Acta Ciencia Indica, Vol. XLII C, No. 4, 209 (2016)

STUDIES ON 2-PYRAZOLIN-5-ONE DERIVATIVES

P.C. MOHANTY

Kendriya Vidyapitha, Charbatia, Cuttack

MRS. S. PATNAIK

B.J.B. (Auto) College, Bhubaneswar

AND

P.K. MISRA

Ex-Deptt. of Chemistry, Ravenshaw College, Cuttack

RECEIVED : 25 December, 2016

In our earlier communications, we reported that 5-pyrazolone [1-4] and its derivatives, 4-acetyl-2-pyrazolin-5-one [5] and 2-pyrazolin-5-thione [6], were associated with significant fungicidal activity against the rice blast pathogen *Pyricularia oryzae* and brown leaf spot pathogen *Helminthosporium oryzae*. Fungicidal property [7] has been noted in 2-mercapto-3-aryl-4-thiazolidone and 2-pyrazolin-5-thione. It was therefore considered worthwhile to synthesise a new heterocyclic compound containing both the fungicidally active moieties-pyrazolone and thiazolidone.

INTRODUCTION

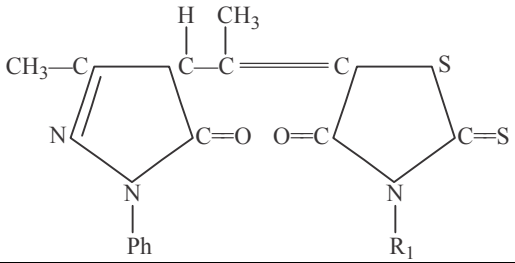
4-Acetyl-1-phenyl-3-methyl-2-pyrazolin-5-one condensed at the active methyl site of 2-mercapto-3-aryl-4-thiazolidone in ethanol to afford the compound [2-(1-phenyl-3-methyl-2-pyrazolin-5-one-4-yl)-2-(2-mercapto-3'-aryl-4'-thiazolidone-5'-ylidene)-ethane). The structure of the compound was established from analytical data and ir spectra. The ir spectra of the compound indicate the characteristic band at 1740 cm^{-1} for ring (>C=O), weak band at 2990 cm^{-1} for heterocyclic –CH stretching vibration, band at 1490 cm^{-1} for $–CH_3$ bonding vibration, and at 1590, 1050, 750 cm^{-1} attributed to –C=H, -C=S >C-S-C< stretching vibration, respectively.

1-Phenyl-3-methyl-2-pyrazolin-5-thione condensed at the 5 position with phenacyl bromide in presence of ethanoland fused sodium acetate to yield 5-ether product of 1-phenyl-3-methyl-2-pyrazolin-5-thioneand phenacyl bromide. It doesnot dissolve in 10% aq. Alkali and does not give any colouration with alcoholic $FeCl_3$ solution.

The ir data indicate the absence of enolic band. Band at 1680 cm^{-1} indicates the presence of characteristic exocyclic carbonyl group absorption, aromatic nucleus at 1370 cm^{-1} and hydrogen atoms of mono-substituted aromatic nucleus at 760 and 740 cm^{-1}. From nmr data in $CDCl^3$ it has been noted that peaks at δ2.2 comes as signlet for 3H of one methyl group, δ3.9 indicates a singlet for 2H, δ6.15 comes as singlet of 1H at C_4 position. Also a multiplet inbetween δ7.4-δ7.9 indicates the presence of phenyl group. The molecular weight of this compound has been determined from the mass spectra and found to be 308 (M^+). Peaks at 308, 203,188, 173, 103, 77, 51 m/e are obtained.

The compounds thus prepared were screened for their antifungal activity against the rice blast pathogen *P. oryzae* and the brown leaf spot pathogen *H. oryzae* by the standard methods [8] of spore germination tests at various concentrations. It is found that only one compound (Sl. No. 9, Table 1) is active against both the pathogens. It was of further interest to note that 5 other compounds (Sl. No. 1, 5, 6, 7, 10, Table 1) were active at 100 ppm. The compound No.1 in Table 2 is found to be more active than the O-ether product earlier reported by Das and Mittra [9].

Table – I



Sl. No.	R_1	m.p. °C	%S Found (Calcd.)	% inhibition of germination at 1000 ppm	
				P. oryzae	H. oryzae
1.	C_6H_5	167	15.65 (15.72)	62.4	56.8
2.	o-C_6H_4Cl	107	14.62 (14.99)	45.9	36.2
3.	m-C_6H_4Cl	72	14.55 (14.99)	49.6	39.7
4.	p-C_6H_4Cl	101	14.32 (14.99)	50	42.1
5.	o-$C_6H_4OCH_3$	85	11.52 (11.61)	69	40
6.	p-$C_6H_4OCH_3$	169	11.53 (11.61)	55	45
7.	p-$C_6H_4OC_2H_5$	62	14.06 (14.19)	32	27
8.	o-$C_6H_4CH_3$	99	15.16 (15.20)	65.9	56
9.	m-$C_6H_4CH_3$	75	15.35 (15.20)	70.1	61
10.	p-$C_6H_4CH_3$	117	15.18 (15.20)	61	52.6

Experimental

All melting points are uncorrected. IR spectra were recorded in Infrared spectrophotometer.

General method for the preparation of 2-(1-phenyl-3- methyl-2-pyrazolin-5-one-4-yl)-2-(2'-mercapto-3'-aryl-4'-thiazolidone-5'-ylidene) ethane : A solution of 1-phenyl-3-methyl-4-acetyl-2-pyrazolin-5-one (0.01 mole) and 2-mercapto-3- aryl thiazolidone (0.01 mole) in ethanol (20 ml) was added dropwise to 40% NaOH (15 ml) and allowed to stand overnight. It was then refluxed for 1 hr on a water bath. Excess of the solvent was removed and the resulting solution was acidified with dil. Acetic acid. An yellow solid mass separated which was filtered, washed with water and finally crystallized from ethanol.

Procedure for the synthesis of S-ether product of 2-pyrozolin-S-thione and phenacyl bromide : 1-Phenyl-3-methyl -2-pyrazolin-5-thione (1.9 g) and phenacyl bromide (1.9 g) were taken in ethanol (10 ml) followed by fused sodium acetate (3g) and was refluxed for 2 hr on a water bath. Excess ethanol was evaporated and cooled and water added. The brown compound

thus isolated was then dissolved in 10% aqueous sodium hydroxide solution. It was allowed to stand at room temperature for 1 hr and filtered. The filtrate and the residue were collected separately. The filtrate was acidified with dil. HCl when no product was obtained. The residue was repeatedly washed with water and dried. It was then recrystallised from ethanol. A cream coloured product was obtained, m.p. 49°, yield 60%.

The compound is insoluble in 10% aqueous sodium hydroxide solution and does not give any colouration with alcoholic ferric chloride solution.

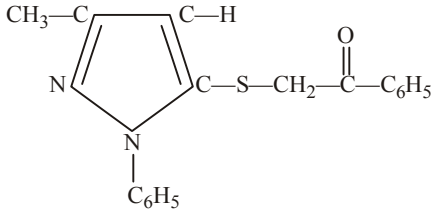


Table 2

Sl. No.	m.p. °C	%S Found (Calcd.)	% inhibition of germination at 1000 ppm	
			P.oryzae	H.oryzae
1.	47	10.54 (10.88)	70	48

Acknowledgement

The authors are thankful to the authority of C.R.R.I., Cuttack for facilities for fungicidal tests.

References

1. Nanda, B., Padmanavan, Savitri, Tripathy, B. and Mittra, A.S., *J. Indian Chem. Soc*., **52**, 533 (1975).
2. Nayak, A., Das, S., Mishra, C.R. and Mittra, A.S., *J. Indian Chem. Soc*., **54**, 485 (1977).
3. Das, N.B. and Mittra, A.S., *J. Indian Chem. Soc.,* **55**, 829 (1978).
4. Das, N.B. and Mittra, A.S., *J. Indian Chem. Soc.*, **56**, 398 (1979).
5. Mohanty, S.K., Sridhar, R., Padmanavan, S.Y., Rao, S. and Mittra, A.S., *Indian J. Chem.,* **15B**, 1146 (1977).
6. Rao, Sundar and Mittra, A.B., *Indian J. Chem.,* **15B**,1062 (1977).
7. Brown, F.C., *J. Amer.Chem. Soc.,* **78**, 6189 (1956).
8. Moore, A. and Montgomery, J., *J. Pomol. Hort. Sci.,* **15**, 253 (1988).
9. Das, N.B. and Mittra, A.B., *J. Indian Chem. Soc*., **55**, 907 (1978).

❑