

Synthetic Resin. IX. Preparation and Characterization of Resins Prepared from Resacetophenone, Quinacetophenone/ Aromatic Hydroxy, Amino and Chloro Compounds/Formaldehyde

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Synopsis

A number of new resins were synthesized from 2,4-dihydroxyacetophenone and 2,5-dihydroxyacetophenone by reaction with substituted hydroxy, amino, and chloro compounds and formaldehyde in presence of various acids and bases as catalyst. The resins were characterized by IR spectra. The solution and chemical properties of the resins were investigated. The solubility parameter was calculated from Small's and Hoy's group contribution methods. The fungicidal properties of the resins synthesized have been evaluated.

INTRODUCTION

The synthesis of resins from hydroxy aromatic substrates like acetophenone, phenacyl bromide, and chalcones has attracted attention¹⁻⁸ in recent years because of their antifungal, antibacterial, and other biomedical applications. We have reported⁹⁻¹³ the synthesis and characterization of resin copolymers from hydroxy aromatic compounds. This communication presents the physico-chemical properties of some resins prepared from substituted hydroxy compounds like 2,4-dihydroxyacetophenone and 2,5-dihydroxyacetophenone (Tables I and II). The fungicidal properties of some of the resins have been reported.

EXPERIMENTAL

Materials

2,4-Dihydroxyacetophenone and 2,5-dihydroxyacetophenone were prepared by Fries migration of resorcinol acetate and hydroquinone diacetate; mp 142 and 202°C, respectively. Hydroxy, amino, and chloro-substituted benzoic acids (E. Merck, India), substituted acetophenones (Sigma), and formaldehyde (B.D.H.) were used. All the solvents used were of analytical grade.

Resin Synthesis

The resins were synthesized by the following methods.

TABLE I
Physico-chemical Properties of Resins Derived from 2,4-Dihydroxyacetophenone

Serial no.	Comonomer	Catalyst	Heating time (h)	Decomposition temperature (°C)	Color	Density	Solubility	Solubility parameter (δ) ranges in solvents that are hydrogen bonded ($(\text{J}/\text{m}^3)^{1/2} \times 10^3$)		
								Weak	Moderate	Strong
1		3	4	5	6	7	8	9	10	11
1.	<i>o</i> -Hydroxybenzoic acid	HCl	8	160	Yellowish gray ^a	1.1944	THF	—	18.6-24.8	18.6-29.7
2.	<i>o</i> -Hydroxybenzoic acid	NaOH	8	300	Yellow ^a	1.241	—	—	24.6-24.8 ^b	20.7-24.8 ^b
3.	<i>o</i> -Hydroxybenzoic acid	CH ₃ COOH	8	300	Yellowish brown ^c	0.9075	—	—	18.6-24.8 ^b	18.6-24.8
4.	<i>o</i> -Hydroxybenzoic acid	Pyridine	8	300	Yellow ^a	1.0617	—	—	—	—
5.	<i>p</i> -Hydroxybenzoic acid	HCl	8	200	Brownish yellow ^c	1.042	DMF	—	19.2-24.8	21.9-24.8
6.	<i>p</i> -Hydroxybenzoic acid	NaOH	8	300	Yellowish brown ^a	0.7947	—	—	24.6-24.8 ^b	20.7-29.7
7.	<i>p</i> -Hydroxybenzoic acid	CH ₃ COOH	10	140	Brown ^c	—	THF	—	18.6-24.8	18.6-24.8
8.	<i>p</i> -Hydroxybenzoic acid	Pyridine	10	300	Pinkish white ^c	—	Pyridine	19.0-19.4 ^b	24.6-24.8 ^b	21.7-21.9
9.	<i>o</i> -Aminobenzoic acid	HCl	6	300	Gray ^c	—	DMSO	—	19.2-24.8	21.9-24.8
10.	<i>o</i> -Aminobenzoic acid	NaOH	6	300	Brown ^a	0.9714	DMSO	—	24.6-24.8	21.9-24.8
11.	<i>o</i> -Aminobenzoic acid	CH ₃ COOH	10	85	Black ^c	1.1641	Nitrobenzene	19.0-19.4 ^b	18.6-24.8	—
12.	<i>o</i> -Aminobenzoic acid	Pyridine	8	300	Yellow ^a	0.7126	—	—	—	21.7-24.8
13.	<i>p</i> -Aminobenzoic acid	HCl	10	300	Reddish brown ^a	—	—	18.8-19.0 ^b	19.2-24.8 ^b	21.9-24.8 ^b
14.	<i>p</i> -Aminobenzoic acid	NaOH	8	300	Brown ^c	—	DMSO	—	24.6-24.8	21.9-24.8
15.	<i>p</i> -Aminobenzoic acid	CH ₃ COOH	10	300	Yellowish gray ^c	1.0034	Benzyl alcohol	17.6-19.9 ^b	18.6-24.8 ^b	21.7-24.8
16.	<i>p</i> -Aminobenzoic acid	Pyridine	12	300	Yellow ^a	—	Pyridine	18.2-20.5 ^b	20.3-24.8 ^b	21.7-24.8 ^b
17.	<i>o</i> -Chlorobenzoic acid	HCl	6	105	Black ^c	0.9131	CHCl ₃	18.8-20.5	18.6-24.8	21.9-24.8
18.	<i>o</i> -Chlorobenzoic acid	NaOH	8	300	Grayish white ^a	1.6078	—	19.0	—	—
19.	<i>o</i> -Chlorobenzoic acid	CH ₃ COOH	10	—	Gray ^c	—	THF	—	18.6-24.6	—
20.	<i>o</i> -Chlorobenzoic acid	Pyridine	10	300	Grayish white ^c	—	Benzyl alcohol	—	—	20.7-24.8
21.	<i>p</i> -Chlorobenzoic acid	HCl	10	230	Pink ^c	0.9852	DMSO	17.6-18.5 ^b	19.2-24.8	21.9-24.8
22.	<i>p</i> -Chlorobenzoic acid	NaOH	10	300	White ^c	1.3824	DMF	—	18.6-24.8	20.7-24.8
23.	<i>p</i> -Chlorobenzoic acid	CH ₃ COOH	8	210	Pinkish white ^c	1.0617	DMF	17.6-20.5 ^b	18.6-24.8	21.9-24.8
24.	<i>p</i> -Chlorobenzoic acid	Pyridine	8	300	Brownish gray ^a	—	DMF	—	19.2-24.8	20.7-21.7
25.	<i>o</i> -Hydroxyacetophenone	HCl	4	300	Brown ^c	—	—	—	—	—
26.	<i>p</i> -Hydroxyacetophenone	HCl	6	300	Black ^c	1.9114	DMF	—	—	—
27.	<i>m</i> -Hydroxyacetophenone	HCl	6	300	Grayish black ^c	1.276	—	—	19.2-24.8	21.9-24.8
28.	<i>o</i> -Aminoacetophenone	HCl	4	290	Black ^c	—	—	—	19.2-24.8	21.9-24.8
29.	<i>p</i> -Aminoacetophenone	HCl	4	300	Black ^c	1.384	—	18.8-19.4 ^b	19.2-24.8 ^b	21.9-24.8 ^b
30.	<i>p</i> -Chloroacetophenone	HCl	6	300	Black ^c	2.2222	—	—	—	—

^a Amorphous. ^b Swelling parameter. ^c Crystalline.

TABLE II
Physico-chemical Properties of Resins Derived from 2,5-Dihydroxyacetophenone

Serial no.	Comonomer	Catalyst	Heating time (h)	Decomposition temperature (°C)	Color	Density	Solubility	Solubility parameter (δ) ranges in solvents that are hydrogen bonded ($(J/m^3)^{1/2} \times 10^{-3}$)		
								Weak	Moderate	Strong
1		3	4	5	6	7	8	9	10	11
1.	<i>o</i> -Hydroxybenzoic acid	HCl	4	300	Black ^c	1.753	—	—	18.6-24.6 ^b	21.9-24.8 ^b
2.	<i>o</i> -Hydroxybenzoic acid	NaOH	8	220	Gray ^c	0.9278	Acetone	17.6-21.5 ^b	18.6-24.8	18.6-29.7
3.	<i>o</i> -Hydroxybenzoic acid	CH ₃ COOH	6	180	Yellow ^a	0.9763	—	17.6-20.5 ^b	19.2-24.8 ^b	18.6-25.8
4.	<i>o</i> -Hydroxybenzoic acid	Pyridine	6	—	Grayish black ^a	0.9331	CHCl ₃	—	18.6-24.8	—
5.	<i>o</i> -Hydroxybenzoic acid	HCl	6	290	Gray ^c	1.381	Pyridine	—	18.6-24.6 ^b	21.9 ^b
6.	<i>p</i> -Hydroxybenzoic acid	NaOH	8	300	Brown ^a	0.8476	—	—	18.6-24.6 ^b	20.7-25.8 ^b
7.	<i>p</i> -Hydroxybenzoic acid	CH ₃ COOH	6	—	Grayish black ^a	—	Methanol	—	18.6-24.8	21.9-24.8 ^b
8.	<i>p</i> -Hydroxybenzoic acid	Pyridine	6	300	Brownish black ^c	0.9282	DMP	—	24.6-24.8	—
9.	<i>o</i> -Aminobenzoic acid	HCl	8	300	Grayish black ^c	1.0629	—	—	19.2-20.3 ^b	—
10.	<i>o</i> -Aminobenzoic acid	NaOH	10	300	Brownish black ^c	1.15	Acetone	—	18.6-24.6 ^b	18.6-21.9 ^b
11.	<i>o</i> -Aminobenzoic acid	CH ₃ COOH	8	300	Brownish black ^c	1.3117	—	—	24.6-24.8 ^b	—
12.	<i>o</i> -Aminobenzoic acid	Pyridine	6	300	Yellowish gray ^a	1.4255	—	—	24.6-24.8 ^b	20.7-25.8 ^b
13.	<i>p</i> -Aminobenzoic acid	HCl	6	300	Black ^c	0.9816	—	—	18.6-24.6 ^b	21.9 ^b
14.	<i>p</i> -Aminobenzoic acid	NaOH	6	300	Brown ^c	1.840	—	—	19.2-24.8 ^b	18.2-25.8 ^b
15.	<i>p</i> -Aminobenzoic acid	CH ₃ COOH	8	200	Yellowish gray ^a	1.9162	THF	—	19.2-24.8	18.6-25.8 ^b
16.	<i>p</i> -Aminobenzoic acid	Pyridine	8	300	Yellowish gray ^a	1.0752	—	19.0-19.4 ^b	19.2-24.8 ^b	20.7-24.8 ^b
17.	<i>o</i> -Chlorobenzoic acid	HCl	8	240	Brownish black ^c	1.6422	Pyridine	18.8-20.5 ^b	19.2-20.3 ^b	18.6-21.9 ^b
18.	<i>o</i> -Chlorobenzoic acid	NaOH	6	160	Grayish yellow ^a	1.1246	Methanol	—	18.6-24.6	20.7-29.7
19.	<i>o</i> -Chlorobenzoic acid	CH ₃ COOH	6	130	Yellowish gray ^a	—	CCl ₄	17.6-20.5	18.6-24.8	18.6-29.7
20.	<i>o</i> -Chlorobenzoic acid	Pyridine	16	180	Grayish black ^a	1.683	DMP	—	19.2-24.8	20.7-24.8
21.	<i>p</i> -Chlorobenzoic acid	HCl	8	—	Brown ^c	1.8647	—	19.0-20.5 ^b	—	—
22.	<i>p</i> -Chlorobenzoic acid	NaOH	6	290	Yellowish gray ^a	—	DMF	—	24.6-24.8	21.9-25.8
23.	<i>p</i> -Chlorobenzoic acid	CH ₃ COOH	6	160	Grayish yellow ^a	2.2224	CHCl ₃	18.2-20.5	18.6-24.8	18.6-29.7
24.	<i>p</i> -Chlorobenzoic acid	Pyridine	16	180	Yellowish white ^a	—	Methanol	18.2-20.5	19.2-24.8	18.6-29.7
25.	<i>o</i> -Hydroxyacetophenone	HCl	4	300	Black ^c	1.1223	—	—	20.3-24.8 ^b	18.6-21.7 ^b
26.	<i>m</i> -Hydroxyacetophenone	HCl	4	300	Black ^c	—	—	—	—	—
27.	<i>p</i> -Hydroxyacetophenone	HCl	4	300	Grayish black ^c	—	—	—	19.2-24.8 ^b	21.7-25.8 ^b
28.	<i>o</i> -Aminoacetophenone	HCl	2	300	Black ^c	1.8973	—	—	—	—
29.	<i>m</i> -Aminoacetophenone	HCl	4	300	Black ^c	—	—	19.4-20.5 ^b	19.2-24.6 ^b	18.6-25.8 ^b
30.	<i>p</i> -Chloroacetophenone	HCl	4	300	Black ^c	1.1862	—	—	19.2-21.7 ^b	18.6-24.8 ^b

^a Amorphous. ^b Swelling parameter. ^c Crystalline.

Method 1

A mixture of 2,4-dihydroxyacetophenone (0.01 mol), substituted aromatic compound (0.01 mol), and formaldehyde (0.1 mol) was added to a round-bottom flask. Hydrochloric acid (2 mL) was added slowly into the reaction mixture. The contents were refluxed at 120°C for 6–10 h. The mixture was periodically shaken. After completion of the reaction, the mixture was poured into ice cold water, filtered, and washed with hot distilled water to remove unreacted material. The product was dried at vacuum. The resins from 2,5-dihydroxyacetophenone were synthesized by this method.

Method 2

A mixture of 2,4-dihydroxyacetophenone (0.01 mol), substituted aromatic compound (0.01 mol), and formaldehyde (0.1 mol) was put in a round-bottom flask, shaken thoroughly to get a homogeneous solution. Then 5 mL of 10*N* sodium hydroxide was added slowly into the reaction mixture. The mixture was refluxed at 120°C for 4–8 h with periodic shaking followed by acidification of the solid obtained.

Method 3

A mixture of 2,4-dihydroxyacetophenone (0.01 mol), substituted aromatic compound (0.1 mol), and formaldehyde (0.2 mol) was put in a round-bottom flask to which 10 mL of 90% glacial acetic acid was added slowly and refluxed at 120°C for 8–10 h with constant stirring. The product was poured into ice cold water followed by filtration with hot distilled water.

Method 4

A mixture of 2,4-dihydroxyacetophenone (0.1 mol), substituted aromatic compound (0.01 mol), and formaldehyde (0.2 mol) was put in a round-bottom flask and refluxed at 120°C for 8–16 h with slow addition of 10 mL of 90% pyridine with constant stirring. After completion of the reaction the product was poured into ice cold water, filtered, washed, and dried. The resins synthesized and their physico-chemical properties are represented in Tables I and II.

Characterization of Resins

The resins were characterized by dilute solution viscometry, using an Ubbelohde suspended level viscometer. The measurements were carried out with 0.5% (w/v) solution in dimethylsulfoxide, tetrahydrofuran, and nitrobenzene at 30°C.

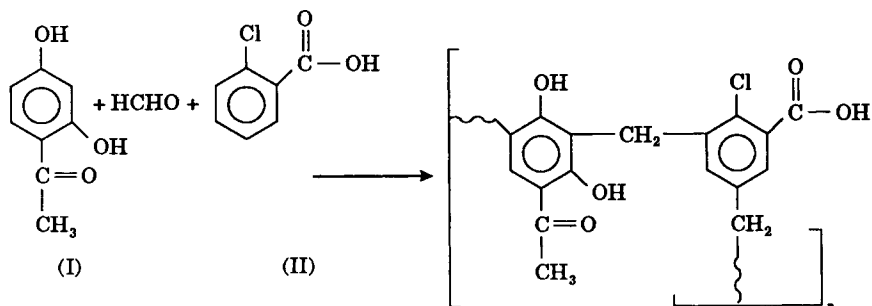
The density of the polymer was determined by means of a small pycnometer in dry benzene at 30°C. The IR spectra was recorded with a Perkin-Elmer 781 spectrophotometer using KBr pellets. The monomer reactivity ratio of resin copolymers were computed using the Kelen-Tüdös equation.

The solubility characteristics were studied by placing (0.01 g) of resin in 2 mL of various solvents and allowing it to stand for 2 weeks.^{14,15} The solvent effect was judged in terms of swelling or dissolution. The solubility parameter of each was then computed.

A number of resins were screened for fungicidal activity following spore germination techniques against the species *Cubularia lunata*, widely known to cause Black Kernel on rice plants.

RESULTS AND DISCUSSION

The polycondensation reaction between 2,4-dihydroxyacetophenone (I) formaldehyde and *o*-chlorobenzoic acid (II) may be represented as follows:



The structure of the repeat unit of this resin was identified from IR spectra of the polymer. The polymer shows characteristic IR bonds (Fig. 1) near 3575, 3030, and 1450 cm^{-1} for O—H stretching (aromatic), C—H stretching (aromatic), and C—H bending of the methylene bridge. The peaks at 1275 and

1690 cm^{-1} are assigned to the $\begin{array}{c} \text{O} \\ || \\ -\text{C}- \end{array}$ stretching of the $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{CH}_3 \end{array}$ group, which are considerably reduced due to the presence of hydrogen bonding. The peak at 630 cm^{-1} was assigned to the C—Cl stretching and at 1575 cm^{-1} for the carboxylate anionic stretching.

Solubility Behavior

The solubility behavior of the resins was determined by using a wide range of solvents of varying solubility parameters in the weak, strong, and moderate hydrogen-bonded category.

Most of the resins were found to be insoluble in the solvents. However, they were found to swell considerably. This fact may be attributed to higher chain symmetry and higher molecular weight of the resin polymers. The solubility parameter ranges of the polymers are shown in Tables I and II.

A plot of solubility parameter (δ) versus hydrogen bonding index (ν) for different solvents was made as shown in Figure 2 for the 2,4-dihydroxyacetophenone-*p*-hydroxybenzoic acid-formaldehyde resin. The values are taken from the approximate midpoint of the solubility map.

The solubility parameter (δ) may also be computed from group molar attraction constant (G) using the relationship

$$\delta = \rho(\sum G/M)$$

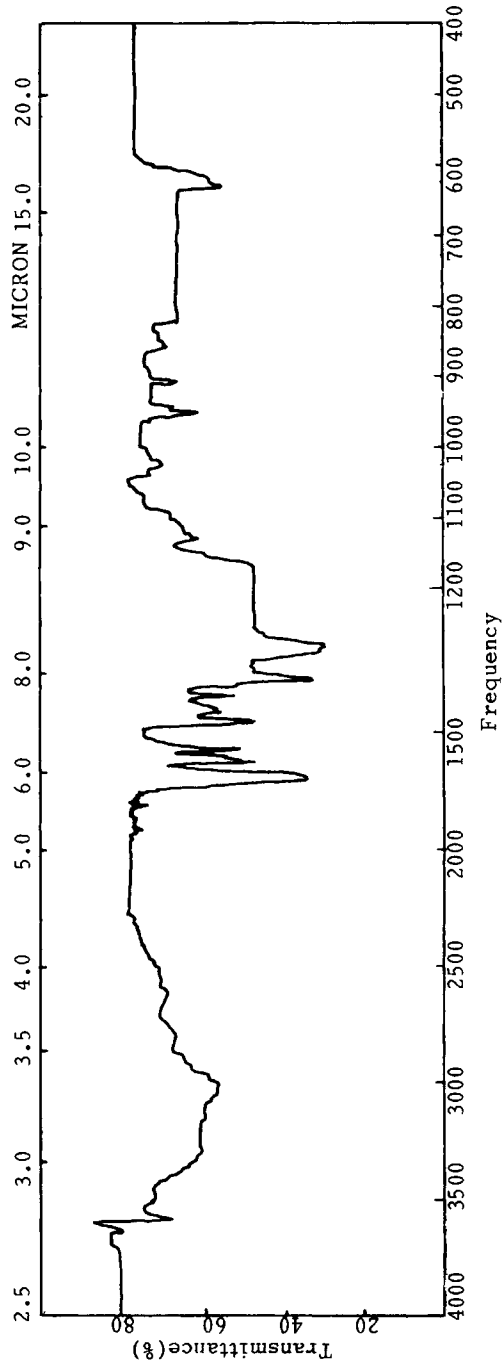


Fig. 1. IR spectra of 2,4-dihydroxyacetophenone-o-Cl-benzoic acid-formaldehyde resin.

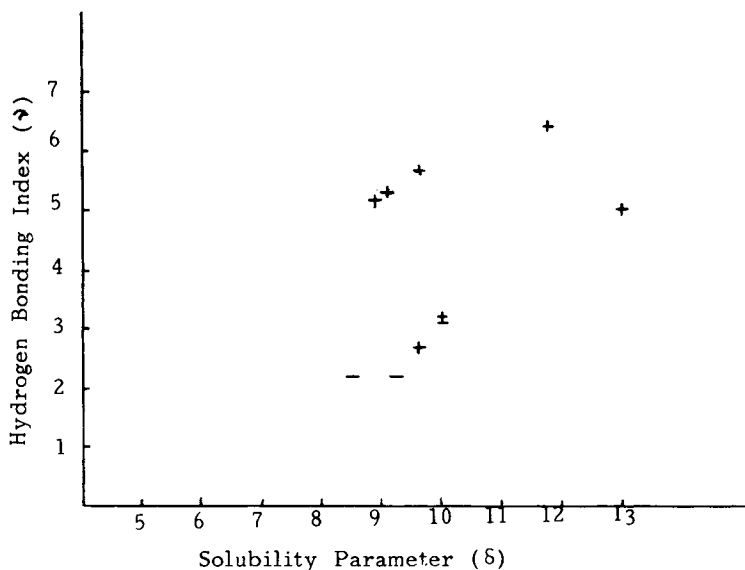


Fig. 2. Solubility map of 2,4-dihydroxyacetophenone-*p*-hydroxybenzoic acid-formaldehyde resin.

where ΣG is the sum of group molar attraction constants, M the formula weight of the polymer repeat unit, and ρ is the density of the polymer. The molar attraction constant G values used have been reported by Small¹⁶ and Hoy,^{17,18} which result in considerably different values as shown in Table III.

Solution Viscosity Behavior

Intrinsic viscosity $[\eta]$ was determined by using Huggins,¹⁹ Kramer,²⁰ and Schultz-Blaschke²¹ equations.

TABLE III
Comparison of Solubility Parameter Values of Resins as Obtained by Different Methods

Name of the resin	δ values in $(\text{cal}/\text{cm}^3)^{1/2}$ as obtained from		
	Small's G value	Hoy's G value	Graph
2,4-Dihydroxyacetophenone- <i>p</i> -hydroxybenzoic acid-formaldehyde resin	10.673	11.044	10.955
2,4-Dihydroxyacetophenone- <i>p</i> -chlorobenzoic acid-formaldehyde resin	11.258	11.469	10.955
2,4-Dihydroxyacetophenone- <i>o</i> -hydroxybenzoic acid-formaldehyde resin	10.4674	11.56193	10.5
2,4-Dihydroxyacetophenone- <i>o</i> -aminobenzoic acid-formaldehyde resin	10.2337	11.2031	11.167
2,5-Dihydroxyacetophenone- <i>o</i> -hydroxybenzoic acid-formaldehyde resin	10.33503	11.4157	10.983

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2c \quad (\text{due to H\u00fcggins})$$

$$\ln \eta_{rel}/c = [\eta] - k_2[\eta]^2c \quad (\text{due to Kramer})$$

$$\eta_{sp}/c = [\eta] + k_3[\eta]\eta_{sp} \quad (\text{due to Schultz-Blaschke})$$

where $k_1 + k_2 \simeq 0.5$.

As seen from Figure 3, $k_1 + k_2 = 0.5707$ is in good agreement with the theoretical value²² of 0.5. The intrinsic viscosity value as obtained for the 2,5-dihydroxyacetophenone-*o*-hydroxybenzoic acid-formaldehyde resin is 2.62 mL/g. The values obtained from the H\u00fcggins-Kramer and Schultz-Blaschke equations are found to be in good agreement with each other.

Monomer Reactivity Ratio

The Kelen-T\u00fcd\u00f6s linear graphical method²³ was chosen to determine the monomer reactivity ratio^{24,25} r_1 and r_2 . Four random copolymers were prepared by condensing each comonomer 2,4-dihydroxyacetophenone (RAP) and 2,5-

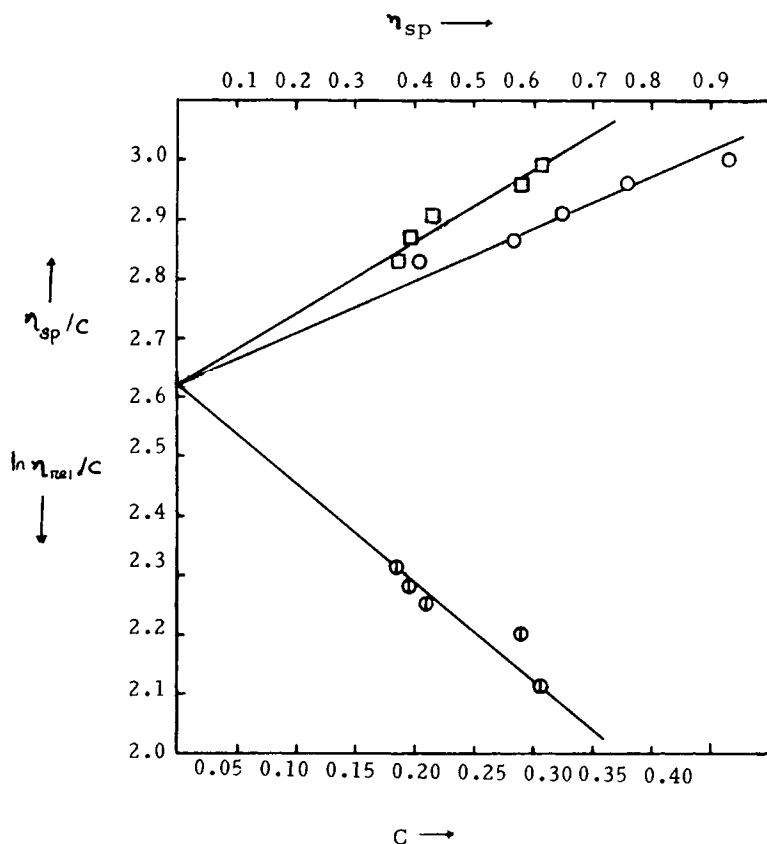


Fig. 3. Plot of $\eta_{sp}/c \sim C$ (\square), $\ln \eta_{rel}/c \sim C$ (\oplus) and $\eta_{sp}/c \sim \eta_{sp}$ (\circ) for the 2,5-dihydroxyacetophenone-*o*-hydroxybenzoic acid-formaldehyde resin.

dihydroxyacetophenone (QAP) with formaldehyde with *o*-chlorobenzoic acid (*o*-ClBA) and *p*-chlorobenzoic acid (*p*-ClBA), respectively.

The resins were prepared by refluxing the different monomers in various molecular proportions in the presence of concentrated hydrochloric acid as a catalyst for 8 h at 120°C. The copolymers were freed from unreacted monomers by repeated washing and dried. The composition of the copolymer was determined by estimating halogen following Volhard's method.²⁶ The coposition of the feed and copolymer is shown in Table IV.

The Kelen-Tüdös equation

$$\frac{X(Y-1)}{\alpha Y + X^2} = \left(r_1 + \frac{r_2}{\alpha} \right) \frac{X^2}{\alpha Y + X^2} - \frac{r_2}{\alpha}$$

where, X is the ratio of mole fraction of monomer in the feed, Y is the ratio of mole fraction in the copolymer, and α is any arbitrary constant given by

$$\alpha = \frac{X_{\min} X_{\max}}{(X_{\min} Y_{\max})^{0.5}}$$

The preceding equation is expressed in the form of a linear relationship.

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \epsilon - \frac{r_2}{\alpha}$$

where

$$\eta = \frac{X(Y-1)}{\alpha Y + X^2}$$

$$\epsilon = \frac{X^2}{\alpha Y + X^2}$$

A graph of η vs. ϵ (Fig. 4) was drawn and the values of r_1 and r_2 computed, as shown in Table IV.

The reciprocal of reactivity ratio expresses the relative reactivity of the unlike and like monomers with a given comonomer. When 2,5-dihydroxyacetophenone (QAP) is copolymerized with *o*-chlorobenzoic acid (*o*-ClBA) and *p*-chlorobenzoic acid (*p*-ClBA), the reciprocal of reactivity ($1/r_1$) is shown to follow the order *o*-ClBA > *p*-ClBA, which can be attributed to the relative degree of polarization of the two monomers. The rate of addition of *o*-ClBA with the common monomer is thus expected to be higher compared to the rate of addition of *p*-ClBA with 2,5-dihydroxyacetophenone.

Antifungal Activity

The fungicidal activity of the resins were studied following the spore germination technique adopted by Horsfall,²⁷ using varying concentrations of the acetone extract of the resins.

TABLE IV
Monomer Reactivity of Quinacetophenone-Chlorobenzoic Acid-Formaldehyde Resin

Food composition in mole		Copolymer composition in mole (%)		Ratio of mole fraction of monomer in feed	Ratio of mole fraction of monomer in copolymer	α	η	ϵ	r_2	r_1	$\frac{1}{r_1}$	$\frac{1}{r_2}$
M_1	M_2	dM_1	dM_2	($X = M_1/M_2$)	($Y = dM_1/dM_2$)							
OC1BA	QAP	OC1BA	QAP									
0.001	0.004	0.1673	0.4762	0.25	0.3513	1.2859	-0.3153	0.1215	0.3227	0.277	3.6062	3.0989
0.0015	0.0035	0.2064	0.4381	0.4286	0.4711		-0.2871	0.2326				
0.002	0.003	0.255	0.3909	0.6666	0.6523		-0.1807	0.3464				
0.0025	0.0025	0.2846	0.3622	1.0	0.7858		-0.1065	0.4973				
0.003	0.002	0.3285	0.3195	1.5	1.0281		0.0118	0.6299				
0.0035	0.0015	0.3811	0.2684	2.3333	1.4198		0.1347	0.7489				
0.004	0.001	0.4114	0.2390	4.0	1.7218		0.1584	0.8785				
PC1BA	QAP	PC1BA	QAP									
0.001	0.004	0.1311	0.511	0.25	0.2572	1.4948	-4.154	0.1398	0.3211	0.505	1.980	3.1143
0.0015	0.0035	0.2059	0.4381	0.4286	0.4711		-2.653	0.2069				
0.002	0.003	0.2930	0.3531	0.6666	0.8318		-0.997	0.2633				
0.0025	0.0025	0.3247	0.3223	1.0	1.01		0.004	0.3984				
0.003	0.002	0.3626	0.2854	1.5	1.2734		0.0997	0.5467				
0.0035	0.0015	0.3907	0.2581	2.3333	1.7174		0.1565	0.7059				
0.004	0.001	0.4102	0.2391	4.0	1.72		0.1550	0.8615				

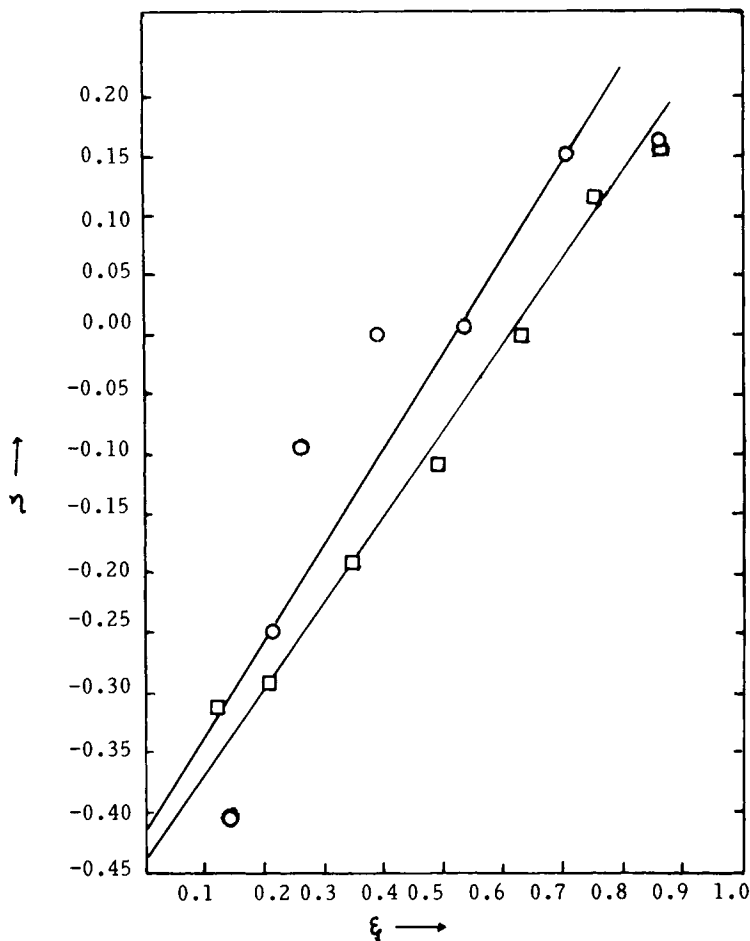


Fig. 4. Kelen-Tüdös plot for the copolymers: \square , 2,5-dihydroxyacetophenone-*o*-Cl-benzoic acid-formaldehyde resin; \circ , 2,5-dihydroxyacetophenone-*p*-Cl-benzoic acid-formaldehyde resin.

The spore germination was carried out with cavity slides incubated in a sterilized moist chamber, prepared by placing a blotting paper at the bottom of a 10-cm petri dish. A drop of diluted resin solution was placed in the cavity and allowed to dry followed by the addition of a drop of the culture suspension in sterilized water. The moist chamber was incubated at 28°C for 24 h.

Observations were recorded after the incubation on the conidial germination. Emergence of a germ tube from the conidium was taken as a criterion for germination. Checks without chemicals were also maintained. From the conidial germination the percentage of inhibition in each dilution was calculated.

The inhibition of conidial germination was plotted against concentration and the dosage response curves were drawn. Figure 5 shows the percentage of inhibition at various concentrations of the resins obtained from 2,5-dihydroxyacetophenone and *o*-chlorobenzoic acid, *o*-hydroxybenzoic acid, *p*-aminobenzoic acid, and *p*-chlorobenzoic acid.

The resins obtained from 2,4-dihydroxyacetophenone were found moderately sensitive to the fungus in comparison to 2,5-dihydroxyacetophenone, which

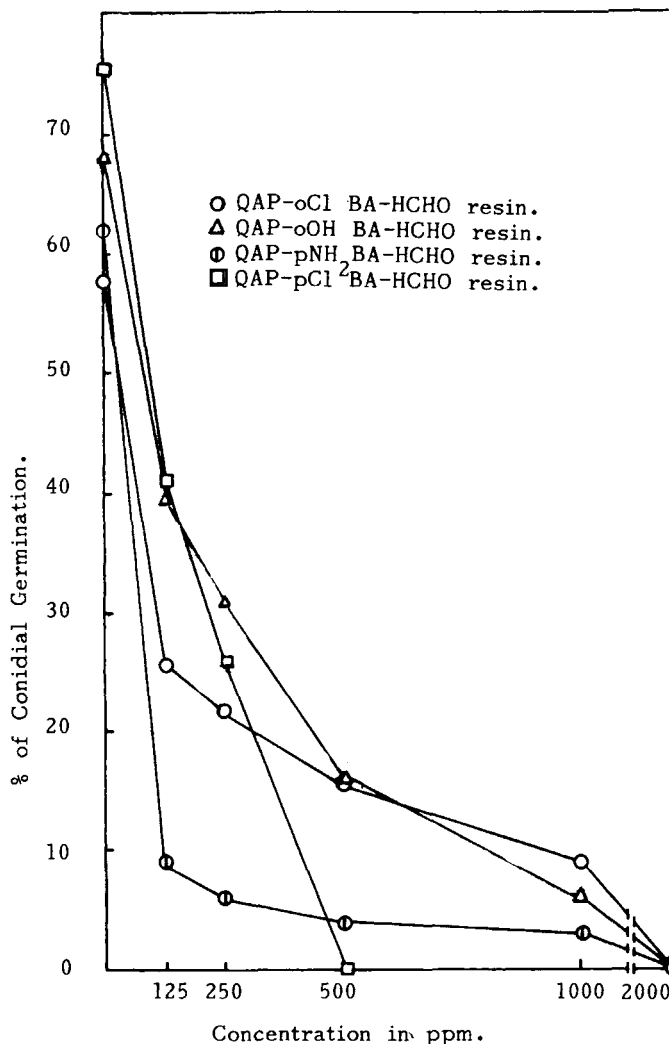


Fig. 5. Percentage of conidial germination vs. concentration in ppm of resins against *Culvularia lunata*: ○, 2,5-dihydroxyacetophenone-*o*-Cl-benzoic acid-formaldehyde resin; △, 2,5-dihydroxyacetophenone-*o*-OH-benzoic acid-formaldehyde resin; ◇, 2,5-dihydroxyacetophenone-*p*-NH₂-benzoic acid-formaldehyde resin; □, 2,5-dihydroxyacetophenone-*p*-Cl-benzoic acid-formaldehyde resin.

was highly sensitive as characterized by complete inhibition at 2000 ppm concentration. In fact resin prepared from 2,5-dihydroxyacetophenone-*p*-chlorobenzoic acid-formaldehyde was found to completely inhibit at 500 ppm concentration and for 2,5-dihydroxyacetophenone-*p*-aminobenzoic acid-formaldehyde resin at a concentration as low as 125 ppm the germination was only 9.49%.

The antibacterial action of the resins may be explained by taking into account the antimetabolism, chelation, and precipitation of chemicals. Oxygen and nitrogen atoms present in the resin can act as hydrogen acceptors in metabolic system, thereby disturbing normal hydrogenation and dehydrogenation reac-

tions in the cell. The reactive free radicals formed by metabolic breakdown form stable crosslinkage with protein and other cellular components.

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