Int. J. Chem. Sci.: 10(1), 2012, 143-149
ISSN 0972-768X
www.sadgurupublications.com

SYNTHESIS, SPECTROSCOPIC AND FUNGICIDAL STUDIES OF COPPER SOAPS DERIVED FROM MUSTARD AND SOYABEAN OILS AND THEIR UREA COMPLEXES

RASHMI SHARMA, MEENAKSHI SAXENA and NISHA SHARMA[a]

Department of Chemistry, S.D. Govt. College, BEAWAR – 305901 (Raj.) INDIA
[a]Department of Botany, S.D. Govt. College, BEAWAR – 305901 (Raj.) INDIA

ABSTRACT

Colloidal surfactants have become one of the most important requirements in day to day life, and have great importance in modern engineering and pharmacological fields. Copper soaps derived from mustard and soyabean oils and their urea complexes have been synthesized using direct metathesis. The synthesized copper soaps and their urea complexes have been confirmed by UV, IR, NMR and ESR spectral analysis. The antifungal activities of copper soaps derived from mustard and soyabean oils and their urea complexes have been evaluated by testing against *Alternaria alternata* and *Aspergillus niger* at different concentrations by agar plate technique. The effect of solvent has been excluded by complete evaporation. It has been observed that the activity increases with the increase in the concentration of the solution. It has been observed that complexes show higher activity than pure soaps, which suggests that complexes are more powerful antifungal agent. The toxicity of copper soaps and their urea complexes are found in the order:

CSoU > CSo

CMU > CM

Key words: Copper surfactants, Anti-fungal studies, IR, NMR, ESR, Edible oils.

INTRODUCTION

Copper soaps derived from edible oils i.e. mustard and soyabean (CM & CSo) play a vital role in various fields due to their surface active properties[1,2]. These oils were particularly chosen as they are easily available commercially and biodegradable in nature. Copper soaps have a tendency of complexation with ‘nitrogen’ and ‘sulphur’ containing ligands. Using urea as a ligand, complexation of synthesized copper soaps have been done to

*Author for correspondence; E-mail: avinash_1965@yahoo.co.in, apurvasaxena06@gmail.com

obtain their urea complexes (CMU & CSoU). Since copper metal is toxic in nature, literature survey reveals that the synthesized copper soaps and their urea complexes may play a significant role in biological activities and have sufficient pharmaceutical, industrial and analytical applications[3-5]. Biocidal studies have been done to asses their comparative toxicity on two easily available fungi *Alternaria alternata* and *Aspergillus niger*.

The studies lead us to the conclusion that copper soap derived from mustard and soyabean oils and their urea complexes may play a significant role in various fields of industries,wood preservation, agrochemical etc[6,7].

EXPERIMENTAL

Copper soaps derived from mustard and soyabean oils and their urea complexes have been synthesized and studied for structural aspects. All chemicals used were of LR/AR grade. Oils were procured directly from the seeds of mustard and soyabean (pure) oils were taken from the market of a reputed brand. The fatty acid compositions of these edible oils[8] were confirmed through GLC of their methyl esters (Table 1). Copper soaps were prepared by refluxing the edible oils i.e. mustard and soyabean oils in their pure form with 2N KOH solution and alcohol for about 3 hr (direct metathesis).The neutralization of excess KOH present was done by 1N HCl. Saturated solution of copper sulphate was then added to it for conversion of neutralized soap into copper soap. Copper soap so obtained was then washed with hot water and dried. The soap was recrystalized using hot benzene. Metal was analyzed by standard procedure (iodometrically). The purified copper soaps derived from edible oil was refluxed with ligand urea in 1 : 1 ratio using benzene as a solvent for one hour. It was then filtered, hot dried; and then recrystallized and purified in hot benzene. The formation of copper soaps and complexes was confirmed by using UV, IR, NMR techniques and elemental analysis. TLC using silica gel was used to check the purity of the soaps and complexes.

In general, copper soaps and complexes are green in colour and soluble in benzene and other organic solvents but insoluble in water. All the soaps and complexes are stable at room temperature. Their physical parameters are reported in Table 2. On the basis of their elemental analysis, 1 : 1 (metal: ligand) type of stoichiometry has been suggested.

In order to study the structure of soaps and complexes, the infra-red (IR) absorption spectra of compounds were obtained on a Perkin-Elmer 5100, 4367 spectrophotometer (4000-200 cm^{-1}) at RSIC, IIT powai, Mumbai. ESR data were also obtained from RSIC, IIT powai Mumbai. ^{1}H NHR are recorded at CSMRI, Bhavnagr, using C_6D_6 as reference. The structures of their urea complexes have been confirmed by using IR, NMR, and ESR technique. The antifungal activities of copper soaps and their urea complexes have been evaluated by testing against two easily available fungi *Alternaria alternata* and *Aspergillus niger,* which was isolated from natural habitat (plants debris) and then purified, characterized and identified. The antifungal activity of copper soaps and their urea complexes were checked by the agar plate technique[10]. The culture medium used for the growth of the organism was natural media i.e. P. D. A. The microscopic photograph diagram of fungi *Aspergillus niger* are shown in Fig. 1. The solution was prepared in ppm of different concentrations (i.e. 10^3 and 10^4 ppm) in methanol-benzene mixture. The effect of solvent has been excluded by complete evaporation. After the solidification the above medium and evaporation of solvent, single fungal hypha/spore were isolated and transferred on agar slants (1%) for multiplication.

After the period of incubation i.e. for 72 hours at $30 \pm 1^{o}C$, the growth of the fungus was measured. The data was statistically analyzed according to the following formula :

$$\% \text{ Inhibition} = \frac{C - T}{C} \times 100 \qquad \ldots(1)$$

Where C = Total area of fungal colony in control plates after 72 hours and T = Total area of fungal colony in test plate after 72 hours.

RESULTS AND DISCUSSION

The percentage fatty acid composition of oils used for copper soap's synthesis is given in Table 1. In the IR spectra of copper soaps a band in the region 750-450 cm^{-1} is due to copper-oxygen (Cu-O) bond, which is characteristic of absorption of metal constituent of each soap molecules, whereas a strong band appears in the region 2970-2840 cm^{-1} confirms the methyl groups in acids of various chain lengths. The low value of magnetic moment for copper ion present in copper soap i.e. 1.9-2.5 B.M. suggests that a binuclear configuration exists in soap solution as follow :

$$Cu_2 (RCOO)_4L_2$$

where R-represents fatty acid composition (Table 1) and L represents the ligand. In the NMR spectra of copper soap–urea complexes, a peak observed at δ-3.2-4.2 confirms the –NH_2 group of urea segment to the metal atom of the soap segment. The antifungal activities of copper soaps and their urea complexes for both the fungi i.e. *Alternaria alternata* and *Aspergillus niger* were checked by agar plate technique. The results of the fungicidal screening data are recorded in Tables 2 and 3. Graphical representations are also shown in Figs. 2 and 3 which suggest that urea complexes of copper soaps show higher activity than pure soaps. It means that complexes are more powerful antifungal agents and N, S, O, etc. containing compounds are able to enhance the performance of copper soaps i.e.

CSoU > CSo

CMU > CM

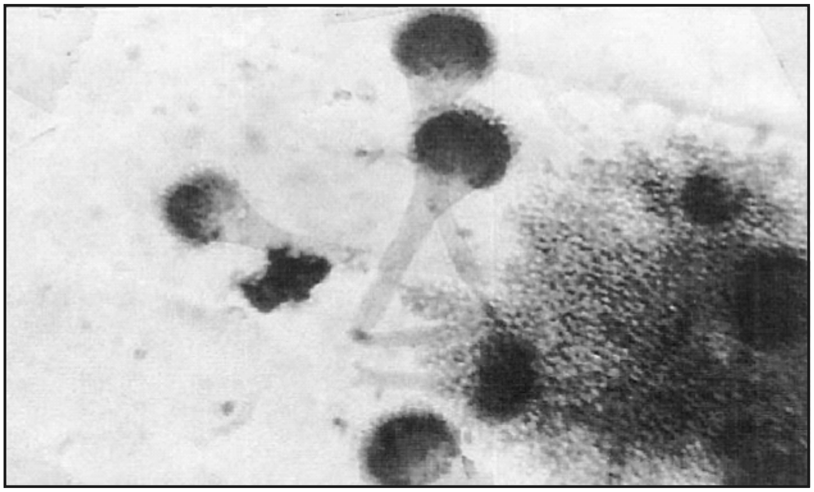

Fig. 1: Microscopic photograph diagram of *Aspergillus niger*

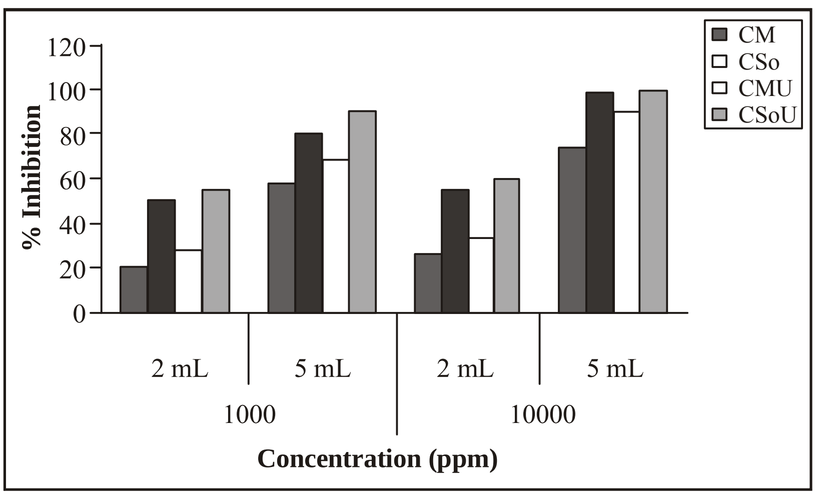

Fig. 2: Antifungal activity of copper (II) soap and their urea complexes for *Alternaria alternate*

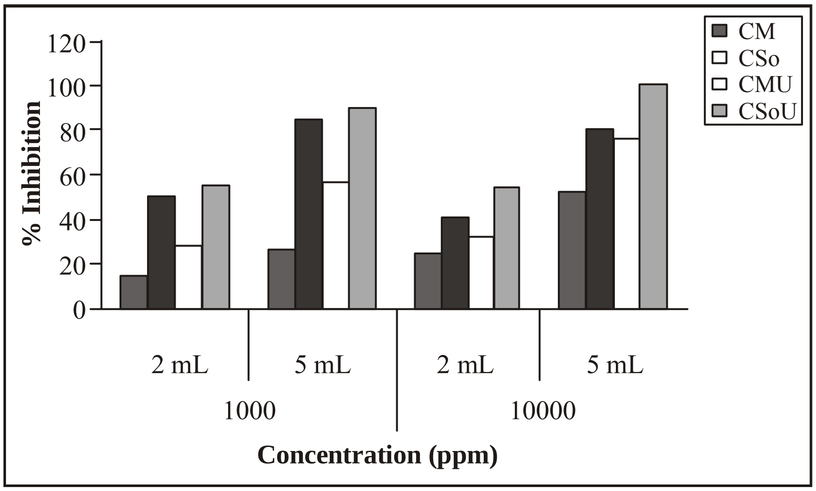

Fig. 3: Antifungal activity of copper (II) soap and their urea complexes for *Aspergillus niger*

The copper soaps and urea complexes have significant fungitoxicity at 10^4 ppm but their toxicity decreases markedly on dilution (10^3 ppm). Their comparative order is as follow:

$$10^3 \text{ ppm} < 10^4 \text{ ppm}$$

Thus, concentration plays a vital role in increasing the degree of inhibition. Also, on increasing the amount of solution from 2 mL to 5 mL, the % inhibition increases suggesting that the % inhibition is affected by the increase in the concentration of the active fungicidal moiety in the analyzed system. Previous studies by various scientists show that enhanced activity of complexes may be due to synergistic mechanism[11] i.e. the free soaps are less active but on complexation, they show more activity in combination with ligands containing 'N' atoms. The toxicity of copper soaps and their urea complexes are as follow :

CSo > CM

CSoU > CMU

In general, CSo and their urea complexes CSoU both are more potent (more toxic) than copper mustard soap (CM) and their urea complexes (CMU). These observations suggest that soap and complexes derived from soyabean oils containing more polyunsaturation and content of shorter fatty acids are more active than soaps and complexes derived from mustard oil containing longer fatty acid content and less unsaturation. All the above results indicate that 'nitrogen' and 'oxygen' containing ligands enhance the fungicidal activity of the soap molecule. These studies will play a significant role in selection and promotion of eco-friendly and biodegradable fungicides, pesticides and insecticides.

Table 1: Fatty acid composition of oils used for copper soap/complex synthesis

Name of oil	% Fatty acid					
	16 : 0	18 : 0	18 : 1	18 : 2	18 : 3	Other acids
Mustard oil	2	1	25	18	10	(C_{20}–C_{22}) – 41%
Soyabean oil	12	4	24	51	9	--

Table 2: Antifungal activity of copper (II) soap and their urea complexes for A*lternaria-alternata*

Name of the soap & complexes	Average % inhibition after 3 days			
	Concentration (ppm)			
	1000		10000	
	2 mL	5 mL	2 mL	5 mL
CM	19.75	58.36	25.50	74.35
CSo	50.56	80.77	54.34	98.50
CMU	28.00	68.28	32.75	89.77
CSoU	54.36	90.00	60.50	100.00

Table 3: Antifungal activity of copper (II) soap and their urea complexes for *Aspergillus niger*

Name of the soap & complexes	Average % inhibition after 3 days			
	Concentration (ppm)			
	1000		10000	
	2 mL	5 mL	2 mL	5 mL
CM	15.38	25.68	24.42	52.06
CSo	51.26	85.56	40.45	80.00
CMU	27.97	56.56	32.69	75.00
CSoU	55.36	89.89	54.35	100.00

ACKNOWLEDGEMENT

The authors would like to thank UGC for financial support, Principal and Head of Department of Chemistry, S.D. Govt. College, BEAWAR for providing Laboratory Facilities.

REFERENCES

1. R. Sharma and S. Khan, RPMP Natural Products, **18**, 429 (2007).
2. M. R. K. Sherwani, R. Sharma, A. Gangwal and R. Bhutra, Indian J. Chem., **42A**, 2527 (2003).
3. N. Singh, N. K. Sangwan and K.S. Dhindsa, Pest Management, Sci., **56**, 28 (2000).
4. G. N. Mukherjee and A. Das, J. Indian Chem. Soc., **78**, 78 (2001).
5. K. N. Mehrotra, V. P. Mehta and T. N. Nagar, Cellulose Chem. Technol., **1**, 38 (1973).
6. Crop. K. Kokai Tokyo Koho JP, **59**, 193, 129, 18 Apr. (1983).
7. J. L. Soyez, Brighton Crop Protection Conference on Pest and Diseases, France, **1**, 451 (1992).
8. F. D. Gunstone, in Introduction to the Chemistry of Fats and Fatty Acids, Chapman and Hall Ltd., London (1985).
9. A. I. Vogel, A Text Book of Qualitative Inorganic Analysis, 4th Edition, Longman, London (1985).
10. J. G. Horsfall, Bot. Rev., **11**, 375 (1945).
11. D. K. Singh, S. Singh and M. Shrivastava, J. Indian Chem. Soc., **82**, 250 (2005).

Accepted : 14.05.2011