A Novel Functions For 4-Aroylpyrazolines and Isoxazolines in Growth Promoting Effects on Some Horticultural Crops.

PARIHAR R.T. [1], BHOYAR A. D. [2], RAJPUT P.R. [3]

[1]Department of Chemistry, Vidnyan Mahavidyalaya, Malakapur, Dist. Buldhana, Maharasthra, India

[2]Department of Chemistry, P.R. Patil College of Engineering and Technology, Kathora Road, Amravati 444607, Maharasthra, India. email: amolbhoyar@rediffmail.com

[3]Department of Chemistry, Vidybharati Mahavidyalaya, Camp, Amravati 444601, Maharasthra, India

Abstract:

Condensation of 2-substituted-3,5-dichloroacetophenones 2a-b obtained from the condensation of 2-hydroxy-3,5-dichloroacetophenone 1 and benzoyl chloride were dissolved in NaOH , on treatment under baker venkatraman transformation in presence of KOH with pyridine gives 1-(2-hydroxy-3,5- dichlorophenyl)-3-substituted-1,3-propanedione 3a-b. Then converted into 3–aroyl-6,8-dichloroflavanones 4a-d by using different aromatic aldehyde in the presence of ethanol, Piperidine. The condensation of 4a-d and phenylhydrazinehydrochlorides, piperidine in DMSO gives 4-aroyl-Δ2-pyrazolines 5a-d.Condensation of 5a- d and hydroxylaminehydrochlorides gives 4-aroyl-Δ2- isoxazolines 6a –d. The above compounds are screened for their activities on horticultural plants and have been found to exhibit significant effects.

Key words: flavanone, isoxazoline, pyrazoline, MeriGold, Indica, Nerium .

Introduction

The newly synthesized chlorosubstituted heterocycles 4-aroylpyrazolines, isoxazolines were assayed for their growth promoting effects on cultivated horticultural plants, namely MeriGold, Indica, and Nerium with predetermined periodicity.

Material and method

All melting points were determined in open capillary tubes and are uncorrected. I.R. spectra were recorded on a Perkin Elmer Infra Red spectrophotometer 1310 using KBr disc. ^{1}H NMR was recorded in $CDCl_3$ on a DRX 300 spectrometer. The reactions were monitored on TLC on silica gel G and the solvent system used was benzene.

2-aroyloxyacetophenone (2a-b) :

2-aroyloxyacetophenones (2a-b) were prepared by the condensation of 2-hydroxyacetophenone (2b) in pyridine medium using appropriate quantity of aromatic acids in presence of $POCl_3$. Thus, 2-benzoyloxy-3,5-dichloroacetophenone (2a) m.p. 66^{O}C, 2-anisoyloxy-3,5-dichloroacetophenone (2b), m.p. 111^{O}C were prepared.

All the above 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 was filtered washed with water followed by sodium bicarbonate (10%) washing finally again with water it crystallized from ethanol to obtained 2–Aroyloxyacetophenone (**2a- b**).

1- (2-hydroxy-3, 5-dichlorophenyl)-3-aryl-1,3-propanediones (3a-b) :

2-benzoyloxy-3,5-dichloroacetophenone (2a) (0.05 mol) was dissolved in dry pyridine (40ml). The solution was warmed up to 60^{o}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–3,5-dichlorophenyl)–3–(4'-methoxyphenyl)-1,3-propanedione (3a).

3a – IR spectrum recorded in KBr (cm^{-1}) 3030, (v), -OH ; 1600, (s), >C=O ;1170, (s), >C–O; 790,(s), C-Cl. PMR spectrum recorded in δ $CDCl_3$ 3.69,(s), 3H, Ar–O-CH_3; 4.56,(s), 2H, –CO–CH_2–CO– (Keto) ; 6.6, (s), 1H, –C=CH- ; 6.92–8.08, (m), 6H, Ar-H ; 12.75, (s),1H,Ar–OH; 15.71,(s),1H,–CHOH=C(enol) TLC : Solvent (Benzene) height : 2.7 cm, solute height : 2.3 cm; Rf value : 0.85 , m.p.112^{0}C, yield 78%.

3–Aroylflavanone (4a-d)

1-(2-hydroxy-3,5-dichlorophenyl)-3-phenyl-1,3 propanedione 3a (0.01 mol) and 3-nitrobenzaldenyde, 4-N,N-dimethylaminobenzaldenyde (0.012 mol) separately was refluxed in ethanol (25 ml) and piperidine (0.5ml) for 15-20 min. yield 3–arylflavanone (4b,4c)resp. 1–(2–hydroxy–3,5-dichlorophenyl)–3–(4'-methoxyphenyl)-1,3-propanedione 3b (0.01mol) and 3-nitrobenzaldenyde, 4-N,N-dimethyl-aminobenzaldenyde (0.012 mol) separately was refluxed in ethanol (25 ml) and piperidine (0.5 ml) for 15–20 min. yield 3–aroylflavanone (4a,4d) resp. All above reaction after refluxing, cooling the reaction mixture was acidified with dil. HCl (1:1). The 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.

4d IR spectrum recorded in KBr (cm-1)

3072, s, C-H aromatic stretching; 2902-2815, s, C-H aliphatic stretching; 1602, s, >C=O; 1554, s, NO2 stretch asymmetrical; 1319, s, NO2 stretch symmetrical; 1272, s, Ar-O-C; 1228, s, C-O-C; 808,s, C-Cl. PMR spectrum recorded in δ CDCl3 3.07, (s), 3H Ar–OCH3 ; 6.66 – 6.69, (dd) , 1 H, CHA – CH ; 7.23-7.26, (dd) , 1H, CH – CHB ; 7.2–8.08, (m), 10H, –Ar–H.; TLC: Solvent (Benzene) height: 2.5cm Solute height: 1.6 cm; Rf value: 0.64, m.p.1900C, yield 78%.

4-aroyl-Δ2- pyrazolines (5a-d)

When 3–aroylflavanones (4a–d) (0.01 mol) and phenylhydrazinehydrochloride (0.02 mol) were refluxed in DMSO 20 ml containing a few drops of piperidine for 1.5 h. separately, After cooling the mixture was diluted with water HCl (1:1). The product thus separated was filtered and crystallized from ethanol–acetic acid to yield 4-aroyl-3,5-diaryl-1-phenyl-Δ2-pyrazolines (5a–d) respectively.

5d IR spectrum recorded in KBr cm-1

3070, (w,b), -OH ; 2908, s, -CH ; 1600, s, >C=O ; 1550, s, -NO2 ; 1168, m, Ar-O-C ; 806, s, C-Cl. PMR spectrum recorded in δ CDCl3 3.08, (s), 3H, Ar–OCH3 ; 4.44, (dd) , 1 H, CHA – CH ; 4.41, (dd) , 1H, CH – CHB ; 6.76–8.08, (m), 16H, –Ar–H. 11.33, s, 1H, Ar-OH. TLC: Solvent (Benzene) height: 2.9cm Solute height: 1.1 cm; Rf value: 0.38, m.p.1800C, yield 70%.

4-aroyl-Δ2- isoxazolines (6a-d)

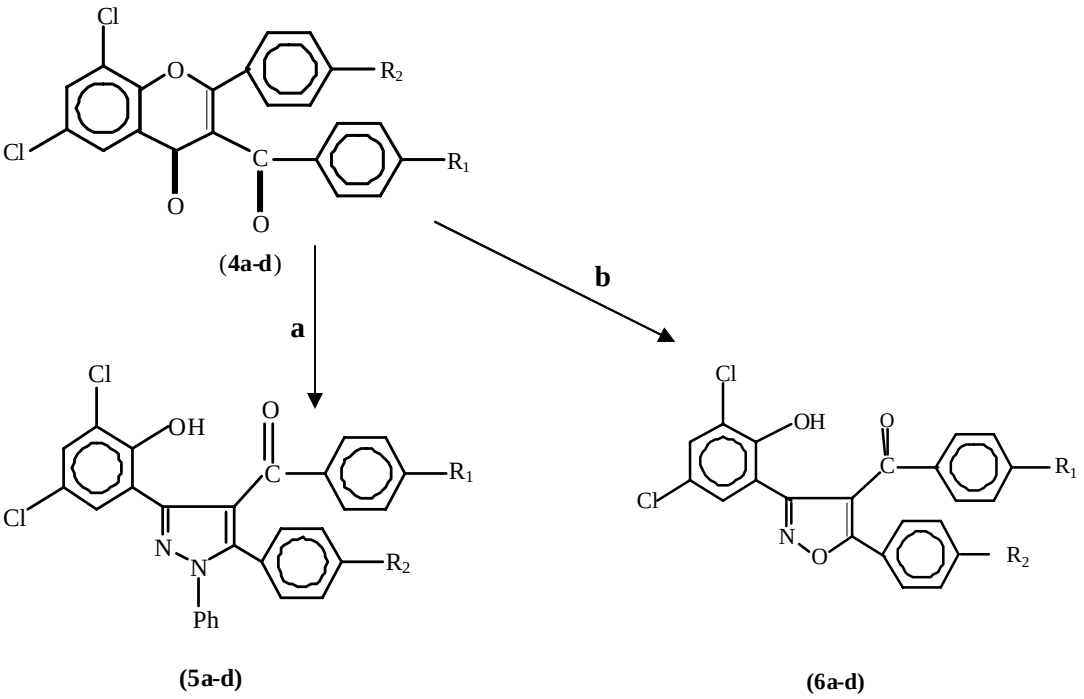
When 3–aroylflavanones (4a–d) (0.01 mol) and hydroxylaminehydrochloride (0.02 mol) were refluxed in DMSO 20 ml containing a few drops of piperidine for 1.5 h. separately, After cooling the mixture was diluted with water HCl (1:1). The product thus separated was filtered and crystallized from ethanol–acetic acid to yield 4-aroyl-Δ2-isoxazolines (6a–d) respectively.

6d IR spectrum recorded in KBr cm-1

3126, (w,b), -OH ; 3076, s, -CH ; 1641, s, >C=O ; 1608, s, >C=N; 1556, s, -NO2 Asymmetric; 1319, s, -NO2 Symmetric; 1168, m, Ar-O-C ; 810, s, C-Cl. PMR spectrum recorded in δ CDCl3 3.07, (s), 3H, Ar–OCH3 ; 6.85, (dd) , 1 H, CHA – CH ; 6.89, (dd) , 1H, CH – CHB ; 6.67–8.08, (m), 10H, –Ar–H. 10.10, s, 1H, Ar-OH. TLC: Solvent (Benzene) height: 2.5cm Solute height: 1.8 cm; Rf value: 0.72, m.p.1550C, yield 75%.

Results and Discussion:

2-hydroxy-3,5-dichloroacetophenone (**1**) on treating with different aromatic acid in the presence of pyridine or NaOH gives a compounds containing aromatic group,



a : $PhNHNH_2$.HCl, Piperidine, DMSO **b** : NH_2OH.HCl, Piperidine, DMSO

These structures are possible for these compounds (**2a, 2b**). The IR spectrum of this compound consist of a ester stretching band at 1790 cm^{-1}, thereby suggested that there is reaction between hydroxyl group and benzoyl chloride (**2a**). However (**2b**) shows a PMR peak at δ2.60 of Ar-OCH_3 this confirms there is presence of OH group and peak at 1820 $^{cm-1}$ for ester group.

The acetophenones (**2a-b**) was formylated by the reaction of pyridine in KOH gives 1-(2-hydroxy-3,5-dichloro- phenyl)-3-aryl-1,3-propanedione (**3a-b**). This on reaction with different aldehyde gives 3-aroylflavanones (**4a-d**). These flavanones on treatment with phenylhydrazinehydrochloride in DMSO medium containing small amount of piperidine gives pyrazolines (**5a-d**) which was confirmed by its spectral analysis

In a similar fashion 3-aroylflavones (**4a-d**) was treated with hydroxylaminehydrochloride in DMSO medium containing small amount of piperidine gives 3,5-diaryl-4-aroylisoxazolines (**6 a-d**) which was characterized by spectral analysis.

Conclusion

A) 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 Merigold, Nerium, Indica all three species. The plants of all three species Merigold, Nerium, Indica 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 synthesised chlorosubstituted heterocyclic compounds *pyrazolines, isoxazolines* 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 in to two groups (A) & (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 of group (B) with the plants from control group (A). 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 1 and 2). The data obtained was subjected to analysis of growth parameters.

Table 1 Effects of newly synthesized compound 3-(2-Hydroxy-3,5-dichlorophenyl) -4-anisoyl-5-(3-nitrophenyl)-1-phenyl-Δ2-pyrazoline (6a) on the growth of cultivated plant.

Periodicity of the observation (in days)	***MeriGold***				***Indica***				***Nerium***			
	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	4	9	4	5	4	6	1	2	11	14	6	8
30	13	17	9	11	7	12	2	3	13	18	7	10
45	20	26	16	19	15	19	4	6	19	25	10	13
60	32	40	22	27	22	27	6	7	23	29	13	16
75	45	57	28	37	32	36	7	9	31	33	16	19
90	54	63	32	40	34	38	8	10	33	37	19	22

C=Control T = Treated

Table 2 Effect of newly synthesized compound 3-(2-Hydroxy-3,5-dichlorophenyl) -4-anisoyl-5-(3-nitrophenyl)isoxazoline. (9a) on the growth of vegetative crops

Periodicity of the observation (in days)	***MeriGold***				***Indica***				***Nerium***			
	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

Results and Discussion

Efforts have been made to investigate and analyze the convergence and divergence of the effect of test compounds on the morphology of plant under investigation. When the first comparison of morphological character was made between those of treated and control group plants, it was interesting to note that all the treated plant exhibited remarkable shoot growth, and considerable increase in the number of leaves as compare to the untreated ones[1-6].

Acknowledgement

The author expresses their sincere thanks to the Dr. K. N. Patil, Ex Principal, VidyaBharti Mahavidyalaya, Amravati and P. G. Department of Botany, SGBAU, Amravati for providing necessary laboratory facilities.

References:

1. Dasgupta, S.N., History of plant pathology and mycology in India, Burma and Ceylon. Pub. Indian Botanical Society, (1958), 118p.
2. Grover, R. K., Plant pathology research in India – an introspection and prospects. Pesticides Annual, (1975).
3. Mehta, P. R., Plant pathology in India – past, present and prospects. Indian phytopath. (1963) 16:1-7.
4. Raychaudhari, S.P., Development of mycological and plant pathological researches, education and extension work in India. Rev. Appl. Mycol. 46, (1963) 577-583.
5. Raychaudhari, S.P., History of plant pathology in India. Annu. Rev. Phatophol. 10 :21-36.
6. Singha, R. S., Plant diseases, fifth edition, oxford and IBH publishing co. New Delhi, (1983).
7. Singha, R. S., Plant diseases, seventh edition, oxford and IBH publishing co. New Delhi, (1985).
8. Frankine. P., Gardner, R., Brent Pearce Roger, L., Mitchell, Physiology of crop plants. First edition (1985)
9. Wareing, P.F. and I.D.J. Phillips, The control of growth and differentiation in plants second edition. New York, Pergamon. (1978).
10. Geirger, W.B. and Conn, J.E., *J. Am. Chem. Soc.* 67, (1945) 112.
11. Laliberate, R., Manson, J., Warik, H and Madewar, G., *Can. J. Chem.* 46, (1968) 1952.
12. Krishna, S.V., Rajsekhar, A., Reddy, T.T.K. and Naidu M.S.R., *Cur. Sci.*, 57(23), (1988), 1291.
13. Bhatt, D.T., Kamdar, G.C., and Parikh, A.R., *J. Indian Chem. Soc*. LXIV, (1984), 816.
14. Ahluwaliya, A.K., Neelukaila and Shashibala, *Ind. J. Chem*. 25B, (1986), 663.
15. Szent, Gyorgi, A., *Biochimia* 2, (1937), 151.
16. Thakar, K.A., and Gill, C.H., *J. Ind. Chem. Soc*. LX, (1983), 668.
17. Hogle, M.B., Pawar B.N. and Nikam, B.P., *J. Ind. Chem. Soc*. LXIV, (1987), 486

-- -- -- -- --