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Transition Metal Complexes of *Croton sparsiflorus* Extract and Their Biological Status

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Transition metal complexes of Hg(II), Zn(II), Mn(II), Cu(II), Cr(II) and Ni(II) with extract of naturally occurring plant *Croton sparsiflorus* of *Euphorbiacea* family have been prepared and characterized on the basis of physico-analytical and IR spectroscopic data. All the metal complexes were also screened for their antimicrobial activity against a bacterial strain (*Bacillus sp*) and a fungal strain (*Rhyzopus oligosporus*). All the complexes exhibited enhanced antimicrobial activity as compared to simple plant extracts.

Key Words: *Croton sparsiflorus*, Extract, Metal ions, Antimicrobial activity.

INTRODUCTION

It has been an old heritage of human history to use herbs for the cure of various ailments. Now within past few decades, medicinal plants are being investigated for their valuable ingredients throughout the world[1]. Medicinal plants have curative properties due to the presence of various active ingredients which are found as secondary plant metabolites in different parts of these plants. These metabolites are grouped as alkaloids, glycosides, corticosteroids, lactones, peptides and essential oils[2].

In plant kingdom among various families, *Euphorbiacea*, is the largest plant family comprising about 5000 species in 300 genera. Most of its types are rich in natural products, for which they are grown commercially[3]. *Croton sparsiflorus* belongs to the same family. It weeds on waste places, road sides, paddy or sugar cane fields and sea shores in Pakistan and India. Its methanol extract has been taken for evaluation of their antifungal potency against various microbes. It possesses appreciable antifungal activity against tested fungi[4]. Alkaloids extracted from *Croton sparsiflorus* are crotsparine ($C_{17}H_{11}NO_3$), crotsparnine ($C_{17}H_{19}NO_2$)[5], crotonosine ($C_{17}H_{17}NO_3$)[6], sparsiflorine ($C_{17}H_{17}NO_3$)[7]. Aroul *et al*.[8], reported that the secondary metabolites including alkaloids were produced and accumulated considerably during reproductive phase.

It is very significant to note that most of these biologically active compounds possess their biological activity due to presence of donor atoms. Due to presence of these donor atoms, they are considered to be the best candidate for complexation with metal ions. These metal ions usually alter their sensitivity and efficiency[9-15]. With the same research interest, an attempt has been made in the present study to examine the effects of metal ions on the antimicrobial activity of extract of naturally occurring plant *Croton sparsiflorus* of *Euphorbiacea* family. For this purpose transition metal complexes of Hg(II), Zn(II), Mn(II), Cu(II), Cr(II) and Ni(II) with extract of naturally occurring plant *Croton sparsiflorus* of *Euphorbiacea* family have been prepared. It was observed that metal ions have significantly enhanced antimicrobial activity of extracts *Croton sparsiflorus* against microbial strains upon coordination.

EXPERIMENTAL

Mature and fresh plant was collected from canal bank, Lahore city. Plant was then identified by a plant taxonomist at the Botany Department, G.C. University, Lahore.

Method of extraction: The dried plant (2.5 Kg) was chopped, ground and then soaked in ethyl alcohol (10 L) for one week. The material afterwards, squeezed and filtered out. Filtrate was, then, shifted to rotary evaporator to separate plant extract from solvent. The resulting residue thus obtained was used as such for the preparation of metal complexes.

Preparation of metal complexes: Generally all the metal complexes were prepared by mixing approximately one part of metal chloride salt of Zn(II), Ni(II), Hg(II), Cu(II), Cr(III) and Mn(II) with two parts of plant extract prepared in 1:1 alcohol:water mixture. After stirring the mixture for 0.5 h, precipitate formed were allowed to settle for 6 h at room temperature and then separated through centrifugation. The settled precipitates were stored and used for further studies[15].

Antimicrobial studies: Antimicrobial activity was determined by previously reported method with little modifications[16,17].

RESULTS AND DISCUSSION

Keeping in view the structures of already extracted active ingredients from *Croton sparsiflorus*, the ethyl extract was treated with Zn(II), Ni(II), Hg(II), Cu(II), Cr(III) and Mn(II) chlorides under various conditions of temperatures and pH. It was established through repeated attempts that stable complexes were obtained at room temperature and pH between 5-6, using 1:1 mixture of ethyl alcohol and water as solvent. Complexes thus obtained are solid and stable over wide range of temperature (Table-1).

TABLE-1
DECOMPOSITION POINTS OF COMPLEXES

No.	Complex	Temperature (ºC)	Physical change
1	Zn-Complex	400	No change
2	Ni-Complex	287	White
3	Mn-Complex	308	Black
4	Cu-Complex	351	Brown
5	Hg-Complex	233	Black
6	Cr-Complex	359	Black

The assignments of the characteristic IR frequencies for the extract and prepared metal complexes are tabulated in Table-2. A comparative scrutiny of infrared spectral data of metal complexes with that of extract material gave clue regarding the donor sites of the extracts. The prominent peaks at or above 3400 cm^{-1} can be attributed to -OH group of carboxylic acid. Similarly the peaks at 2933, 2851 and 1450 cm^{-1} can be assigned to -CH stretching. These peaks have been shifted towards lower or higher frequencies in metal complexes indication interaction of metal ions with donor sites. Furthermore the appearance of new bands in the range 652-450 cm^{-1} can be attributed to M-O bond in almost all metal complexes[17].

TABLE-2
IR DATA OF PLANT EXTRACT AND METAL COMPLEXES

No.	Complex	IR Absorption bands (cm^{-1})
1	Extract	3830 (w), 3781 (w), 3746 (w), 3708 (w), 3666 (m), 3445 (m), 2933 (s), 2851 (s), 1458 (m).
2	Zn-Complex	3736 (w), 3713 (w), 3665 (w), 3623 (w), 3548 (m), 2966 (m), 2474 (w), 2218 (w), 1450 (s), 905 (m), 688 (m), 573 (m), 455 (m).
3	Ni-Complex	3751 (w), 3713 (w), 3620 (w), 3584 (m), 3501 (m), 3452 (m), 3028 (m), 1646 (m), 1453 (s), 866 (m).
4	Mn-Complex	3739 (w), 3664 (w), 3548 (w), 3488 (m), 3411 (m), 3360 (m), 3190 (m), 3156 (m), 2625 (m), 2856 (m), 2493 (w), 2343 (w), 1794 (w), 1455 (s), 1076 (w), 860 (m), 723 (m), 621 (m), 407 (s).
3	Cu-Complex	3774 (w), 3734 (w), 3665 (w), 3419 (m), 2480 (m), 2343 (m), 1447 (s), 1075 (m), 859 (s), 721 (m).
6	Hg- Complex	3745 (w), 3781 (w), 3663 (w), 3587 (m), 3547 (m), 3513 (m), 3381 (m), 3191(m), 2855 (m), 1512 (s), 1458 (s), 582 (s).
7	Cr-Complex	3667 (w), 3610 (w), 3550 (m), 3501 (m), 3342 (m), 3124 (m), 1645 (m), 1510 (s), 1354 (s), 1085 (m), 847 (m), 477 (s).

All the metal complexes (1-6) have been screened for their antibacterial activity against *Bacillus* species and the results obtained are shown in Table-3. A comparison of zone of inhibition for the extracts, complexes, salts and solvents indicates that the complexes of Hg and Ni have exceptionally good antibacterial activity (zone of inhibition 6.2 and 6.0 mm, respectively), as compared to plant extract (zone of inhibition 1.1 mm). The complexes of Cr, Zn and Mn showed intermediate antibacterial effect (zone of inhibition 4.0-5.4 mm).

TABLE-3
ANTIBACTERIAL ACTIVITY DATA OF METAL COMPLEXES AGAINST *Bacillus* SPECIES

No.	Zone of Inhibition (mm)				
	Component	Extract	Salt (M-Cl)	Solvent	Complex
1	Mn-Complex	1.1	0	4.5	5.6
2	Zn-Complex	1.1	1.6	4.5	5.6
3	Cu-Complex	1.1	2.9	4.5	5.4
4	Hg-Complex	1.1	3.2	4.5	6.2
5	Cr-Complex	1.1	1.5	4.5	5.8
6	Ni-Complex	1.1	1.7	4.5	6.0

Table-4 shows the results of antifungal activity of the complexes as compared to plant extract. It reveals that complexes of Hg, Ni and Zn possess excellent antifungal activity (zone of inhibition 5.0 mm) as compared to the plant extract (zone of inhibition 1.5 mm), while the complexes of Cr and Mn have intermediate antifungal activity (zone of inhibition 4.8 and 4.6 mm, respectively).

TABLE-4
ANTIFUNGAL ACTIVITY DATA OF METAL COMPLEXES AGAINST *Rhyzopus oligosporus*

No.	Zone of inhibition (mm)				
	Component	Extract	Salt (M-Cl)	Solvent	Complex
1	Mn-Complex	1.5	1.1	4.0	4.6
2	Zn-Complex	1.5	2.0	4.0	5.0
3	Cu-Complex	1.5	3.0	4.0	4.5
4	Cr-Complex	1.5	2.2	4.0	4.8
5	Ni-Complex	1.5	2.1	4.0	5.0
6	Hg-Complex	1.5	1.3	4.0	5.0

Overall it has been observed that all the metal complexes have higher antimicrobial activity as compared to simple plant extract (Figs. 1 and 2). This enhancement in antibacterial activity of these metal complexes can be explained on the basis of chelation theory[18]. When a metal ion is chelated with a ligand, its polarity will be reduced to a greater extent due to overlap of ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further the chelation process increases the delocalization of π-electrons over the whole chelate ring which results increases the lipophilicity of metal complexes. Consequently the metal complexes can be easily penetrated into the lipid membranes and block the metal binding sites of micro-organisms enzymes. These metal complexes also affect the respiration process of the cell and thus block the synthesis of proteins, which restrict further growth of organism.

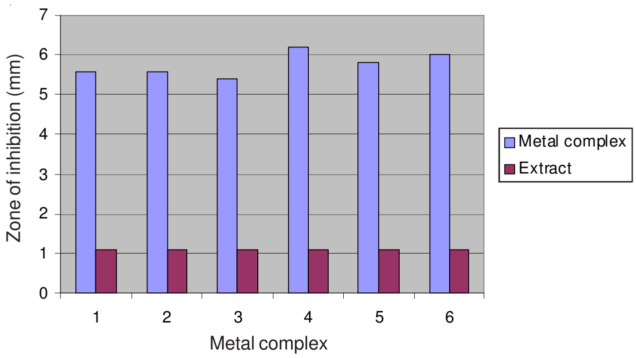

Fig. 1. Comparative antibacterial activity of metal complexes with reference to extract against *Bacillus* species (1) Mn-complex, (2) Zn-complex, (3) Cu-complex, (4) Hg-complex, (5) Cr-complex (6) Ni-complex

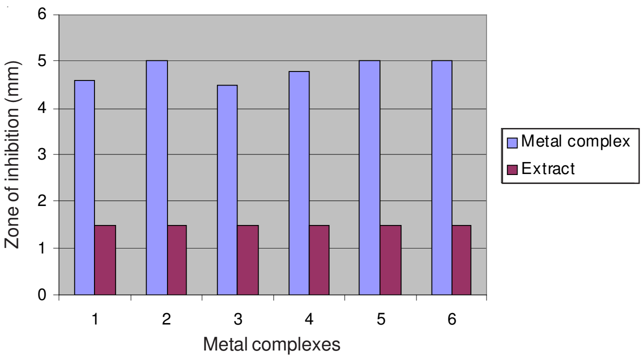

Fig. 2. Comparative antifungal activity of metal complexes with reference to extract against *Rhyzopus oligosporus* (1) Mn-complex, (2) Zn-complex, (3) Cu-complex, (4) Cr-complex, (5) Ni-complex (6) Hg-complex

Conclusion

Above results clearly indicate that the complexes formed from toxic extract from *Croton sparsiflorus* have better inhibitory effect on microbes as compared to the pure plant extract.

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