

THE STRUCTURE-ACTIVITY RELATIONSHIPS OF SOME TRIPHENYLTIN(IV) DERIVATIVES OF HETEROCYCLIC DITHIOCARBAMATES

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Four newly synthesized triphenyltin complexes of heterocyclic dithiocarbamates have been screened for their fungicidal activity against two wide spread fungal pathogens namely *Macrophomina phaseolina* (Tassi) Goid and *Alternaria melongena* (Rang. and Samb.) to study their radial growth and sclerotial formation. The triphenyltin complexes of 4-methyl piperazine and 4-methyl piperidine dithiocarbamates exhibit stronger fungicidal property than the corresponding complexes of piperadine and morpholine dithiocarbamates.

Keywords : Fungal pathogens; Food poison technique; Radial growth; Sclerotial formation.

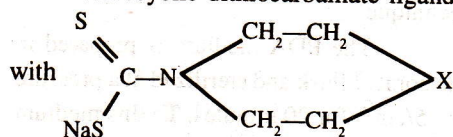
Introduction

Elemental sulphur has been in use as a fungicide for a long time and even today it is one of the best for the control of powdery mildew diseases. The sulphur containing ligands like dithiocarbamates, benzothiazoline etc. have versatile pharmacological activities^{1,2} and this activity increases manifold on complexation with different metals. Several investigators have shown^{3,4} that the antifungal activities of salts, esters and oxidation products of di-N-substituted dithiocarbamate derivatives are higher if the substituents on the N atom are methyl groups⁵.

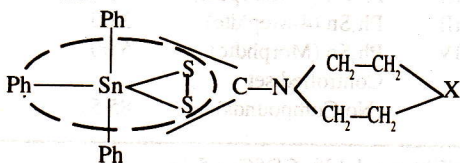
The carbamate fungicides form a very important group among fungicides. Most of these are foliage fungicides, while some are used for soil and seed treatments. In this paper, the fungicidal activity of some newly synthesized triphenyltin complexes, has been reported.

Materials and Methods

Four heterocyclic dithiocarbamate ligands



composition have been synthesized by a reported procedure⁶. The triphenyltin (IV) complexes of the above four heterocyclic dithiocarbamate ligands have been synthesized⁷ by the reactions of triphenyltin chloride (Ph_3SnCl) with the corresponding ligands in 1:1 stoichiometric ratios in refluxing benzene solution. After removing the solvent and on recrystallisation, yellow solids are being obtained. These complexes are reported to have the following structure⁷.



When X = CH₂ ; Lignad = piperadine dithiocarbamate (Pipdte)

" X = CH-CH₃ ; " 4-methyl piperadine dithiocarbamate (4-MePipdte)

" X = N-CH₃ ; " 4-methyl piperazine dithiocarbamate (4-MePzdtc)

" X = O; " morpholine dithiocarbamate (Morphdte)

The fungicidal activity of the complexees was assessed against two fungal pathogens *Macrophomina phaseolina* and *Alternaria melongena*. These two fungal pathogens were isolated from the infected plant of groundnut (*Arachis hypogaea L.*) and brinjal (*Solanum melongena L.*) crops respectively. The isolations were made on 2 percent potato dextrose agar (PDA) and were purified by using mono hyphal tip technique⁸.

The PDA medium is prepared in the conical flask and sterilized at a pressure of 15/cm² for 20 minutes. To this medium was added requisite quantity of different triphenyltin compounds to get 250 ppm concentration. These compounds were mixed thoroughly by stirring. The medium

was than poured into Petri plates (90mm diameter) and each containing 25ml of poisoned medium. Small fungal bit (3mm diameter) of test pathogens cut from the periphery of 5 days old culture with a sterile cork borer and transferred aseptically into the centre of the petri plates. These plates were incubated at 26 ± 1° C until control plates filled up. Controlled set were kept without adding any compounds of triphenyltin. The colony diameter was recorded diagonally after 60 hours of incubation and sclerotial formation was recorded visually. The experiment was replicated four times.

Results and Discussion

A technique employing poisoning of nutrient medium (poisoned food technique)⁹ with test compound to evaluate its fungicidal property reveals substantial property in the tested compounds. Radial growth of the pathogen *M. phaseolina* was significantly reduced in all the triphenyltin compounds *in vitro* as compared to radial growth of the controlled set (85.5 mm) (Table 1). The compound III {Ph₃Sn (4-MePzdtc)} exhibited stronger fungicidal

Table 1. Fungicidal Activity of the Compounds of Triphenyltin Dithiocarbamates.

Compound	Average radial growth of <i>M. phaseolina</i> in mm (range)	Sclerotial formation mm (range)	Average radial growth of <i>A. melongena</i> in mm (range)	Sclerotial formation
I. Ph ₃ Sn (4-MePipdte)	9.00	+	4.12	+
II. Ph ₃ Sn (4-MePipdte)	4.62	+	3.25	+
III. Ph ₃ Sn (4-Mep ^z dte)	3.00	-	3.00	-
IV. Ph ₃ Sn (Morphdte)	5.00	+	10.75	+
Controlled set (No Compounds)	85.5	+++	87.50	+++

SEM = + 1.138; CD5% = 5.16

- = Nil; + = Few; ++ = Several; +++ = Abundant;

property i.e. no fungal growth and no sclerotia formation in pathogen *M.phaseolina* was recorded.

Less radial growth (9mm; 4.62mm; 5mm with sclerotia formation) was recorded in compounds I [(Ph₃ Sn(Pipdte)); II (Ph₃ Sn(4-MePipdte))] and IV [Ph₃ Sn (Morphdte)]. Similarly, all the triphenyltin compounds significantly reduced the radial growth of the pathogen *A.melongena* in comparison to radial growth of the controlled set (87.5mm). No radial growth and no sclerotia formation was recorded in compound III (Ph₃ Sn(4-MePzdtc)]. Less radial growth (4.12mm; 3.25mm) with sclerotia formation was recorded in compound I (Ph₃ Sn(Pipdte)] and II [Ph₃ Sn(4-Mepipdte)]. Radial growth of pathogen were recorded in compound IV (Ph₃ Sn(Morphdte)].

With regard to the structure-activity relationship, compound III showed strong fungicidal activity towards both pathogens.

In case of *M.phaseolina*, compounds II and IV and in case of *A.melongena*, compounds I and II showed satisfactory results in reducing the radial growth. Compound I in case of *M.phaseolina* and compound IV in case of *A. melongena* showed less fungicidal activity. Hence, the subsequent fungicidal potential of the complexes have been categorized in the order given below:-

In case of pathogen *M. phaseolina*, compound III > II > IV > I whereas in case

of pathogen *A. melongena*, compound III > II > I > IV.

From the above studies, it can be concluded that the presence of the methyl group on the N atom enhances the fungicidal activities of the triphenyltin complexes of heterocyclic dithiocarbamates.

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