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COPPER (II) FUNGICIDES : RELATIVE EFFICACY OF FUNGICIDAL ACTION OF SOME COPPER (II) MONOSUBSTITUTED ACETATES AGAINST *ALTERNARIA SOLANI* CAUSAL ORGANISM OF EARLY BLIGHT OF "POTATO" (*Solanum Tuberosum* L.)

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The relative efficacy of fungicidal action of Copper (II) acetate, glycolate, chloroacetate, cyanoacetate and glycinate are reported against *Alternaria solani* causing early blight of potato (*Solanum tuberosum* L.). Copper (II) acetate and glycolate show complete inhibition of spore germination of the pathogen in all of the concentrations (25-1000 ppm.). On the other hand copper (II) chloroacetate, cyanoacetate and glycinate inhibit the spore germination by 57 to 78 per cent in the concentrations of 25 and 50 ppm. The degree of inhibition of spore germination of the pathogen decreases with the decrease in the degree of ionization of the complexes.

**Keywords :** Copper (II) Fungicidas. Monosubstituted Acetates; *Alternaria solani*; *Solanum tuberosum* L.;

#### INTRODUCTION

THERE has been a great surge of efforts to replace the simple salts of copper (II) by some coordination complexes of copper (II), which are less phytotoxic (Martin *et al.*, 1942). In our earlier communication, we have reported fungicidal activity of some copper (II) alkanoates and it has been concluded that the toxicity of the complexes decreases with an increase in the size of the carboxylate ligands attached to the copper atom. In continuation, the present investigation deals with the fungicidal activity of some copper (II) monosubstituted acetates against *Alternaria solani* (Ell. and Martin). Jones and Grout, pathogenic to 'potato' (*Solanum tuberosum* L.) and a correlation between the toxicity of the complexes and the degree of ionization of the complexes is suggested.

#### EXPERIMENTAL

The following complexes were tested in the present study :—

(1)  $\text{Cu}(\text{CH}_3\text{COO})_2$ . (2)  $\text{Cu}(\text{OHCH}_2\text{COO})_2$ . (3)  $\text{Cu}(\text{ClCH}_2\text{COO})_2$ . (4)  $\text{Cu}(\text{CNCH}_2\text{COO})_2$ . (5)  $\text{Cu}(\text{NH}_2\text{CH}_2\text{COO})_2$ .

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All the complexes were synthesised by literature route. The purity and chemical composition of the complexes were ascertained on the basis of elemental analysis, IR, UV and magnetic susceptibility measurements (Nene & Thapliyal, 1979).

The relative efficacy of fungicidal activity of the above mentioned compounds was investigated by spore germination method (Tyagi, 1980). The pathogen (*Alternaria solani*) was obtained from the leaves of infected potato crop (*Solanum tuberosum* L), later purified and identified. The culture of the pathogen was maintained on P.D.A. medium and spore germination was studied from one week old culture of the same. Spore suspension was prepared in sterilized water for all complexes. For each of the complex, 7 different concentrations (25, 50, 75, 100, 200, 500 and 1000 ppm) and a control (in sterilised water) was taken. The plates were incubated at  $28\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  and 100 per cent relative humidity for 24hrs. For each concentration, 10 observations were taken and the mean value of these are incorporated in Table I.

TABLE I

*Percentage inhibition of spore germination of the Alternaria solani in presence of some copper (II) monosubstituted acetates*

Complexes	Control	Concentrations of complexes in ppm							<i>pKa</i> of the parent carboxylic acids
		25	50	75	100	200	500	1000	
Copper(II) acetate: $\text{Cu}(\text{CH}_3\text{COO})_2$	4.3	100	100	100	100	100	100	100	4.75
Copper (II) glycolate; $\text{Cu}(\text{OHCH}_2\text{COO})_2$	5.2	100	100	100	100	100	100	100	3.83
Copper(II) chloroacetate; $\text{Cu}(\text{ClCH}_2\text{COO})_2$	3.4	70.4	78.2	99	100	100	100	100	2.86
Copper(II) cyanoacetate; $\text{Cu}(\text{CNCH}_2\text{COO})_2$	6.74	57.3	67.8	100	100	100	100	100	2.45
Copper(II) glycinate; $\text{Cu}(\text{NH}_2\text{CH}_2\text{COO})_2$	4.5	67.0	72.7	78.5	90	100	100	100	2.34

## RESULTS AND DISCUSSION

From Table I, it is obvious that spore germination of the pathogen is completely checked in all the treatments of copper (II) acetate and glycolate complexes indicating their toxicity. The remaining complexes viz. Copper (II) chloroacetate, cyanoacetate and glycinate are more effective at higher concentrations (1000, 500, 200, 100 and 75 ppm) as the spore germination is completely inhibited in these operations; however, copper (II) glycinate showed 78.5 per cent inhibition of spore germination of the pathogen at the concentration of 75 ppm. The lower concentrations (50 and 25 ppm) of these complexes are found to inhibit the spore germination of the pathogen by 78-57 per cent. This varying degree of inhibitory effect of all these complexes at the

concentrations of 50 and 25 ppm. Comes about due to a difference in the toxicity of the complexes.

The degree of ionization of the  $\text{Cu}^{++}$  complexes depends on the extent of covalent nature of the Cu-O (Carboxylate) bond. Lew and Thompson (1963) suggested that the covalent nature of the Cu-O bond is increased with a decrease in the  $pK_a$  value of the parent carboxylic acids and hence the complexes are less ionic in nature. It is, therefore, expected that ionic compounds will provide more free ions which will eventually increase the toxicity of the complexes. It is supported by our results (Table I).

It may be suggested from these observations that there is lesser inhibition of spore germination of the pathogen in case of copper (II) cyanoacetate than that in copper (II) glycinate, whereas the  $P_k a$  of the former compound (2.45) is lower than that of the later compound (2.34). This unexpected behaviour of copper (II) cyanoacetate appears due to its polymeric structure, in which nitrogen atom of the cyano group is coordinated to the copper atom of the other dimeric unit of the complex by donating electrons to the Cu atom, consequently covalent nature of Cu-O bond increase (Tyagi *et al.*—*Communicated*). Therefore, the toxicity of the Copper (II) cyanoacetate is lower than that of the copper (II) glycinate.

It is apparent from the present investigation that the lower concentrations (25 and 50 ppm) of copper (II) chloroacetate, cyanoacetate and glycinate may safely be recommended as spray for the control of leaf spot diseases caused by *Alternaria solani*. These are effective at lower concentrations and therefore are economical.

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