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Synthesis and Antifungal Activity of Chlorosubstituted 1-Phenyl-Δ2-Pyraoles and 1-Phenyl-Δ2-Pyraolines on Plant Pathogen Alternaria Solani

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ABSTRACT

Alterneria leaf blight is one of the most important disease of potato worldwide. During 2009 – 2010 in the Kashmir valley surveyed that he disease was prevalent in all the potato growing areas. The overall mean disease incidence and intensity ranged from 24.54 to 28.23%. In early stages of disease development , small irregular to circular dark brown spot on lower leaves appear meaning 0.5 mm in size. The aim of the present study was to investigate the antifungal and antibacterial activities on Alterneria solani. Alterneria solani was procured from genuine agricultural agencies. The compound synthesis in part I was screened invitro for their antifungal & antifungal activities by disc diffusion method.

Keywords : Alterneria Solani , Antifungal and Antibacterial Activities , Pyrazoles, Pyrazolines

I. INTRODUCTION

In order to synthesized flavanones , flavones, Pyrazolines and Pyrazoles the reaction sequence were followed as out line in the scheme I. The required 1-(2-hydroxy-3,5-dichoroacetophenone which on condensation is converted into 2-aroyl-3,5-dicholoroacetophenone (3) were reacted under BVT in the presence of KOH with pyridines gives 1-(2-hydroxy-3,5dichorophenyl)-3-substituted-1,3-propanedione (4) and then converted into 3-aroylflavanones (5) by using different aromatic aldehyde in the presence of ethanol-piperidine. The reaction of (5) and the iodine in the presence of ethanol yield flavones (7). The condensation of (7) and phenylhydrazine hydrochloride in the presence of ethanol and piperidine gives pyrazoles (8) . The compounds prepare were characterized and characterized and screened for their antifungal activity.

II. METHOD AND MATERIAL

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 on silica gel G and the solvent system used was benzene.

2-Aroyloxyacetophenone (3a – c).

2 hydroxy-3,5-dichloroacetophenone (0.04 mol) and benzoyl chloride (0.05 mol) where dissolved in dry pyridine (30 ml) with $POCl_3$ in NaOH (10%) (3a), 2 hydroxy-3,5-dichloroachoro -acetophenone (0.04 mol) and anisic acid (0.05 mol) where suspended in dry pyridine (30 ml) with $POCl_3$ in NaOH (10%) 30 ml (3b) and 2 hydroxy-3,5-dichloroacetophenone (0.04 mol) and valeric acid (0.05 mol) where suspended in dry pyridine (30 ml) with $POCl_3$ in NaOH (10%) 30 ml (3c). All the above reaction mixture was kept 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 (3a-c).

1-(2-hydroxy-3,5-dichlorophenyl)-3-aryl-1,3-propanedione (4a-c)

When 2-Aroyloxyacetophenone (3a-c) (0.05 mol) was dissolved in dry pyridine 40 ml. the solution was warmed upto 60^0C and pulvariesd KOH (15 g) was added slowly with constant stirring. After 4hr the reaction mixture was acidified by adding acid cold 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 to get 1-(2 hydroxy-3,5-dichlorophenyl)-3-aryl-1,3-propanedione (4a-c) respectively.

4b – IR spectrum recorded in KBr (cm^{-1}) 3429, (s), -OH ; 2981, (s), -CH ; 1261, (s), > C=O ; 772, (s), -C-Cl . PMR spectrum recorded in δ $CDCl_3$ 3.90, (s), 2H – $CO\text{-}CH_2\text{-}CO$- ; 2.65, (s), 1H, -O-CH_3- ; 8.06 - 7.27, (m), 6H, -Ar-H ; 12.72, (s), 1H, -Ar-OH. TLC : Solvent (Benzene) height 3.4.cm, solute height :2.4 cm ; Rf value : 0.70, m.p. 96^0C, yield 82 %.

3-Aroylflavanone (5 a-d)

A mixture of 1-(2-hydroxy-3,5-dicholorophenyl)-3-phenyl-1,3-propanidione (4a) (0.01 mol) and benzaldehyde (0.02 mol) was refluxed in ethanol (25 ml) and piperidine (0.5 ml) for 15-20 min. yield 3-benzoyl-2-phenyl-6,8-dichloroflavanone (5a) . 1-(2-hydroxy-3,5-dicholorophenyl)-3-(4'methoxyphenyl)-1,3-propanedione (4b) (0.01 mol) and anisaldehyde (0.02 mol) was refluxed in ethanol (25 ml) and piperidine (0.5 ml) for 15-20 min. yield 3-anisoyl-(4'-methoxyphenyl)-6,8-dichloroflavanone (5b). 1-(2-hydroxy-3,5-dicholorophenyl)-3-butyl-1,3-propanedione (4c) (0.01 mol) and propionaldehyde (0.02 mol) was refluxed in ethanol (25 ml) and piperidine (0.5 ml) for 15-20 min. yield 3-valeroyl-2-ethyl-6,8-dichlorocromanone (5c). 1-(2-hydroxy-3,5-dicholorophenyl)-3-butyl-1,3-propanedione (4c) (0.01 mol) and valeraldehyde (0.02 mol) was refluxed in ethanol (25 ml) and piperidine (0.5 ml) for 15-20 min. yield 3-valeroyl-2butyl-6,8-dichlorocromanone (5d). all above reactions after refluxing, cooling the 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 is then crystallized from ethanol-acetic acid mixture.

5a – IR spectrum recorded in KBr (cm^{-1})

3070, (s), -C-H ; 1773, (s), >C=O ; 1699, (s), >C=O ; 1296, (s), -C-O ; 767, (s), -C-Cl . PMR spectrum recorded in δ $CDCl_3$ 5.40, (D), 1H –CH-CH ; 5.60, (d), 1H, -CH-CH- ; 6.48 – 8.21, (m), 14H, -Ar-H ; TLC : Solvent (Benzene) height 2.6.cm, solute height :1.2 cm ; Rf value : 0.46, m.p. 152^0C, yield 75 %.

4-Aroyl-Δ^2-pyrazolines (6 a-b) and 4-alkoyl-Δ^2-pyrazolines (6 c-d)

3-benzoyl-2-phenyl-6,8-dichloroflavanone (5a) (0.01 mol) and phenylhydrazine hydrochloride (0.02 mol) was refluxed in ethanol (20 ml) and piperidine (0.5 ml) for 1.5 hr. yield 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-1,5-diphenyl-Δ^2-pyrazolines (6a). 3-anisoyl-2-(4'-methoxyphenyl)-6,8-

dichloro-flavanone (5b) (0.01 mol) and phenylhydrazine hydrochloride (0.02 mol) was refluxed in ethanol (20 ml) and piperidine (0.5 ml) for 1.5 hr. yield 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(4'methoxyphenyl)-1-phenyl-Δ^2-pyrazolines (6b). 3-valeroyl-2-ethyl-6,8-dichlorocromanone (5c) (0.01 mol) and phenylhydrazine hydrochloride (0.02 mol) was refluxed in ethanol (20 ml) and piperidine (0.5 ml) for 1.5 hr. yield 3-(2-hydroxy-3,5-dichlorophenyl)-4-valeroyl,5-ethyl-1-phenyl-Δ^2-pyrazolines (6c). 3-valeroyl-2butyl-6,8-dichlorocromanone (5d) (0.01 mol) and phenylhydrazine hydrochloride (0.02 mol) was refluxed in ethanol (20 ml) and piperidine (0.5 ml) for 1.5 hr. yield 3-(2-hydroxy-3,5-dichlorophenyl)-4-valeroyl-5-butyl-1-phenyl-Δ^2-pyrazolines (6d). all above reactions after refluxing, cooling the 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 is then crystallized from ethanol-acetic acid mixture.

6a – IR spectrum recorded in KBr (cm $^{-1}$)

3208, (vb), -OH ; 3003, (s), -C-H ; 1675, (s), >C=O ; 1599, (m), >C=N ; 764, (s), -C-Cl . PMR spectrum recorded in δ $CDCl_3$ 5.10, (D), 1H –CH-CH ; 5.45, (d), 1H, -CH-CH- ; 6.8 – 8.2, (m), 20H, -Ar-H ; 13.4, (m), 1H, -Ar-OH ; TLC : Solvent (Benzene) height 2.9.cm, solute height :1.5 cm ; Rf value : 0.51, m.p. 165^{0}C, yield 85 %.

3-Aroylflavanone (7a-d)

3-Aroyl-6,8-dichloroflavanone (5 a-d) was refluxed for 10 minutes in ethanol (20 ml) with crystal of iodine. all above reactions after refluxing, cooling the mixture was acidified with dil HCl (1:1). The product thus separated was filtered washed with sodium thiosulphate solution (10%) and finally again with water. It is then crystallized from ethanol to get 3-Aroylflavanone (7a-d) .

7a – IR spectrum recorded in KBr (cm $^{-1}$)

3070, (vb), -C-H ; 1694, (s), >C=O ; 1663, (s), >C=O ; 1587, (s), -C=C ; 750, (s), -C-Cl . PMR spectrum recorded in δ $CDCl_3$ 3.1, (D), 1H –CH-CH ; 3.5, (d), 1H, -CH-CH- ; 6.8 – 8.2, (m), 12H, -Ar-H ; TLC : Solvent (Benzene) height 2.1.cm, solute height :1.3 cm ; Rf value : 0.62, m.p. 172^{0}C, yield 80 %.

4-Aroylflavanones (8 a-b) and 4-Alkoyl-pyrazoles (8 c- d)

3-benzoyl-2-phenyl-6,8-dichloroflavone (7a) (0.01 mol) and phenylhydrazine hydrochloride (0.02 mol) was refluxed in ethanol (20 ml) and piperidine (0.5 ml) for 1.5 hr. yield 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-1,5-diphenyl-Δ^2-pyrazoles (8a). 3-anisoyl-2-(4'-methoxyphenyl)-6,8-dichloro-flavone (5b) (0.01 mol) and phenylhydrazine hydrochloride (0.02 mol) was refluxed in ethanol (20 ml) and piperidine (0.5 ml) for 1.5 hr. yield 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(4'methoxyphenyl)-1-phenyl-Δ^2-pyrazoles (8b). 3-valeroyl-2-ethyl-6,8-dichlorocromone (7c) (0.01 mol) and phenylhydrazine hydrochloride (0.02 mol) was refluxed in ethanol (20 ml) and piperidine (0.5 ml) for 1.5 hr. yield 3-(2-hydroxy-3,5-dichlorophenyl)-4-valeroyl,5-ethyl-1-phenyl-Δ^2-pyrazoles (8c). 3-valeroyl-2-butyl-6,8-di-chlorocromanone (7d) (0.01 mol) and phenylhydrazine hydrochloride (0.02 mol) was refluxed in ethanol (20 ml) and piperidine (0.5 ml) for 1.5 hr. yield 3-(2-hydroxy-3,5-dichlorophenyl)-4-valeroyl-5-butyl-1-phenyl-Δ^2-pyrazoles (8d). All above reactions after refluxing, cooling the 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 is then crystallized from ethanol-acetic acid mixture.

8a – IR spectrum recorded in KBr (cm $^{-1}$)

3228, (vb), -OH ; 1674, (s), >C=O ; 1598, (s), >C=N ; 1441, (m), >C=C< ; 749, (s), -C-Cl . PMR spectrum recorded in δ $CDCl_3$ 6.5 – 8.2, (m), 13H, -Ar-H ; 11.4, (s), 1H, -Ar-OH ; TLC : Solvent (Benzene) height

2.5.cm, solute height :1.9 cm ; Rf value : 0.76, m.p. 175^{0}C, yield 80 %.

Photochemical Study :

The photochemical screening of *Alterneria solani* reported in the presence of alkaloids, tannins, steroids, prines, carbohydrates and proteins.

Antifungal Assay

The well diffusion method was used to determined the antifungal activity of *Alterneria solani.*

The culture media for pathogens was prepared by using folloeing composition for one liter distilled water.

Peptone	:	5.0 g/lit
Sodium Chloride	:	5.0 g/lit
Beef extract	:	1.5 g/lit
Yeast extract	:	1.5 g/lit
Agar	:	15.0 g/lit
pH (Approximately)	:	7.4 $\pm$ 0.2

The culture medium thus prepared was sterilized in autoclaves at 15 lbs/inch pressure and 121^{0}C temp. for 15 min. After sterilization , it was cooled down to about 50^{0}C and poured into pre sterilized petri plates of 8.5 cm in diameter each and allowed to solidify the nutrient agar medium of about 14mm depth. The petri plates were kept with nutrient broth at 37^{0}C for 4 hr. in an incubator.

The plates were dried again for 30 min. and without further delay discs soaked in the test compound . the plates were kept in incubator at 37^{0}C for about 18 – 24 hrs. soon after incubation period is over the degree of sensitivity to get compound was determined by measuring the visible clear area of growth free zones produces by the diffusion of the antibodies in to media from the discs by vernier caliper in mm. the result obtained are tabulated in the following table.

III. RESULT AND DISCUSSION

The newly synthesized compound is assayed against *Alterneria solani.* And the antifungal effects were effects under controlled laboratory conditions. On comparison of the result , the dominant inhibitory effect of butyl group substituted compounds against *Alterneria solani* is found remarkable. The cholorosubstituted pyrazoles and pyrazolines showed their prominent effect against *E. amylovora* and *A. tumefacience*.

IV. CONCLUSION

The fungus causes disease in crop plant , which affects on yield. Plants are natural source of remedy of fungal diseases. *Alterneria solani* is comes widely in nature. The antifungal study was carried out with an objective to investigate antifungal potentials. The butyl and chloro group substituted compounds shows better activity than other substituents against fungi.

Table 1 : Antifungal activity data of compound 6 a – d and 8 a- d .

Sr. No.	Test Compounds	Zone of inhibitions (mm) *Alterneria solani*
1	6a	13
2	6b	14
3	6c	14
4	6d	14
5	8a	11
6	8b	12
7	8c	13
8	8d	13

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