## SYNTHESIS AND PHYSIOLOGICAL ACTIVITY OF NEW SCHIFFBASES OF DEHYDROACETIC ACID AND THEIR METAL CHELATES*

SCHIFFBASES play a prominent role in modern coordination chemistry, in view of their excellent chelating capacities and biological applications[1]. Acid hydrazides are well known for their antituberculous activity apart from their extensive use in agriculture and industry[2-4]. On the other hand thiosemicarbazide and thiosemicarbazones have attracted special attention due to their activity against viruses, protozoa, smallpox and certain kinds of tumour[5-7]. In a previous communication[8], we have reported the potential fungitoxicity of some transition metal chelates derived from dehydroacetic acid [3-acetyl, 6-methyl, 2H-pyran-2,4 (3H) dione] (I), against *Rhizoctonia solani*. With a view to prepare schiffbases of dehydroacetic acid which will have potential biological importance, we have synthesised dehydroacetic acid benzoyl hydrazone (DBH) (II *a*), dehydroacetic acid salicyl hydrazone, (DSH) (II *b*), and dehydroacetic acid thiosemicarbazone, (DTS) (II *c*). These schiffbases were synthesised by the procedure of Mahesh and Gupta[9] and characterised by analytical and infrared data. These schiffbases were found to be excellent chelating agents, precipitating metal ions in quantitative yield. Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes have been synthesised and characterised. The metal chelates are stable to air and moisture, decompose at higher temperature, insoluble in common organic solvents, indicating their dimeric or polymeric nature. Infrared spectra of the schiffbases and complexes have indicated that these schiffbases act as monobasic and dibasic tridentate ligands with O : N : O and O : N : S donor sequence. Structural elucidation of these complexes will be described elsewhere. The schiffbases as well as their corresponding metal chelates were screened *in vitro* for their biological activity against *Sarocladium oryzae* and *Xanthomonas oryzae*, the causative organisms of 'sheath rot' and 'bacterial leaf blight' in rice plants respectively and found to be potentially toxic. The activity of some of these chelates is good in comparison with commercial pesticides.

### *Experimental*

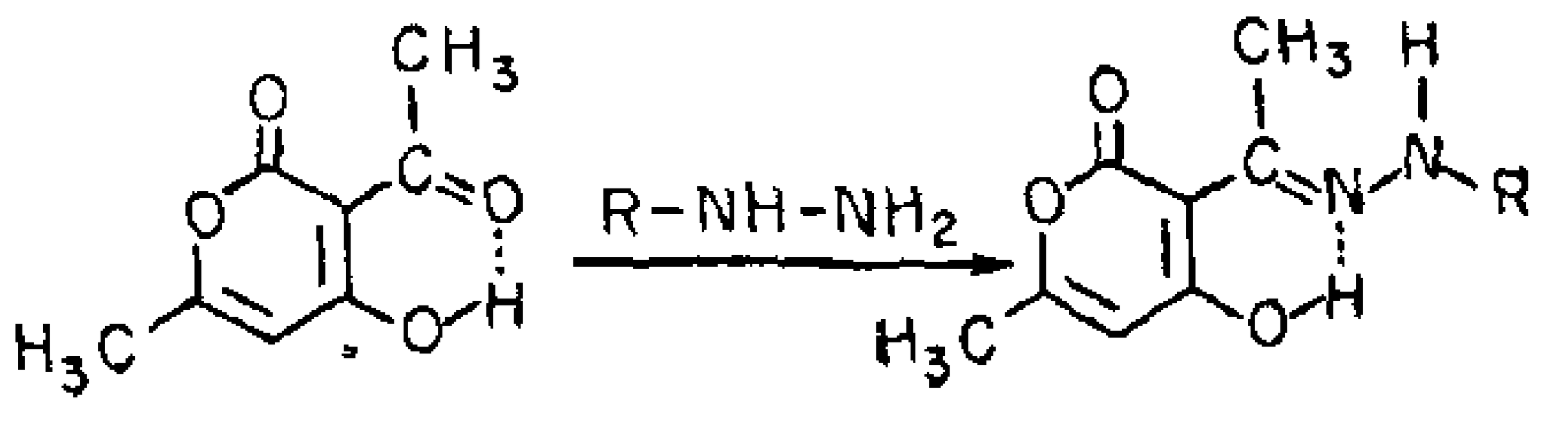
Dehydroacetic acid (0·05 mole) was separately refluxed with benzoyl hydrazide (0·05 mole), salicyl hydrazide (0·05 mole) and thiosemicarbazide (0·05 mole) in methanol for about an hour, under normal conditions[9]. The products, II *a–c* separated during reflux were filtered and recrystallised from EtoH–DMF as yellow shining crystals in 50–60% yield.

*Dehydroacetic acid benzoylhydrazone*(*II a*) : m.p. 207–8° C (found C, 62·91, H, 4·87, N, 9·75; calculated for $C_{16}H_{14}O_4N_2$ C, 62·94, H, 4·90, N, 9·79); $IR^{KBr}_{\nu_{max}}$ : 3375 (–OH) 1685 (>C=O of lactone) 1630 (>C=O) 1605 (>C=N).

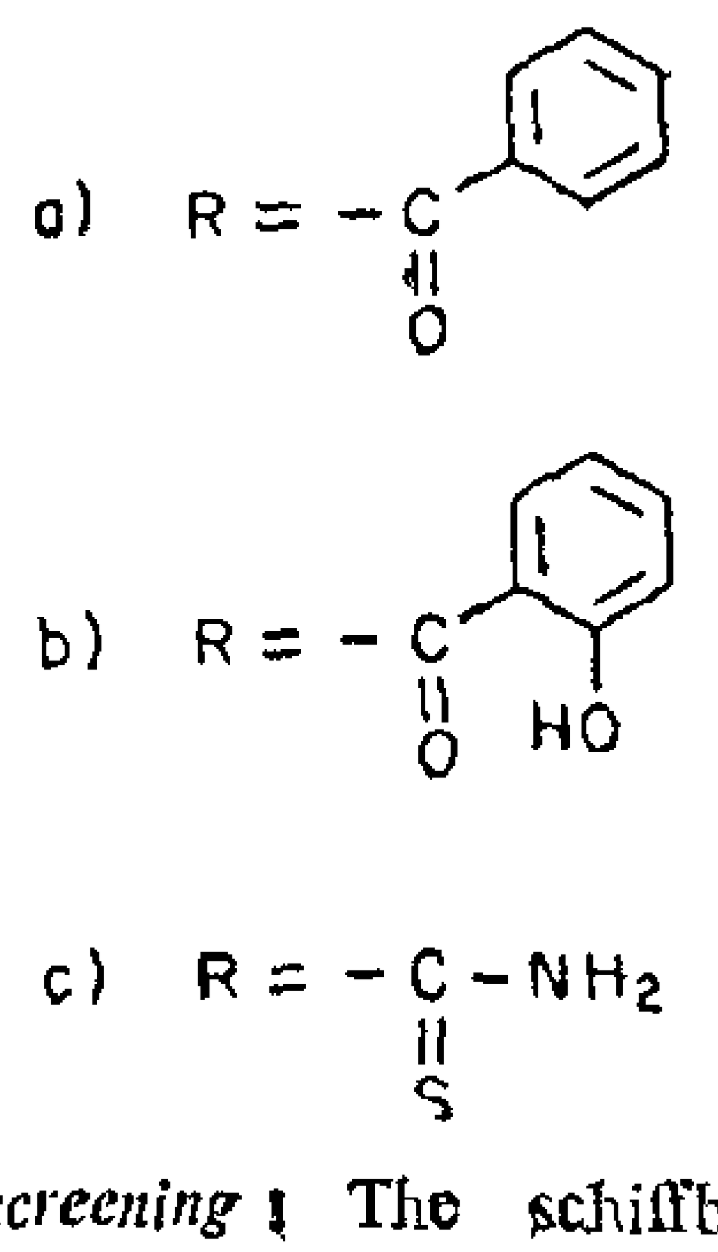
*Dehydroacetic acid salicyl hydrazone* (*II b*) : m.p. 236–8° C (found C, 59·32, H, 4·91, N, 9·19; calculated for $C_{16}H_{15}O_5N_2$ C, 59·41, H, 4·95, N, 9·24); $IR^{KBr}_{\nu_{max}}$ : 3375 (-OH) 1685 (>C=O of lactone) 1635 (>C=O) 1608 (>C=N).

*Dehydroacetic acid thiosemicarbazone* (*II c*) : m.p. 190–1° C (found C, 44·23, H, 4·50, N, 21·56, S, 13·10; calculated for $C_{10}H_{11}O_3N_3S$, C, 44·81, H, 4·56, N, 21·58, S, 13·27); $I.R.^{KBr}_{\nu_{max}}$ : 3360 (–OH) 1675 (>C=O of lactone) 1,600 (>C=N) 760 (>C=S).

The metal chelates were synthesised by mixing clear solutions of A.R. metal chlorides (0·01 mole) and sodium salts of the ligands (0·02 mole) in aqueous medium. The precipitation is almost instantaneous and quantitative. The metal chelates were filtered, washed with distilled water followed by solvent ether and dried in vacuum.




I II (a–c)




*Biological screening* : The schiffbases and their corresponding metal chelates were screened *in vitro* for their biological activity by adopting inhibition zone technique[10]. Four day old culture of *Sarocladium oryzae* was employed in potato dextrose agar (PDA) medium for fungicidal test. For bactericidal test two day old culture of *Xanthomonas oryzae* was used in Hayward medium. The replications in each case were three. The schiffbases exhibited toxicity in the range of 800–1,000 ppm. Due to synergistic combination of the coordinated metal ions with the ligands, the toxicity has been augmented to a great extent and the metal chelates showed toxicity in the range of

50–500 ppm. The Cu(II) chelate of IIc exhibited maximum toxicity. The toxicity of the metal chelates was found to be generally in the following order Cu > Ni > Zn > Fe > Mn > Co.

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## RECOGNITION OF SHORT JUVENILITY IN *PONCIRUS*

THE presence of a long juvenile period of seven to eight years in *Poncirus* and *Citrus* is a major handicap in quick evaluation of hybrid progenies. Attempts made in the past to shorten the juvenility by the use of chemicals have met with no success while regulation of temperature and photoperiod resulted in temporary breakdown of juvenility of 9 to 18 month old seedlings of grape fruit[1]. Furr *et al.*[2], also observed terminal flowering in 18 months old grape fruit which did not persist but reverted back to juvenile phase again. No published evidence is available to show the appearance of short juvenility in *Poncirus*. Therefore, in this note, we report about the short juvenility in *Poncirus* which has been identified and selected at this station.

In a survey, during 1975, at Horticultural Experiment Station, Chethalli, three (nine months old) seedlings of trifoliate orange [*Poncirus trifoliata* (L) Raf.] were found flowering. They produced perfect axillary flowers which set fruit but the fruits dropped off after 15 days. These plants were then transplanted to the main field for further observations. During the succeeding season (1976) two seedlings reverted back to juvenile phase while one continued flowering and produced fruits (Fig. 1). One of the interesting features in this seedling is that this keeps on flowering even during off seasons when other trifoliate plants remain dormant.

FIG. 1

A comparison of some characters of this short juvenile seedling with juvenile seedling and its fruiting behaviour through three successive years are presented in Table I. It is evident that this precarious seedling was slow in growth and had continuous flowering and fruiting. From the fruiting behaviour it is evident that short juvenility recognized by us is different from the one observed by Furr *et al.*[2]. The plant isolated at this station has given continuous flowering which shows that it is not due exclusively