

TABLE II
Some IR bands of AZM, AZSB, AZH and their metal chelates

Ligand	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Assignment
~ 3600	3600	3600	3600	3600	3600	ν_{NH_2}
~ 3400	3200	3220	3250	3250	3300	ν_{OH} (bonded)
1610-1635	1570	1580	1585	1585	1600	$\nu_{\text{C=O}}$ (bonded)
1500	1500	1500	1500	1500	1500	δ_{NH}
1435-1460	1410	1420	1425	1425	1430	δ_{OH} (bonded)
~ 1270	1250	1255	1260	1260	1265	δ_{CH}

The important I.R. band frequencies for the free ligands and their metal chelates are given in Table II. The bands corresponding to the ν_{OH} become broadened, less intense and suffer a frequency shift when the ligand is bonded to the metal ions to give the chelates. All the spectra of the metal chelates show an overlap of the bonded $\nu_{\text{C=O}}$ with $\nu_{\text{C=C}}$ near 1600 cm^{-1} and a red shift is observed. This indicates that the quinone structure is influenced by the substituents; that is to say it lowers the C=O character and increases the C-C bond order. The intensity of the bands due to δ_{OH} decreases apparently due to the displacement of a proton from the α -OH group on complex formation.

From the foregoing results as well as those obtained from the elemental analysis of the solid chelates, we conclude that the reaction between the metal ions and the complexing agents under investigation occurs via the formation of a covalent linkage with the oxygen of the α -OH group and the carbonyl group.

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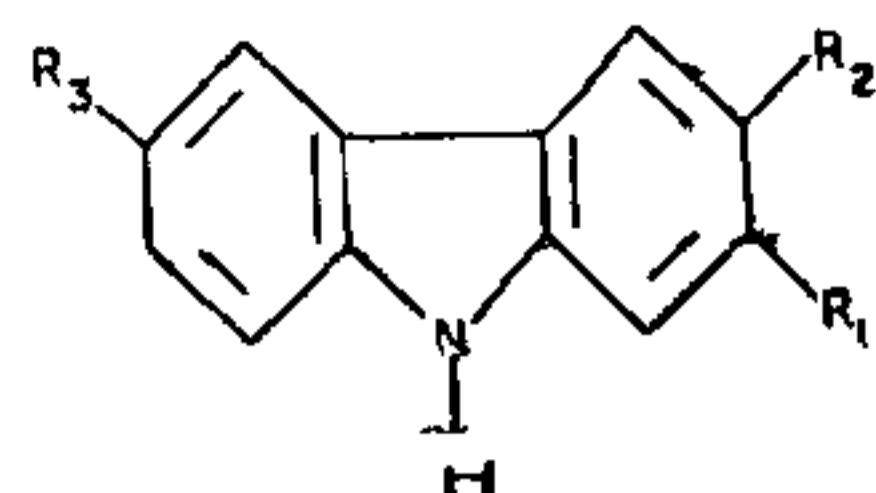
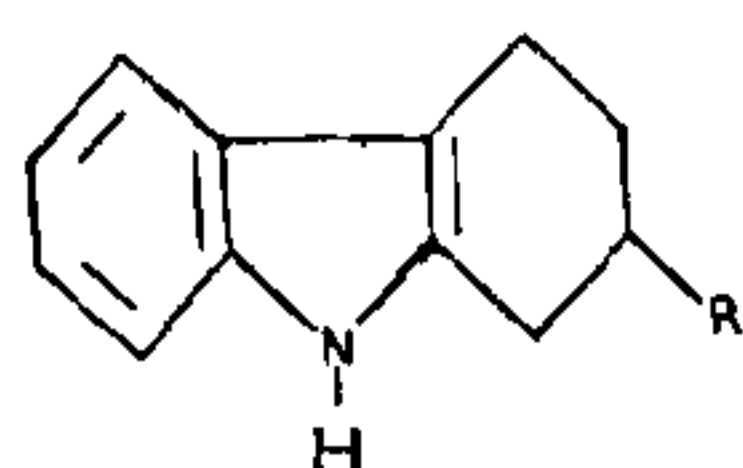
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INVESTIGATION ON THE TOXICITY OF SOME CARBAZOLE DERIVATIVES AND PLANT EXTRACTS

PREVIOUS studies on the insecticidal properties of carbazole derivatives¹ revealed that tetrahydrocarbazole, 2-methyl tetrahydrocarbazole and 3-methyl tetrahydrocarbazole are more toxic to houseflies (*Musca domestica* L.) than the corresponding carbazoles. Such high toxicity of tetrahydrocarbazole derivatives is due to the presence of partially reduced carbazole moiety¹. This¹ interested us to study the toxicity of tetrahydrocarbazole(I), carbazole(III), glycozoline(IV) and glycozolidine(V) (carbazole alkaloids), along with extract of root-bark of *Glycosmis pentaphylla* (Retz) DC (which contains two carbazole alkaloids—glycozoline and glycozolidine) on mosquito larvae (*Culex* Sp.). The percentage of mortality of house-flies (*Musca domestica* L.) at different concentrations of tetrahydrocarbazole(I) and 2-methyl tetrahydrocarbazole(II) are also presented in this communication.

Tetrahydrocarbazole(I) and 2-methyl tetrahydrocarbazole(II) were prepared by Borsche method described previously¹. The dried and powdered root-bark of *Glycosmis pentaphylla* (Retz.) DC was extracted with benzene in a Soxhlet for 48 hours. The benzene extract was freed from solvent and used for toxicity tests on mosquito larvae. The neutral mass of this extract (after the separation of acidic and basic constituents by washing with alkali and acid respectively) was also used for toxicity tests. Glycozoline²(IV) and glycozolidine³(V) were isolated from the neutral mass of the benzene extract of the root-bark of *Glycosmis pentaphylla* (Retz.) DC. by chromatography and characterised in the usual way.



(I) $R = H$; (II) $R = CH_3$; (III) $R_1 = R_2 = R_3 = H$; (IV) $R_1 = H$, $R_2 = CH_3$, $R_3 = OCH_3$; (V) $R_1 = OCH_3$, $R_2 = CH_3$, $R_3 = OCH_3$.

Toxicity tests on Mosquito larvae :

Toxicity tests on mosquito larvae (*Culex*. Sp.) were performed with 0.5% ethanolic solution of carbazole, tetrahydrocarbazole, glycozoline, glycozolidine, benzene extract of the root-bark of *Glycosmis pentaphylla* (Retz) DC. and the neutral mass obtained therefrom (which contains carbazole derivatives). The ethanolic solution (1.5 ml) of the above substances were sprayed on the mosquito larvae in 50 ml of water. Five replications were made for each compound. Ethanol was used as control. Results are presented in the Table I.

TABLE I

Treatment	Concentration in gm/100 ml	% of mortality mean
Tetrahydrocarbazole(I)	0.5	100 (90)*
Carbazole (III)	0.5	8.68 (17.16)
Glycozoline (IV)	0.5	1.33 (6.55)
Glycozolidine (V)	0.5	3.89 (11.39)
Benzene extract of the root-bark of <i>Glycosmis pentaphylla</i> (Retz) DC.	0.5	11.07 (19.46)
Neutral mass from the above benzene extract	0.5	88.79 (70.45)
Ethanol (Control)	..	1.11 (6.02)

F value	84.08 (Significant at 1% level)
CD at 1%	15.76
at 5%	11.63

* Figures in the brackets represent angular transformation.

From the above data, it is evident that tetrahydrocarbazole and the neutral mass from the benzene extract of root-bark of *Glycosmis pentaphylla* (Retz) DC are toxic to mosquito larvae (*Culex* sp.). The

toxicity of tetrahydrocarbazole is greater than the neutral mass. But naturally occurring carbazoles, viz., glycozoline, glycozolidine and carbazole are not toxic. Therefore, the neutral mass from the benzene extract of root-bark of *Glycosmis pentaphylla* (Retz) DC. may contain some other toxic constituent.

Toxicity tests on house-flies :

Toxicity tests on house-flies (*Musca domestica* L.) at different concentrations were carried out by Spraying Method developed in our Laboratory¹.

Table II shows that the percentage of mortality increases as the concentration increases. The graph drawn by concentration against % of mortality is a straight line (Fig. 1). No synergistic activity of tetrahydrocarbazole with pyrethrum extract was found.

TABLE II

The mortality of house-flies after 24 hours interval in tetrahydrocarbazole at different concentrations

Compound	Concentration in gm/100 ml	% of mortality Mean
Tetrahydrocarbazole (I)	0.5	78.88 (62.65)*
do	0.4	65.94 (54.27)
do	0.3	45.06 (42.19)
do	0.2	36.42 (37.11)
do	0.1	16.32 (23.81)
do	0.05	15.16 (22.95)
do	0.02	8.76 (17.26)
Ethanol (Control)		7.55 (16.00)
F value	30.60 (Significant at 1% level)	
CD at 1%	12.92	
CD at 5%	9.50	

* Figures in the brackets represent angular transformation.

Table III shows that the percentage of mortality gradually increases as the concentration increases, but it is more or less the same from 0.2 to 0.4%, which is evident from the graph (Fig. 1).

During our previous investigation¹, we noticed that tetrahydrocarbazoles are more toxic to house-flies than the corresponding carbazole derivatives. The present investigation also shows that tetrahydrocarbazole is toxic to mosquito larvae (*Culex* sp.), while carbazole is not. This is due to the presence of partially reduced ring of the carbazole moiety.

TABLE III

The mortality of house flies after 24 hours interval at different concentrations of 2-methyl tetrahydrocarbazole

Compound	Concentration in gm/100 ml	% of mortality Mean
2-Methyl-tetrahydrocarbazole (II)	0.5	85.5 (67.62)*
do.	0.4	75.1 (60.07)
do.	0.3	74.0 (59.34)
do.	0.2	73.8 (59.12)
do.	0.1	39.8 (39.11)
do.	0.05	32.7 (34.88)
do.	0.02	29.1 (32.65)
do.	0.01	21.0 (27.28)
Ethanol (Control)		7.6 (16.00)

F value	29.4
	(Significant at 1% level)
CD at 1%	19.44
CD at 5%	15.12

* Figures in the brackets represents angular transformation.

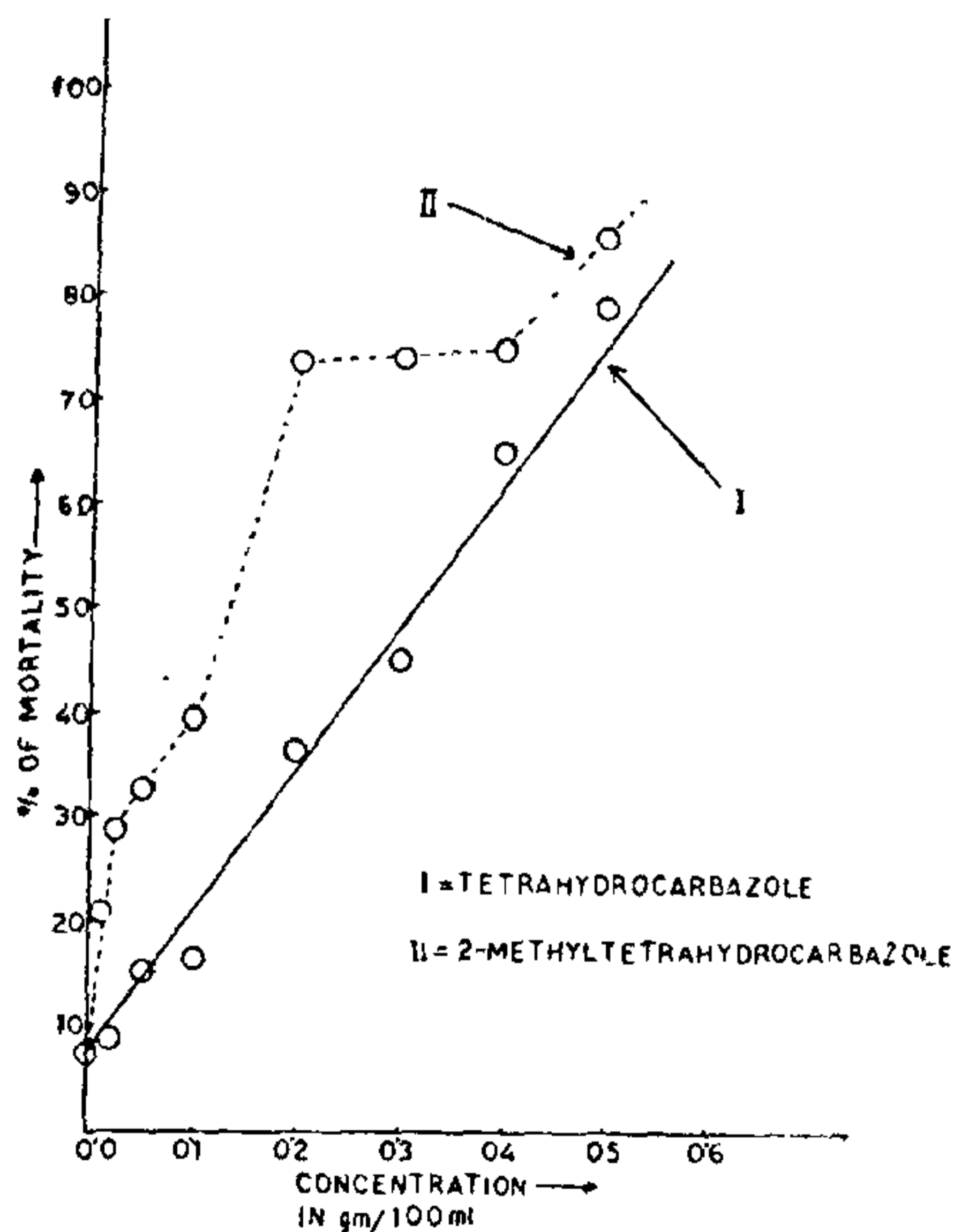


FIG. 1. Concentration-mortality relationship of house-flies (*Musca domestica* L.) in tetrahydrocarbazole and 2-Methyl tetrahydrocarbazole.

The authors are thankful to CSIR, New Delhi, for the award of Junior Research Fellowship to DNC. and also to UGC, New Delhi, for financial assistance to the Senior author (B. P. D.).

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SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN ALLOYS WITH SALICYLALDEHYDE HYDRAZONE

SALICYLALDEHYDE hydrazone has been recommended as a spectrophotometric reagent and its various complexes with bivalent metal ions have been isolated¹⁻³. It forms a yellow coloured complex with copper (II) at room temperature in the pH range 7.5 to 8.7. The complex shows maximum absorbance at 400 nm. In the present study, attempts have been made for the micro determination of copper (II) spectrophotometrically in alloys.

Experimental

Salicylaldehyde hydrazone (SH) was synthesised by refluxing salicylaldehyde (1 mole) with hydrazine hydrate (anhydrous 1 mole) in ethanolic medium for about 4-6 hours. The crude compound thus obtained was recrystallized from ethanol to get bright yellow flakes (m.p. 97°C). The purity of SH was checked by thin layer chromatography and elemental analysis. Calcd. C, 61.76%; H, 5.88%; N, 20.58%; Found: C, 61.6%; H, 5.8%; N, 20.2%. Acetone solutions of the ligand were used.

Solutions of metal ions were standardised by conventional methods. Absorbance was measured with a Unicam SP 600, spectrophotometer, with 10 mm matched glass cells.

Results and Discussion

Physico-chemical characteristics of the complex

The absorbance of the Cu (II)-(SH) (1:1) complex was found to remain constant at λ_{max} 400 nm in the pH range 7.5 to 8.7. For complete development of the colour, 30 times molar excess of the reagent per mole of copper (II) is required. The colour reaction obeys Beer's law up to 5.6 ppm of copper and the optimum range of concentration for accurate determination of copper, obtained from Ringbom's plot is