in all these areas, the soils are reported to be in the acidic range[13] An acidic nature of the soil may be a prerequisite for not only *I. glutinosus* but perhaps also for other apodan species. The soil analysis presented here offers the first analytical evidence of the requirements of the animals of this interesting amphibian order.

A comparison of habitat variations of the three orders of Amphibia is interesting. The Urodela are restricted in their distribution consequent on the special requirements of low temperature and aquatic medium. The Anura appear to exhibit greater adaptability in regard to temperature as well as other environmental requirements. The paucity of individuals as well as of species of Apoda appears to be determined by the special habitat characteristics of the animals of this order. From the present study it is evident, among the factors governing the severe restriction of Apoda to tropical and pan-tropical regions, are the characteristic physico-chemical features of the soil.

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ANTIFUNGAL ACTIVITY OF SOME NOVEL LANTHANON THIOSEMICARBAZONE COMPLEXES

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ABSTRACT

Antifungal activities of some newly synthesized and well-characterized lanthanon complexes of salicylidine- and 2-hydroxy-1-naphthalidine thiosemicarbazones have been determined. The ligands and their resulting complexes have been shown to be toxic against the two pathogenic fungi, *viz.*, *Aspergillus niger* and *Draschelera australiensis* and the results indicate that the toxicity decreases on metallation. Overall, the 2-hydroxy-1-naphthalidine-thiosemicarbazonelanthanon complexes are more toxic to fungi than the corresponding lanthanon derivatives of salicylidinethiosemicarbazones.

INTRODUCTION

SCHIFF bases and thioureas are amongst the most important nitrogen and sulphur containing ligands, which show remarkable pharmacological activity and have wide biological applications[1]. Perhaps, the group N–C–S is of considerable chemotherapeutic interest and is responsible for the pharmacological activity[2]. It has been indicated that the microbiol activity of these compounds is due to their ability to chelate traces of metal ions[3].

A study of the antifungal activity of some thiosemicarbazones and their lanthonon complexes has been undertaken in the present investigations. The antifungal activity of the chelating agents, salicylidinethiosemicarbazone ($STSCH_2$) and 2-hydroxy-1-napthalidinethiosemicarbazone (OH-$NTSCH_2$) and their lanthanide metal complexes has been evaluated against the pathogenic fungi, *Aspergillus niger* and *Draschelera australiensis*.

Experimental

($STSCH_2$) and (OH-$NTSCH_2$) were prepared by refluxing the equimolar amounts of salicylaldehyde or 2-hydroxy-1-naphthaldehyde and the thiosemicarbazide in alcohol. These were further recrystallized from the same solvent and analyzed[4].

The lanthanonthiosemicarbazone complexes of different compositions were synthesized by refluxing tris-(isopropoxy) lanthanon and thiosemicarbazone for a period of ~12 to 18 hours in dry benzene. The resulting compounds in 2 : 3 and 1 : 2 molar ratios (M : L), *e.g.*, Ln_2(STSC/OH-NTSC)$_3$ and Ln(STSC/OH–NTSC) (STSCH/OH–NTSCH) (where Ln = La, Pr, Nd and Sm) were isolated and dried in vacuum at 50–60° C/0·5 mm for 2–3 hours. Other details have already been reported in our previous communications[4,5].

Acetone was used as a solvent for preparing different concentrations (*e.g.*, 100 and 200 ppm, w/v) of the chelating agents and their complexes and these were incorporated in potato-dextrose-agar medium. The petriplates were inoculated with a block of 5 mm diameter of *Aspergillus niger* and *Draschelera australiensis* and each treatment was replicated three times with a control in which no chemical was added. The plates were incubated at 28 ± 1° C for four days and the growth inhibition per cent was calculated on the basis of the average diameter of the fungal colony (Vincent[6]).

Results and Discussion

Amongst the two ligands tested, 2-hydroxy-1-naphthalidinethiosemicarbazone has been found to be more fungitoxic than the salicylidinethiosemicarbazone (per cent growth inhibited at 100 and 200 ppm, for *Aspergillus niger* fungi $STSCH_2$/OH–$NTSCH_2$ = 46 and 72/64 and 78, and for *Draschelera australiensis* fungi $STSCH_2$/OH–$NTSCH_2$ = 56 and 100/76 and 100). It may be due to two benzene rings in the former along with the phenolic oxygen at the ortho position. The hydroxy group increases the toxicity of both the ligands and according to Horsfall the hydrogen of the phenolic group is so reactive that it enables the toxicant to combine with the constituents of the fungus resulting to inhibit its function.

Comparatively, both the chelating agents, *e.g.*, $STSCH_2$ and OH–$NTSCH_2$ show higher fungitoxicity than their corresponding lanthanon complexes [per cent growth inhibited at 100 and 200 ppm, for *Aspergillus niger* fungi, Ln_2(STSC/OH–NTSC)$_3$ = 22–27 and 30–56/38-52 and 46–65, Ln(STSC/OH–NTSC) (STSCH/OH–NTSCH) = 29–38 and 38–61/47–60 and 60–74, and for *Draschelera australiensis* fungi, Ln_2(STSC/OH–NTSC)$_3$ = 28–41 and 34–59/50–56 and 64–76, Ln(STSC/OH–NTSC) (STSCH/OH–NTSCH) = 35–52 and 42–77/56–62 and 51–81]. This may be due to the fact that the sulphur and nitrogen of thioketo (>C=S) and azomethine (>C=N) groups, respectively in the chelating agents are present in the free state and these can, therefore, combine with the fungi cells rather easily and check their growth. However, on complexation, the ligand is coordinated to the central metal atom through these donor atoms and as a result of which the toxicity of the complexes decreases. According to Waker, the fineness of the particles of the fungicides is also important in the toxicity determination along with the solubility. This too might be an additional factor for the lower activity of lanthanonthiosemicarbazone derivatives. As regards the solubility, both the ligands are more soluble than their corresponding complexes and as a result of which these might be absorbed easily by the fungal hyphae. It is also observed that 1 : 2 (M : L) complexes are more toxic than the 2 : 3 (M : L) complexes owing to the larger ratio of the ligand to metal and also due to the uncoordinated thioketo sulphur in the former type of complexes[4,5]. Further, the fungi *Draschelera australiensis* undergoes more irreversible toxic effects than *Aspergillus niger*.

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