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Coumarin Polymers Derived from Salicylaldehyde-Formaldehyde Polymer

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ABSTRACT

Coumarin and 3-aryloxycoumarin polymers were prepared by the Perkin reaction of salicylaldehyde-formaldehyde polymer with acetic anhydride and with simple and substituted phenoxy acetic acids, respectively. All the coumarin polymer samples were characterized by elemental analysis, IR spectrometry, and TGA. Coumarin polymer samples were screened for their antifungal activity against a variety of fungi.

INTRODUCTION

A number of coumarin derivatives are known to be physiologically active, and some of them are reported to possess antibacterial and antifungal properties [1-3]. Recently, various 3-phenoxycoumarins have been reported as good fungicides [4]. Salicylaldehyde-formaldehyde (SAL-F) polymer has been reported to be a polymeric ligand [5]. There are no reports on work done in connection with the modification of SAL-F polymer affording bioactive polymer. In light of the above observations about the physiological activity of coumarin derivatives, it was thought interesting to prepare polymers containing coumarin nuclei in the polymer chain and to test their physiological properties.

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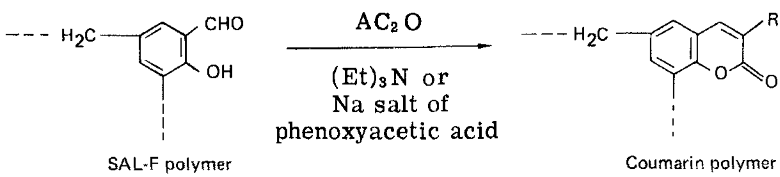
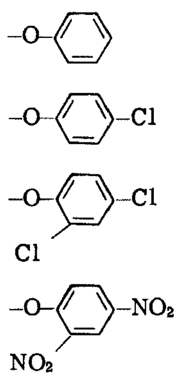
The synthesis was carried out by the application of the Perkin reaction as modified by Oglialoro [6] involving reaction of SAL-F polymer with acetic anhydride and/or the Na-salt of a phenoxyacetic acid such as 4-chloro, 2,4-dichloro or 2,4-dinitrophenoxy acetic acid.



where R = –H



These polymer samples were characterized by elemental analyses and IR spectral characteristics. Thermal properties of the polymers were estimated by thermogravimetric analysis. The toxicity of these coumarin polymers against various fungi was evaluated.

EXPERIMENTAL

Materials

All the chemicals used were of chemically pure grade.

The fungicidal activities of the coumarin polymers were tested against the plant pathogenic organisms Penicillum expansum, Botrydepladia thiobromide, Nigrospora sp. Trichotesium sp., and Rhizopus nigricans.

Polymer Preparation

Salicylaldehyde-formaldehyde (SAL-F) polymer was prepared by the acid-catalyzed method reported earlier [5]. It is soluble only in DMF. Its molecular weight, estimated both by VPO and conductometric titration, is 800 ± 50 [7].

Coumarin Polymer

A mixture of SAL-F polymer (0.17 mol), anhydrous triethyl amine (2.0 mL), and acetic anhydride (0.52 mol) was refluxed for 15 h. The resultant reaction product was then stirred in a slight excess of well-cooled aqueous hydrogen carbonate solution to remove the acetoxy cinnamic acid derivative. The solid was filtered, washed with boiling water, and air-dried.

The yellow powder was then treated with boiling DMF (10 mL) to remove unreacted SAL-F polymer. The yield was 1.0 g. This polymer sample is designated as COU. It is insoluble in common organic solvents.

3-Phenoxycoumarin Polymers

A mixture of SAL-F polymer (0.17 mol), acetic anhydride (0.85 mol), and sodium phenoxyacetate (0.34 mol) was heated at 190-200°C for 15 h. The reaction mixture was then worked up in the manner described above. The product was in the form of a brownish yellow powder. It did not melt up to 360°C and was insoluble in common organic solvents. The yield was 1.6 g. The polymer sample is a 3-phenoxycoumarin derivative and is designated as PCOU-1.

Other 3-aryloxycoumarin polymers were similarly prepared by reacting SAL-F polymers with sodium 4-chloro-, with 2,4-dichloro-, and with 2,4-dinitrophenoxyacetates. The designations of all the polymers are shown in Table 1.

Measurements

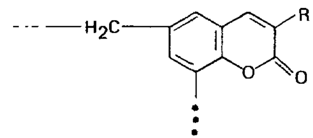
Elemental Analysis

Chlorine content of 3-(4-chloro- and 2,4-dichlorophenoxy) coumarin polymers was estimated by the Carius method. Nitrogen content of 3-(2,4-dinitrophenoxy) coumarin polymer was estimated by the Dumas method.

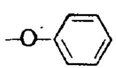
IR spectra of all the polymer samples were taken in KBr on a UR-10 spectrophotometer.

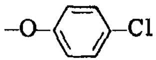
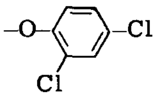
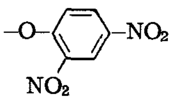
Thermogravimetry of all the polymer samples was carried out on a Linseis thermobalance at a heating rate of 10°C/min.

TABLE 1. Elemental Analyses of Coumarin Polymers



Polymer sample	% C		% H		% Cl		% N	
	Required	Found	Required	Found	Required	Found	Required	Found
SAL-F	71.64	68.84	4.47	4.27	-	-	-	-
COU R = H	75.94	72.44	3.79	5.71	-	-	-	-
PCOU-1	76.8	71.79	4.0	4.21	-	-	-	-

R = 

PCOU-2	67.48	69.08	3.16	4.3	12.47	10.8	-	-
R = 								
PCOU-3	60.00	63.86	2.5	3.48	22.18	21.1	-	-
R = 								
PCOU-4	51.47	55.67	2.14	3.21	-	-	7.5	7.18
R = 								

Antifungal Activity

The fungicidal activity of all the coumarin polymer samples (at 1000 ppm concentration) was evaluated following the method described in our earlier communication [8]. Plant pathogenic organisms used were Penicillium expansum, Botrydepladia thiobromide, Nigrospora sp., Trichothesium sp., and Rhizopus nigricans.

RESULTS AND DISCUSSION

All the coumarin polymer samples are pale yellow to dark brown solids. They are insoluble in common organic solvents.

The C and H content of the parent SAL-F polymer sample and those of the coumarin polymers very nearly agree with those predicted on the basis of the structures of the respective repeat units. The chlo-

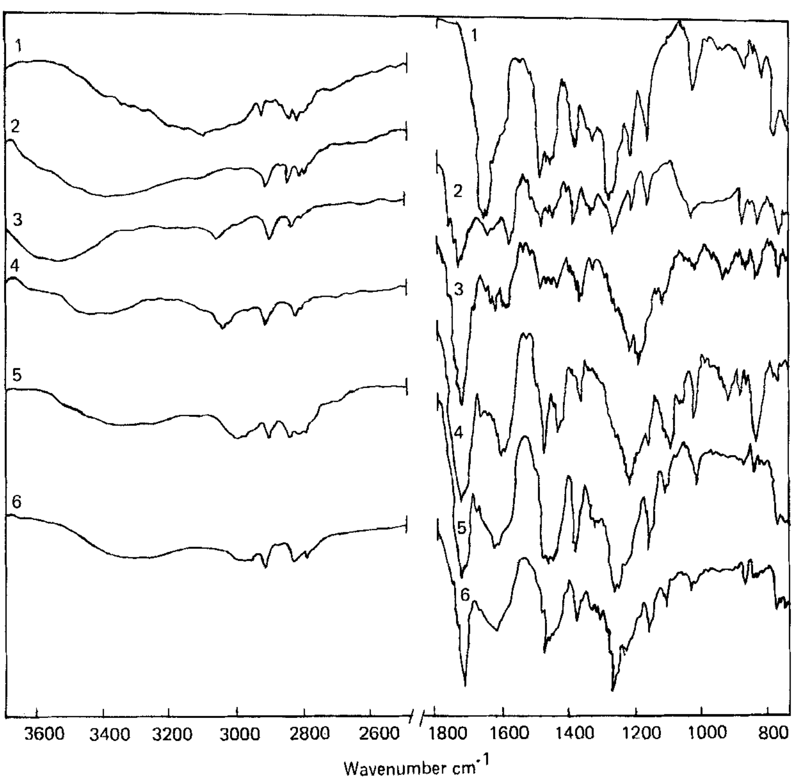


FIG. 1. IR spectra of polymer samples. (1) SAL-F. (2) COU. (3) PCOU-1. (4) PCOU-2. (5) PCOU-3. (6) PCOU-4.

rine or the nitrogen content of chlorine- or nitrogen-containing coumarin polymers agree well with the expected values. This suggests that the salicylaldehyde units of almost all the repeat units of SAL-F polymer are transformed during the Perkin reaction.

The IR spectra of all polymer samples are shown in Fig. 1. The important features of the IR spectrum of the polymer sample SAL-F are a broad band due to a chelated OH [9] extending from 3450 to 2600 cm^{-1} and with inflections around 2920 and 2850 cm^{-1} attributed to asymmetric and symmetric stretching of CH of $-CH_2-$ bridges, and a carbonyl band at 1670 cm^{-1} due to –CHO of the salicylaldehyde nuclei of the repeat units [10, 11]. The IR spectra of the coumarin polymers comprise bands characteristic of aromatic system and $-CH_2-$ bridges at the expected positions. These spectra resemble each other in their general shape and the relative intensities of the bands. Comparison of the IR spectra of the coumarin polymers with that of the parent polymer reveals characteristic differences. The carbonyl band due to aldehyde –C=O at 1670 cm^{-1} has almost disappeared and that due to the δ-lactone system of the coumarin nucleus appears in the spectra of the coumarin polymers at 1730 cm^{-1} [12]. Even the broad band characteristic of chelated OH has disappeared or almost disappeared in the spectra of the coumarin polymers, depending upon the nature of the polymer. From these spectral data it can be inferred that the salicylaldehyde nuclei of almost all the repeat units have participated in the Perkin reaction.

Typical TG thermograms are shown in Fig. 2 and the percent weight loss at various temperatures in TG experiments are presented in Table 2. Examination of these data reveals that each coumarin polymer and the parent SAL-F polymer sample degrade in one stage. They are all stable up to around 300°C. Beyond this temperature the coumarin polymers degrade more rapidly than the parent polymer sample. The SAL-F polymer sample suffers a weight loss of about 50% when heated up to 500°C. However, the coumarin polymers suffer a weight loss up to 90 to 95% when heated up to 500°C depending upon the nature of the polymer. These results show that the coumarin polymers are thermally less stable than the parent SAL-F polymer.

The percentage inhibition of the growth of several fungi by the coumarin polymer samples is furnished in Table 3. Examination of the results reveals that all the polymers are less toxic against various fungi than simple coumarin and 3-phenoxycoumarin [1-4]. Coumarin, and particularly 3-phenoxycoumarin, are found to have measurable activity against fungi at relatively very low concentration (40 to 200 ppm) [4]. The lower activity of polymer is due to their poor miscibility in the medium.

In the present experiments the required concentration of polymer for the complete inhibition of growth of fungi is in the range of 700-1500 ppm depending upon the nature of polymer. The chlorine-containing PCOU-2 and PCOU-3 samples are more toxic and are required in a smaller dose than the other coumarin polymers. This probably happens because of the presence of chlorine in these polymers.

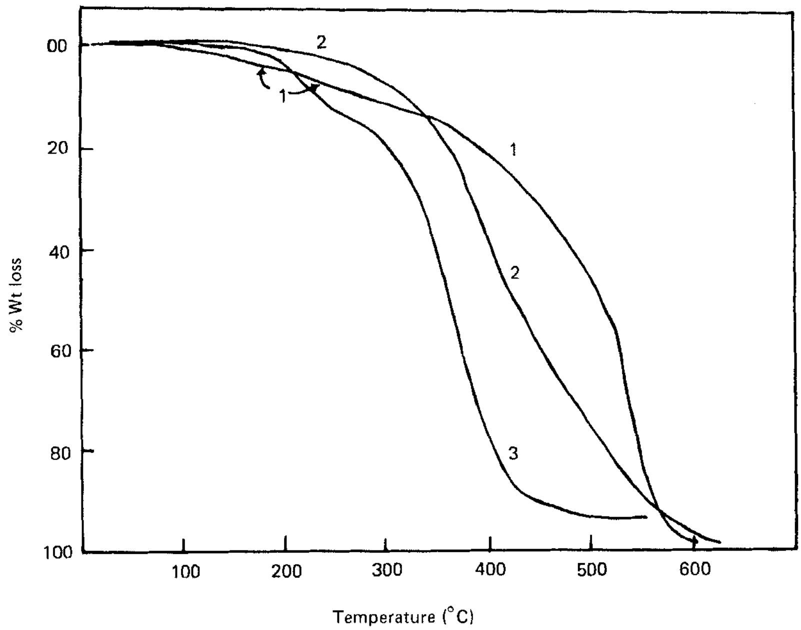


FIG. 2. TG thermograms of polymer samples. (1) SAL-F polymer. (2) COU polymer. (3) PCOU-1 polymer.

TABLE 2. Thermogravimetric Analysis of Coumarin Polymers

	% Weight loss at a temperature (°C) of				
Polymer sample	200	300	400	500	600
SAL-F	5	10	22	47	97
COU	-	6	36	75	90
PCOU-1	4	20	30	90	95
PCOU-2	1	13	27	85	95
PCOU-3	1	10	23	82	98
PCOU-4	6	15	35	85	98

TABLE 3. Antifungal Activity of Coumarin Polymers

Polymer sample	Zone of inhibitions at 1000 ppm (%) for fungi				
	Penicilliam expansum	Botrydepladia thiobromide	Nigrospora sp.	Trichothesium sp.	Rhizopus nigricans
COU	85	80	100	100	79
PCOU-1	100	100	82	84	90
PCOU-2	100	85	100	100	100
PCOU-3	100	88	100	100	100
PCOU-4	100	80	100	80	100

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