midazoles, thereby making it difficult for the formation of charge-transfer complex[11]. On the other hand, presence of a methyl group in the benzere ring of benzimidazcle, facilitated the reaction resulting in an increased yield of the debenzylation product.

In comparison with the already known methods of debenzylation, the iodine catalysed process appears to be simple and promising. Application of this method to other N-benzyl heterocycles is under investigation.

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STUDIES ON THE ANTIFUNGAL ACTIVITY OF SOME MIXED LIGAND METALLIC COMPLEXES OF SALICYLIC ACID

MIXED ligand complexes of salicylic acid with Cu(II), Ni(II), Co(II) and Fe(II) as metals and 8-hydroxy quinoline, nicotinic acid, pyridine and β-picoline as secondary ligands were synthesised and screened for their antifungal activity. The compounds were found considerably active against many of the fungi.

Introduction

Activity of certain drugs has been found to be related to their affinity for linking with metal ions in complex formation or chelation. It is reported that in rheumatic fever the nonchelating analogues of salicylic acid, meta and para-hydroxy benzoic acids are relatively ineffective compared to salicylic acid[1]. The fungicidal ability is related to metal binding strength[2-4].

In the pre ent study, mixed ligand metallic complexes of salicylic acid as primary and pyridine, β-piccline, 8-hydroxy quinoline and nicotinic acid as secondary ligands were synthesised and tested for their antifungal activity.

Experimental

Mixed ligand complexes of Cu(II), Ni(II), Co(II), Fe(II) were prepared taking salicylic acid as primary and pyridine, β-picoline, 8-hydroxy quinoline and nicotinic acid as secondary ligands. All reagents were of ANALAR grade and the complexes were isolated using the method of Khadikar *et al.*[5]. Individual metal in each complex was estimated using reported methods[6]. The composition of salicylic acid complex is assumed to be $ML_2 . 2H_2O$ while that of mixed ligand complex is $ML_2X_2 . 2H_2O$ where M is the metal, L the primary ligand and X the secondary ligand (pyridine or β-picoline). In the case of oxine or nicotinic acid secondary ligand, the composition is $MLX . 2H_2O$. The results are given in Table I.

TABLE I

Analytical data of the complexes

Sl. No.	Complex	Appearance	% of metal		% of nitrogen	
			Calc.	Found	Calc.	Found
1.	$Cu(SA)_2 . 2H_2O$	Green	17·00	16·88	..	..
2.	$Cu(SA)_2(Py)_2 . 2H_2O$	Bluish green	11·95	11·88	5·27	5·20
3.	$Cu(SA)_2(Pico)_2 . 2H_2O$	Bluish green	11·34	11·32	5·00	4·91
4.	Cu (SA) (Oxine) . $2H_2O$	Greenish yellow	16·69	16·66	3·68	3·57
5.	Cu (SA) (Nico) . $2H_2O$	Bluish green	17·71	17·56	3·90	3·76
6.	$Ni(SA)_2 . 2H_2O$	Light green	15·92	16·00	..	..
7.	$Ni(SA)_2(Py)_2 . 2H_2O$	Light green	11·14	11·02	5·31	5·25
8.	$Ni(SA)_2(Pico)_2 . 2H_2O$	Light green	10·57	10·49	5·04	5·01
9.	Ni (SA) (Oxine) . $2H_2O$	Yellow	15·62	15·55	3·72	3·68
10.	Ni (SA) (Nico) . $2H_2O$	Light green	16·59	16·47	3·95	3·83
11.	$Co(SA)_2 . 2H_2O$	Pink	15·95	15·90	..	..
12.	$Co(SA)_2(Py)_2 . 2H_2O$	Pink	11·18	11·06	5·31	5·30 .

TABLE I (*Contd.*)

Sl. No.	Complex	Appearance	% of metal		% of nitrogen	
			Calc.	Found	Calc.	Found
13.	$Co(SA)_2(Pico)_2 . 2H_2O$	Pink	10·61	10·54	5·04	5·04
14.	$Co(SA)(Oxine) . 2H_2O$	Orange	15·67	15.54	3·72	3·65
15.	$Co(SA)(Nico) . 2H_2O$	Pink	16·64	16·52	3·95	3·87
16.	$Fe(SA)_2 . 2H_2O$	Dark green	15·14	15·10	..	..
17.	$Fe(SA)_2(Py)_2 . 2H_2O$	Dark green	10·59	10·42	5·31	5·28
18.	$Fe(SA)_2(Pico)_2 . 2H_2O$	Dark green	10·06	9·98	5·05	4·83
19.	$Fe(SA)(Oxine) . 2H_2O$	Brown	14·86	14·53	3·72	3·66
20.	$Fe(SA)(Nico) . 2H_2O$	Dark green	15·78	15·64	3·96	3·82

SA = Salicylic Acid; Oxine = 8-hydroxy quinoline; Nico = Nicotinic Acid; Py = Pyridine; Pico = β-picoline.

TABLE II

Anti-fungal activity of the complexes

Sl. No.	Organisms (Compound No. as given in Table I) →	Control D.M.F.	Anti-fungal activity in terms of mean diameter (in mm) of zone of inhibition appearing around the cup *																	
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1.	*Asperigillus flavus*	..	16	18	18	20	20	14	14	16	16	16	12	14	14	16	16	12	14	14	14	14
2.	*Trichophyton equingia*	..	18	18	18	22	22	16	16	18	18	18	14	16	16	18	16	18	15	18	14	14
3.	*Helminthosporium rostatum*	..	14	14	14	16	16	12	12	12	12	12	12	12	12	12	12	12	11	12	14	12
4.	*Chryptococcus neoformans*	..	16	18	18	20	20	16	18	18	20	20	14	14	14	16	16	14	14	14	16	16
5.	*Trichoderma viride*	..	20	20	20	22	22	14	14	14	16	16	14	16	16	18	18	14	14	14	16	16
6.	*Fusarium oxysporum*	..	14	16	16	18	18	14	14	14	16	18	12	12	12	14	14	12	12	14	14	14
7.	*Colletotrichum fulcatum*	..	18	18	18	20	20	16	16	18	18	18	14	14	14	16	16	12	14	14	16	14
8.	*Curvillaria lanata*	..	18	20	20	22	20	16	14	16	18	16	14	14	14	16	14	14	14	14	14	14
9.	*Colletotrichum capsici*	..	16	16	16	18	18	14	14	14	16	16	14	14	12	12	14	14	12	12	12	12
10.	*Alternaria solani*	..	18	18	18	20	20	14	16	16	18	18	16	16	16	16	12	12	12	12	12	12

* including the diameter of the cups.
D.M.F. = Dimethyl formamide.

Antifungal Activity

The complexes were dissolved in dimethyl formamide to get 1% conc Cup diffusion[7] method was followed for determining antifungal activity. Sabroud's agar media was used for culturing the organism. The melted media was aseptically poured into petridishes and then 2 ml inoculum was added to the dish. After settling, 4 cups of 6 mm dia. were cut by sterile cork borer and these cups were filled by test solution. A control was also run. These inoculated plates were then incubated for 72 hours at 24° ± 1. The inhibitory effect was noted against the test organism by measuring the diameter of zones of inhibition appearing around the cups. The experiments were performed in triplicate and the mean values were recorded in Table II.

Discussion

A perusal of Table I indicates that the mixed ligand metallic complexes of salicylic acid as primary ligand and pyridine, β-picoline, 8-hydroxy quinoline and nicotinic acid as secondary ligands using Cu, Ni, Co, Fe as metals had the expected chemical composition. The anti-fungal activity was compared with simple metallic complexes of salicylic acid which is reported as an anti-fungal agent and as a standard for the purpose for various experiments. The mixed ligand complexes were found to possess higher activity against some organisms and hence it can be presumed that the mixed ligands potentiate the activity to a considerable extent against *T. eqningia, T. viride, A. flavus*; the former two being the cause of many dermal infections. The complexes were, however, active against *C. fulcatum A. solani, C. neoformans* also.

Copper complexes were found to be comparatively more active while those of iron were least active.

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A SOFT FRUIT ROT OF *AEGLE MARMELOS*

FOLLOWING a cyclonic storm, quite a good number of raw fruits of *Aegle marmelos* were found damaged while still attached to the tree. The rotten fruits were brought to the laboratory and the following studies were made.

Small bits of surface sterilized rotten fruits were plated on PDA and Czapek's media and incubated at 28° C (± 2° C). The fungus showing consistent growth on the plated bits was isolated, purified and maintained on PDA. It was identified as *Fusarium solani* (Mart.) Sacc.

The pathogenicity tests were conducted under aseptic conditions following the knife injury method of Tandon and Mishra[2]. Inoculations were done on injured and uninjured raw fruit surfaces and incubated at 28° C for 15 days to observe the symptoms and for making enzymatic studies. Respective controls were also maintained.

The results revealed that no rotting occurred in intact uninjured fruits while the inoculated injured fruits developed the brownish soft rot with three distinct zonations of colour: (i) the severely macerated black regions near and at the site of injury containing white mycelia and spores, (ii) inner to it was dark-brown and considerably macerated tissue showing brownish watery secretions from which the mycelia were occasionally isolated and (iii) innermost dull brown regions which were visibly affected and sharply distinct from the yellowish apparently healthy tissue. The pathogen was reisolated from outer two zones only.

The seeds were yellowish-brown and pulpy in less effected regions while completely transformed into watery substances in severely infected dark-black region. The rotting advanced more quickly in tissue of the hard pericarp (3/4 area blackened within 15 days) as compared to its advancement in depth (1·6 cm out of 5·5 cm fruit diameter) within the same period. The rotten tissue emitted pungent odour.

Since the tissue maceration and release of watery substances were noticed well ahead of mycelial growth, certain hydrolysing enzymes were determined for their possible role in present host-pathogen interaction. Two pectolytic, *viz.*, Polymethylgalacturonase (PMG) and Polygalacturonase (PG) and one cellulolytic, *viz.*, Cellulase (Cx) were taken into consideration as