A Study : Synthesis of Hydrazones and their Zn(II), Cd(II) and Hg(II) chelates : Characterization, Fungal and Bacteriocidal

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ABSTRACT

Salicyldehyde-benzene-1, 2-dicarboxyloyl hydrazone (S.B.H.), salicyldehyde-ethanedicarboxyloyl hydrazone (S.E.H.). were synthesized by the reaction of already synthesized hydrazides of phthalic acid, succinic acid, anthranilic acid and oxalic, acid, respectively with salicyldehyde in proper ratio. The metal complexes of these hydrazones were prepared with Zn(II), Cd(II) and Hg(II). All the Compounds were characterized and screened for their biocidal activity against gram + ve (S aureus) and gram - - ve (E. coli) bacteria and two common fungi (A. niger and C. albicans) by several dilution method in slant and broth culture media. A comparative study of the activities of the synthesized Compounds with their metal Complexes has been given and explained.

(Key words : metal chelate, hydrazones, fungal activity, bacteriological studies)

INTRODUCTION

Fungus is a great menace both to humans as well as the vegetable kingdom. Among all methods of controlling the growth of fungus chemical control is the most effective method. A large variety of organic compounds like phenol, dithiocarbamates, sulphide, sulphones, quinone and organometallic compounds have been used is biocidal agents. Since the beginning of dithiocarbamates (Tisdale et. al., 1934) many

other derivatives of this compound have been prepared and used. It is reported that matel complexes of dithicarbamates acid have been found more active than the acid itself. A survey of literature further reveals that anti microbial activity of a potential active ligand is in enhanced several times on its coordination with suitable metal ions both in simple as well as in mixed ligand complexes. (Sorenson, 1978, Sharma et. al., 1981,1983,1985,1986,1987).

A part from the synthetic studies the chemistry of hydrazones is gaining much importance due to their anti fungal (molodykh. et. al., 1980, Tokkokoho. 1981, piscopo. et.al., 1983 and ahluwalia, et. al., 1972,1974, insecticidal. (bottger, 1951), anti-tubercular (mokhtar, 1979; Zakalyuzhny et. al., 1975), anti-cancerous (sosnovsky et. al., 1985) and anti-inflammatory (aminabhavi et. al., 1983; makurva, 1985) agents. Our earlier observation (jauhari, et. al., 1987, Beena et. al., 1987). In this field have indicated an increased activity of hydrazones in the form of their metal complexes. In this present paper, we are reporting our extended studies on the synthesis and biocidal studies of the listed hydrazones and their zn(II), cd(II) and Hg(II) Complexes with a view to explore the possibility of their uses in agriculture.

MATERIALS AND METHODS

1. PREPARATION OF LIGANDS :-

All the chemicals used were of AR grades salicyldehyde- benzene 1, 2-dicarboxyloyl hydrazone (S.B.H.), salicyldehyde-ethanedicar-boxyloyl-hydrazone (S.E.H.) were synthesized by refluxing the mixture of acid hydrazides with salicyldehyde in proper ratio in methanol over an oil bath for about 4 hours as reported earlier Beena et. al., 1987.

2. PREPARATION OF METAL COMPLEXES :-

The reported metal complexes were prepared by refluxing a mixture of an equimolar (2.0×10^{-2}M) amount of metal acetate/metal nitrte with the synthesized ligands in the case of S.B.H., S.E.H. in 1:2 ratio in the case of methanol over an oil bath for 4 hours. The obtained precipitate was washed successively with water, methanol, a little D.M.F. and finally with ether. The crude products were further recrystallized either from their methanol or DMF solution or from 1:1 mixture of nitrobenzene and benzene. The purity of the ligand and their metal Complexes was further checked by T.L.C. method. All the Compounds were kept over P_2O_5 in a desiccators. (yield 60 – 70%) The structure of the synthesized ligands and their metal chelates were determined by their elemental analysis (C.D.R.I., Lucknow) molecular weight determined (Cryscopic method) and Conductance data (Toshniwal digital Conductivity bridge) as given in Table-1.

I.R. SPECTRAL STUDIES:-

The I.R. spectra of all the compounds were recorded on Beckmann I.R.-20 spectrophotometer in KBr matrix. The most significant difference which emerge from a comparison of the I.R. frequencies of the active donor sites of the free organic molecules with its metal Complexes were (i) disappearance of the V OH bands (2500-

2700cm^{-1}) in the Complexes all the four ligands, (ii) lowering in the intensity as well as in band position of > C = O group (1600-1680cm^{-1}), of the ligand S.B.H., S.E.H. in their metal Complexes, (iii) lowering in the V C = N bands (1480-1530cm^{-1}) of the ligand by 20-30cm^{-1} in metal Complexes.

On the basis of observation number (i), (ii) it is concluded that the ligand S.B.H., S.E.H. behave as a bianionictetrdentate ligand and their co-ordination takes place through phenolic and carboxyl groups. The non-electrolyte nature of the Complexes can be explained by the Charge neutralization of the metal ion through the deprotonation of phenolic group (Rastogi et. al. 1978) some new bands developed in the I.R. spectra of metal Chelates in the region of 500-550cm^{-1}, 400-450cm^{-1} and 300-400cm^{-1} also support the formation of M-O, M-N and M-O=C bonds respectively in the resulting complexes (Agrawal et. al. 1970, Dutta et. al., 1962, Gillard et. al., 1964, 1969).

ANTIFUNGL AND ANTIBACTERIAL ACTIVITY

A. For the antimicrobial study of the compounds, serial dilution method (Donald et. al., 1955: Spooner 1972, Reeves et.al.1978) was adopted. The incubated micro-organism were allowed to grow in slant and broth culture media using aseptic conditions.

RESULT AND DISCUSSION

A study of the Table 1 and 2 reveals that all the synthesized ligands and their metal chelates are fairly stable non-ionic in nature and can be easily prepared. A Comparative study of the biocidal activity of the compounds listed in Table (II) indicates that in some cases the activity of the ligands have considerably changed in co-ordination with suitable metal ions.

The order of activity given in the Table (III) infers that the biocidal activity of a synthesized potentially active molecule and its metal complexes is dependent both the nature of metal ions and the nature of the parent acid chosen for the synthesis of hydrazones which make them specific in nature against a particular bacteria or fungi. However the compounds of Zn and Hg have been found more effective biocidal against the chosen bacteria and fungi.

TABLE I – PHYSICO-CHEMICAL DATA

Compound	Molecular weight (calcul-ated)	M.P./d.p. ^{0}C	Percentage analysis (calculated)			Molar- con-ductance ohm^{-1}cm^7 mol^{-1}
			C	H	N	
S.E.H.	346 (354)	208	60.5 (60.1)	4.58 (5.08)	15.8 (15.87)	--
S.B.H.	412 (402)	212	66.2 (65.67)	4.60 (4.47)	12.90 (13.93)	--
Zn(II)-S.E.H.	420 (417.38)	>360	51.5 (51.75)	3.56 (3.83)	12.8 (13.41)	0.1
Cd(II)-S.E.H.	458 (464.41)	>360	46.4 (46.51)	3.50 (3.44)	11.98 (12.05)	0.2
Hg(II)-S.E.H.	500 (552.59)	235	38.4 (39.67)	2.67 (2.89)	10.00 (10.13)	0.1
Zn(II)-S.B.H.	472 (465.38)	>360	57.0 (56.36)	3.60 (3.43)	11.9 (12.03)	0.2
Cd(II)-S.B.H.	520 (512.41)	>360	53.00 (51.52)	3.5 (3.12)	10.82 (10.91)	0.2
Cd(II)-S.B.H.	520 (512.410	>360	53.00 (51.520	3.5 (3.12)	10.82 (10.91)	0.2
Hg(II)-S.B.H.	615 (600.59)	270	45.0 (43.95)	2.80 (2.66)	9.60 (9.32)	0.1

TABLE II – FUNGICIDAL AND BCTERIOCIDAL ACTIVITY (uG)

Substance	Bacteria 48 hrs. at 27^0C		Fungi 96 hrs. at 37^0C	
	S. aureus	E. coli	A. niger	C. albicans
S.E.H.	100	100	100	100
S.B.H.	100	100	100	100
Zn(II)-S.E.H.	6.25	6.25	50	100
Cd(II)-S.E.H.	100	100	100	100
Hg(II)-S.E.H.	50	50	100	100
Zn(II)-S.B.H.	100	100	100	100
Cd(II)-S.B.H.	12.5	100	100	100
Hg(II)-S.B.H.	25	12.5	25	50

TABLE III – ORDER OF M.I.C. VALUES IN TERMS OF METALIONS

Complex	Bacteria		Fungi	
	S. aureus	E. coli	A. niger	C. albicans
M(II)-S.E.H.	Zn > Hg > Cd	Zn > Hg > Cd	Zn > Cd = Hg	Zn = Cd = Hg
M(II)-S.B.H.	Cd > Hg > Zn	Hg > Cd = Zn	Hg > Cd = Zn	Hg > Cd = Zn

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