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NOTE

Synthesis and Fungicidal Evaluation of Some 1,3,4-Thiadiazoles against *P. oryzae* and *R. solani*

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A series of 2-amino-5-[(substituted phenoxy methylene)]-1,3,4-thiadiazoles from cresols, 2/4-chlorophenols and 4-chloro-3-methyl phenols have been synthesized. All such thiadiazoles have shown moderate activity towards the mentioned fungi.

Key Words: Fungicidal evaluation, 1,3,4-Thiadiazoles, *P. oryzae*, *R. solani*

Fungicidal activity in thiadiazole derivatives has been recognized since a long time[1,2]. In this connection a number of compounds of same class have shown appreciable activity against *A. niger* and *H. oryzae*[3]. With this view in mind and in continuation of our ongoing research for new antifungal agents[3], we report herein the synthesis of some 2-amino-5-[(substituted phenoxy methylene)]-1,3,4-thiadiazoles and their evaluation against *P. oryzae* and *R. solani*, respectively.

All the chemicals and solvents used were LR grade. The structures of thiadiazoles were routenly checked by spectral and microanalytical data. IR (KBr) spectra were scanned on Perkin-Elmer 710 and PMR; $\delta(CDCl_3)$ on Varian A 60 D spectrophotometer respectively. All the melting points reported were recorded in open capillaries and are uncorrected. Phenoxy acetic acids of cresols, 2/4-chlorophenols and 4-chloro-3-methyl phenols were synthesized according to the procedure reported earlier[4].

2-Amino-5-[(methyl phenoxy methylene)]-1,3,4-thiadiazoles (I–VI)

A mixture containing equimolar quantities of thiosemicarbazide, phenoxy acetic acid and conc. sulphuric acid was warmed at 60–80°C for 6 h. The reaction mixture was cooled up to 5°C in ice-cold water and then neutralized by concentrated ammonium hydroxide. The solids thus obtained were filtered and crystallized from ethenol (Table-1).

Fungicidal screening

Agar growth technique[5] has been applied for the fungicidal screening of

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thiadiazoles (**I–VI**) against the two selected fungi, *viz.*, *P. oryzae* and *R. solani* at 500 ppm. It was performed by adding a solution of test compound in acetone and water (20 : 80 v/v) mixture to pre-sterilized petridishes containing Czapeks agar, and mixing thoroughly. One week old culture of the test compound was inoculated in the centre of each petridish. The bioassay was done in three replicates. The plates were incubated at 28 ± 1°C for 96 h. The percentage inhibition of mycelial growth or spore germination was calculated as:

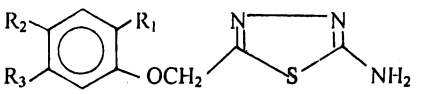
$$\% \text{ Inhibition} = \frac{(C - T)}{C} \times 100$$

where C = average diameter of the fungal colony (in mm) in control plate and T = average diameter of the fungal colony (in mm) in treated plate.

Commercially available carbenedazim has been used as a reference for comparison.

The various physico-chemical and analytical data of thiadiazoles have been summarized (Table-1).

TABLE-1
PHYSICO-CHEMICAL AND ANALYTICAL DATA OF 2-AMINO-5-[(SUBSTITUTED PHENOXY METHYLENE)]-1,3,4-THIADIAZOLES



S. No.	m.f.	R_1	R_2	R_3	m.p. (°C)	Yield (°C)	Fungicidal screening	
							P. oryzae	*R. solani*
I.	$C_9H_8N_3OS_3Cl$	H	Cl	H	200	55	42	30
II.	$C_9H_8N_3OSCl$	Cl	H	H	224	50	32	16
III.	$C_{10}H_{11}N_3OS$	CH_3	H	H	214	59	16	14
IV.	$C_{10}H_{11}N_3OS$	H	H	CH_3	202	52	18	17
V.	$C_{10}H_{11}N_3OS$	H	CH_3	H	208	58	15	16
VI.	$C_{10}H_{11}N_3OSCl$	H	Cl	CH_3	196	60	36	22
	Carbendiazim						100	100

Spectroscopic data

IR (KBr) ν_{max} cm^{-1}; 3300–3200 ν(NH), 1260, 1040 ν(C—O—C), 1630–1615 ν(C=N; Cyclic) PMR δ ($CDCl_3$); **I:** 8.0–8.5 (Br 1-NH), 6.7–7.38 (m, Ar—H), 3.81 (t, 2H, OCH_2); **V:** 7.8–8.4 (Br 1-NH), 6.6–7.74 (m, Ar—H), 3.78 (t, 2H OCH_2).

Microanalytical data

I: $C_9H_8N_3OSCl$; Calcd. (Found)% : C 44.72 (44.58), N 17.39 (17.24). **III:** $C_{10}H_{11}N_3OS$; C 54.29 (54.38), N 19.00 (18.88). **VI:** $C_{10}H_{11}N_3OSCl$; C 44.96 (46.78), N 16.43 (16.74).

All the thiadiazole derivatives have shown satisfactory spectral and micro-analytical data, confirming their structures. Fungicidal screening data of these thiadiazoles indicate that they are more active towards *P. oryzae* rather than

R. solani. Their activity towards each of the fungi has been found to be significantly varied with changes in the position of substituents. In general, the chlorosubstituted derivatives have shown greater activity than those of methyl substituted thiadiazoles. Introduction of methyl group **(VI)** has considerably lowered the activity of these compounds towards both of the fungi. Maximum activity towards each of the fungi has been shown by **(I)**, indicating that chloro group at *para* position plays a significant role in their activities.

The fungicidal action of these compounds may be due to the disruption of reproductive action of fungi, or of the function of thiadiazole nucleus, but at a relatively slower rate than the reference carbendiazim. These observations indicate that the proposed thiadiazoles are associated with moderate fungicidal activities towards *P. oryzae* and *P. solani*. Commercially these moderately active thiadiazoles could be exploited to eradicate the various diseases caused by powdery mildew, apple and pear scab, spot of stone fruits, brown rust of wheat etc. except diseases caused by downy mildew.

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