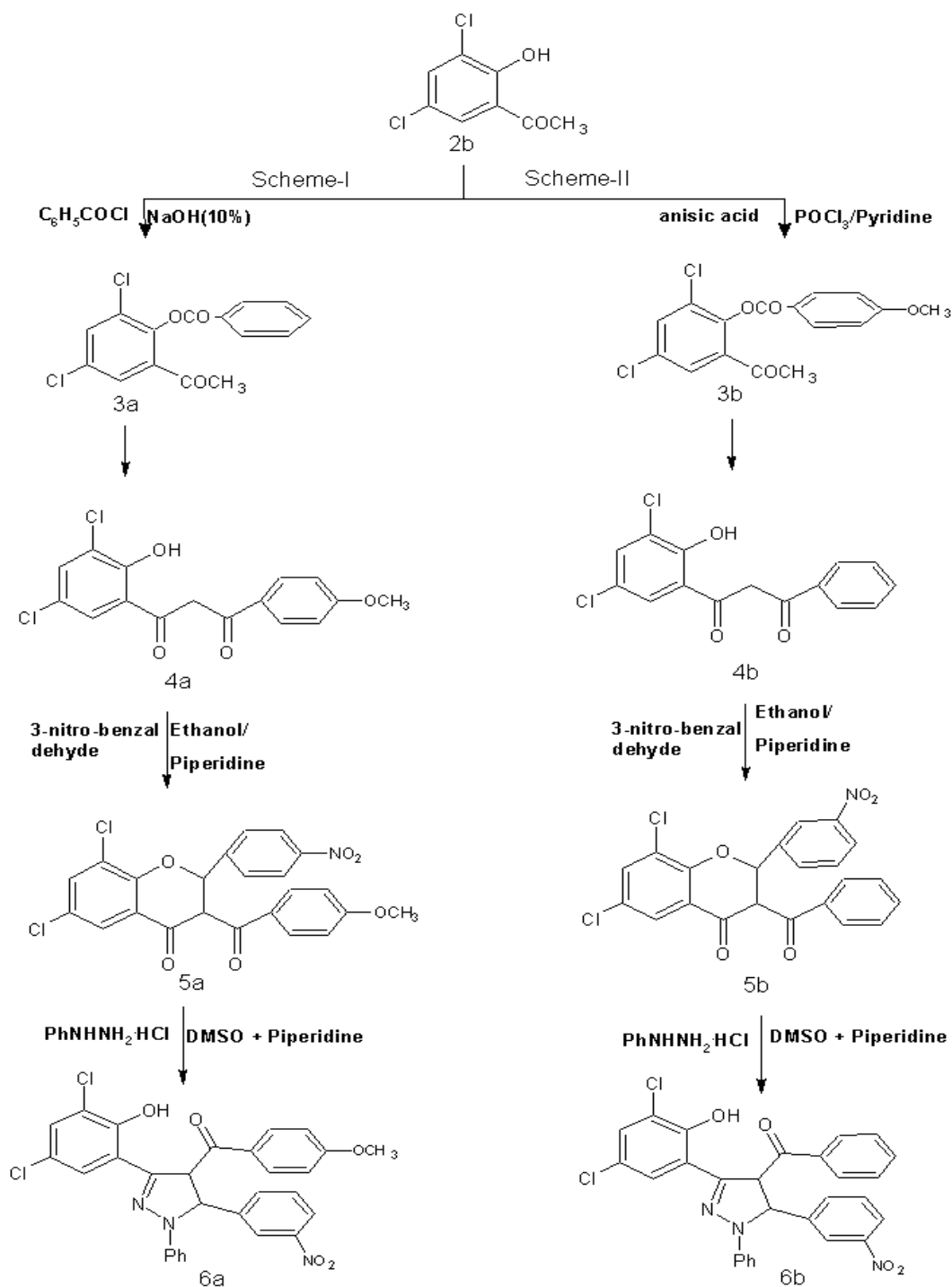
A mixture of 3-benzoyl-2-(3-nitrophenyl)-6,8-dichloroflavone(6b)(0.01mol) was reflux in DMSO (20 ml) and piperidine for about 1.5 hrs. After cooling, the reaction mixture was acidified with dil. HCl (1.1). The product thus separated was filtered, washed first with sodium bicarbonate solution (10%) and then with water. Finally it was crystallized from ethanol-acetic acid mixture to get the compound (6b), m.p. 198°C, yield 80%

IR (KBr): 3060 (-OH phenolic stretching); 1610 (>C=O stretching); 1375 (>C=N stretching); 790 (C-Cl stretching); PMR: δ 3.10 (s, 3H, -ArOCH₃); δ 6 to 8. (m, 11H, -ArH); δ 11.68 (s, 1H, -ArOH)

Table-1: Characterization data of synthesized new compound

Compound	Molecular Formula	M.P. (°C)	Yield (%)	Rf
2	C ₈ H ₆ O ₂ Cl ₂	53	75	0.84
3a	C ₁₅ H ₁₀ O ₃ Cl ₂	66	76	0.66
4a	C ₁₅ H ₁₀ O ₃ Cl ₂	110	75	0.71
5a	C ₂₃ H ₁₅ O ₆ NCl ₂	175	68	0.78
6a	C ₂₃ H ₁₄ O ₆ 2Cl ₂	190	75	0.72
3b	C ₁₆ H ₁₂ O ₄ Cl ₂	66	76	0.66
4b	C ₁₆ H ₁₂ O ₄ Cl ₂	114	75	0.81
5b	C ₂₂ H ₁₃ O ₅ NCl ₂	187	80	0.65
6b	C ₂₂ H ₁₂ O ₅ N ₂ Cl ₂	198	80	0.64

The compound (3a-6a) and (3b-6b) were studied the vegetative growth promoting effects of some newly synthesized chlorosubstituted heterocycles with special reference to horticulture crop.



Scheme-1 and 2

For growth promoting effects

The beds of black cotton soil, 2.5 x 2.5 meter size were prepared on an open field of the small plants of *Tagets erecta*, *Canna indica*, *Nerium indicum*. all three species.

The plants of all three species *Tagets erecta*, *Canna indica*, *Nerium indicum*. under examination were planted in these beds separately by conventional method. The plant beds were irrigated as and when required with tap water. The spraying solutions of newly synthesized chlorosubstituted heterocyclic compound *isoxazoles* were prepared in dioxane (0.01 dilution) separately and sprayed thrice at fortnightly

intervals (15, 30, 45 days). The plants from each bed were divided into two groups (A) and (B). The groups (A) plants were kept unsprayed and termed as control group. Whereas the plants from group (B) designated as treated group (B) plants were sprayed with the compounds being tested.

All the field experiments were conducted to compare the treated plants and control plants. The samples were taken at 15, 30, 45, 60, 75 and 90 days after planting stage. The plants were carefully examined and number of leaves and heights of shoots were recorded (Table-2a-2b). The data obtained was subjected to analysis of growth parameters.

Table-2a: Effect of newly synthesized compound 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(3-nitrophenyl)isoxazole (6a) on the growth of horticulture crop.

Periodicity of the observation (in days)	<i>Tagets erecta</i>				<i>Canna indica</i>				<i>Nerium indicum.</i>			
	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
15	10	13	6	8	7	10	3	4	12	15	4	7
30	14	17	10	13	9	13	5	7	16	18.5	7	10
45	19	24	13	17	16	20	8	10	21	24	10	13
60	24	30	19	21	21	25	8	11	24	29	13	16
75	32	36	24	26	23	27	10	13	30	32	15	18
90	47	49	30	38	31	35	12	15	35	39	17	21

Table-2b: Effect of newly synthesized compound 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(3-nitrophenyl)isoxazole. (6b) on the growth of horticulture crop.

Periodicity of the observation (in days)	<i>Tagets erecta</i>				<i>Canna indica</i>				<i>Nerium indicum.</i>			
	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
15	6	8	4	7	5	8	1	2	10	12	7	9
30	10	14	7	11	8	12	2	3	14	16	10	12
45	16	19	10	15	10	15	4	5	17	20	13	15
60	21	26	14	19	14	20	6	8	22	25	16	18
75	27	31	20	24	19	24	9	11	28	32	19	21
90	35	39	24	30	23	27	10	13	34	39	12	24

The efforts have been made to investigate and analyze the convergence and divergence of the effects of test compounds on the morphology of treated plants,

When the first 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 remarkable shoot growth, and considerable increase in the number of leaves as compared to those untreated ones.

When all the treated plants were compared among themselves, it was distinctly observed that, the *Tagets erecta* showed the pronounced vegetative growth than *Canna indica*, *Nerium indicum*. There has been fair amount of satisfaction in carrying out the present study.

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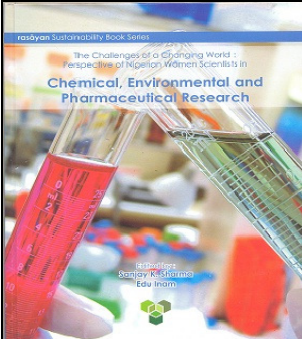
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