Asian Journal of Chemistry Vol. 5, No. 2 (1993), 378–380

Studies of Some Antifungal Agents

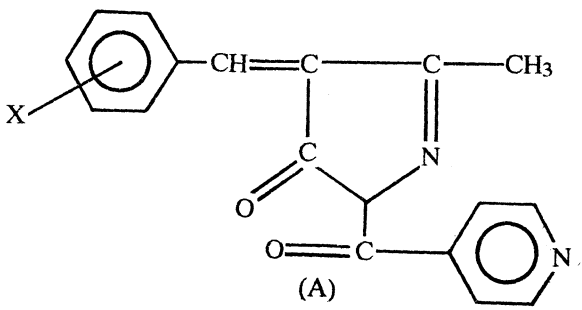
C.P. SINGH* and SAHEDEV KUMAR PRAJAPATI
Department of Chemistry, Sahu Jain P.G. College
Najibabad–246 763, India

A series of N'-(4-pyridoyl)-3-methyl-4-(substituted arylidene)-2-pyrazolin-5-ones have been synthesised to study their antifungal activity. All the compounds have been screened for their antifungal activity against the rice blast pathogen *Pyricularia oryzae* and brown leaf spot pathogen *Helminthosporium oryzae* and found to be antifungal.

INTRODUCTION

In these days of intensive agricultural practices pesticides are invaluable in the promotion of farm productivity and protection of agricultural products during storage. Therapeutical importance of pyrazolones and its derivatives has been studied by several investigators as fungicides[1]. Some halogenated and non-halogenated pyrazolones have been screened as fungicides[2,3]. Working on the generalization that N-heterocycles incorporated wth CO group show significant pesticidal activity. In view of these observations, some N^1-(4-pyridoyl)-3-methyl-4-(substituted arylidene)-2-pyrazolin-5-ones have been synthesised which posses an additional CO group directly linked with 2-pyrazolin-5-one ring leading thereby to a possible enchaced fungicidal activity.

N^1-(4-Pyridoyl)-3-methyl-4-(substituted arylidene)-2-pyrazolin-5-ones of type (A) have been obtained by the reaction of N^1-(4-Pyridoyl)-3-methyl-2-pyrazolin-5-one[4] with substituted benzaldehydes, using glacial acetic acid as condensing agent. The homogeneity and purity of the compounds were checked through TLC and their structures established by IR, NMR spectral studies and elemental analyses.



(A)

X = –OH, –Cl, –Br, $-NO_2$ and $-OCH_3$

EXPERIMENTAL

All the chemicals used were either BDH or E. Merck grade.

Synthesis of N^1-(4-pyridoyl)-3-methyl-4-(X)arylidene-2-pyrazolin-5-ones

A mixture of substituted benzaldehyde (0.01 M) and N^1-(4-pyridoyl)-3-methyl-2-pyrazolin-5-one (0.01 M) in glacial acetic acid of sufficient quantity was refluxed on a water bath for 4 hrs. and resulting solution kept in a refrigerator until a solid product separated out. It was filtered off, washed well with water, dried and recrystallised from a mixture of glacial acetic acid and DMF.

By analogous procedure, several substituted 2-pyrazolin-5-ones have been synthesised; their characteristics are recorded in Table 1.

TABLE 1
CHARACTERISTICS OF N^1-(4-PYRIDOYL)-3-METHYL-4-(X) ARYLIDENE-2-PYRAZOLIN-5-ONES

Sl. No.	X	M.pt. °C	Yield (%)	M.f.	% of Nitrogen Found (Calcd.)	R_f value
1.	2-Hydroxy	105	55	$C_{17}H_{13}N_3O_3$	13.60 (13.68)	0.87
2.	3-Hydroxy	130	68	$C_{17}H_{13}N_3O_3$	13.64 (13.68)	0.94
3.	4-Hydroxy	170	75	$C_{17}H_{13}N_3O_3$	13.62 (13.68)	0.88
4.	4-Methoxy	185	60	$C_{18}H_{15}N_3O_3$	13.02 (13.08)	0.77
5.	2-Chloro	145	70	$C_{17}H_{12}N_3O_2Cl$	12.95 (13.00)	0.82
6.	2-Hydrocy-5-bromo	189	65	$C_{17}H_{13}N_3O_3Br$	10.79 (10.85)	0.74
7.	3-Hydroxy-6-bromo	195	80	$C_{17}H_{13}N_3O_3Br$	10.80 (10.85)	0.81
8.	4-Nitro	205	75	$C_{17}H_{12}N_4O_4$	16.63 (16.66)	0.92
9.	4-Hydroxy-3-methoxy	225	72	$C_{18}H_{16}N_3O_4$	12.40 (12.43)	0.67

*The R_f values for all the compounds on silica gel plates (thickness 0.5 mm) with developer as acetone/dimethyl formamide (2 : 1) in saturated chambers at room temperature (29 ± 1°C).

IR spectra in KBr were recorded on a Perkin Elmer grating IR spectrophotometer. The spectra had characteristic peaks at 1720 cm^{-1}, ν(C=O);

1280 cm^{-1}, ν(>C=N); 1562 cm^{-1} (heterocyclic five-membered 2-pyrazolin-5-one ring) and 720, 770 cm^{-1} (substituted benzene ring).

The structure of N^1-(4-pyridoyl)-3-methyl-4-(4-nitroarylidene)-2-pyrazolin-5-one was also confirmed by ^{1}H–NMR spectra studies. In $CDCl_3$ solution, the following δ(ppm) values were obtained: 2.48 (s, 3, C_1–CH_3); 2.56 (s, 1, C*H*); 7.16 (bs, 4, ArH, *ortho* and *meta* to NO_2); 7.12 (dd, 2,4-pyridinecarbonyl, ortho to C=O, J=9 and 2 Hz); 7.04 (dd, 2,4-pyridinecarbonyl; *meta* to C=O, J = 9 and 2 Hz).

Fungicidal Activity

All the synthesised compounds have been assayed for antifungal activity against *P. oryzae* and *H. oryzae* using spore germination test at various concentrations using the standard method[5]. It was observed that compounds Nos. 7 and 8 did not exhibit significant activity while the remaining compounds showed high activity against the pathogen *P. oryzae*. Compounds Nos. 2 and 5 cause 100% inhibition of *P. oryzae* spore at 1000 ppm concentration, Highest activity was exhibited by compound No. 5, which inhibited 90% of *P. oryzae* spore germination at 250 ppm concentration. Compounds Nos. 1, 2, 6, 7, 8 and 9 did not exhibit significant fungicidal activity against the pathogen *H. oryzae* while the remaining compounds Nos. 3, 4 and 5 showed significant fungicidal activity. Compound No. 3 causes 70% inhibition of *H. oryzae* spore at 1000 ppm concentration.

ACKNOWLEDGEMENTS

The authors wish to express their cordial thanks to Dr. A.N. Singh (Principal) and Dr. A.C. Ojha, Head, Chemistry Dept., Sahu Jain College, Nijibabad providing for laboratory facilities. The authors also wish to express their sincere thanks to U.G.C. (New Delhi) for financial assistance.

REFERENCES

1. G.B. Crippa and S. Maffei, *Gazz. Chim.* (Ital.)., **72**, 67 (1942).
2. B. Nanda, S. Padmanavan, B. Tripathi and A.S. Misra, *J. Indian. Chem. Soc.*, **52**, 533 (1975).
3. A. Nayak, S. Das, C.R. Misra and A.S. Misra, *J. Indian. Chem. Soc.*, **54**, 485 (1977).
4. C.P. Singh, Ph.D. Thesis, Synthesis and Studies of 1,2-Diazoles and Diazolones, Rohilkhand University, Bareilly, 1980.
5. A. Moore and J. Montgomery, *J. Promol. Hort. Sci.*, **15**, 253 (1938).

(*Received:* 10 October 1991; *Accepted:* 10 July 1992) AJC–449