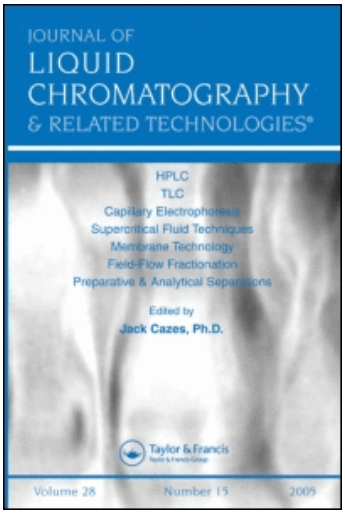

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REVERSE-PHASE LIQUID CHROMATOGRAPHY OF PHENOL-FORMALDEHYDE ALL-ORTHO OLIGOMERS

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ABSTRACT

High Performance Liquid Chromatography was proven to be a powerful method for the separation and quantitation of ortho-linked Phenol-Formaldehyde oligomers. A homologous series of oligo [(2-hydroxyl-1,3-phenylene)methylene] s (dinuclear to octanuclear compounds) was analyzed. The samples were separated by reverse-phase chromatography and monitored at 280 nm. Optimum conditions were obtained on a μ-Bondapack C_{18} column employing isocratic ambient elution with a metanol/water 80:20 (v/v) mixture. Four reference mixtures of oligomers of known composition were used to assure the reliability of the method. Subsequent analysis of two samples of all-ortho novolac resins was performed in order to substantiate further the validity of the technique.

INTRODUCTION

Among the phenolic resins, Phenol-Formaldehyde (P-F) novolacs in which all phenolic nuclei are linked by an ortho-ortho methylene bridge, represent a class of substances of special interest and broad utility since it exhibits shortened curing periods over the conventional products(1).

In the past, GLC has been used extensively to separate quantitatively low molecular wieght P-F condensation products. This

technique, combined with other analytical methods (IR, UV, paper chromatography, GPC, ^{1}H NMR, and mass spectroscopy), provided structural information such as the ratio of ortho/para linkages and the number-average molecular weight, but failed to give the exact composition of the resin. Recently (2), ^{13}C NMR spectroscopy has proved to be a more powerful tool for the analysis of these resins. In this field, however, HPLC analysis has received only marginal attention and has been mainly applied to alkaline-catalyzed P-F condensates (3) or to individual phenolic compounds (4).

Our interest in the application of coordinating metal phenolates in the ortho-site specific P-F condensations (5) and in the control of practical syntheses of faster curing novolacs (6) prompted us to develop an accurate quantitative technique for the rapid characterization of resins of this type. This paper reports the quantitation of ortho-linked P-F oligomers and related resins by reverse-phase HPLC.

EXPERIMENTAL

Apparatus

HPLC was performed using a Model 6000A pump (Water Associates, Milford, Mass.), a U6K injector (Waters), and a Model 440 UV detector (Waters). The samples were separated at ambient temperature on a 30 cm x 3.9 mm i.d. μ-Bondapak C_{18} high efficiency column (Pat.No.27324, Waters) and monitored at 280 nm. The recorder was an OmniScribe (Houston Instruments, Austin, Texas) instrument. A mobile phase of 80% methanol in water with a flow rate of 2.0 ml/min was used throughout this work. Actual sample mass, injection volume, and other LC operating parameters are indicated in each chromatogram. All the samples were dissolved in methanol and filtered on Millipore FHLP 0.5 μm filters prior to the injection. Standard solutions of each oligomer were prepared at various concentrations in order to cover a range of 0.3 to 6.0 μg per injection.

Chemicals

The oligo[(2-hydroxy-1,3-phenylene)methylene]s dinuclear to octanuclear derivatives) used were prepared in our lab according to a previously described (5) ortho-specific P-F oligomerization with a purity of 99+% by HPLC. The resin NOVO-A was prepared in benzene from bromomagnesium phenoxide and paraformaldehyde (3:2 mol/mol); colorless homogeneous powder, m.p. 56-60 °C (6). The resin NOVO-B was prepared in xylene (5 mol) from phenol and paraformaldehyde (3:2 mol/mol); pale yellow glassy solid, m.p. 46-50 °C (7). RS-HPLC grade methanol, obtained from Carlo Erba, Milano, was used without further purification. Redistilled water (Carlo Erba) was filtered on Sep-Pak C_{18} cartridges and degassed immediately prior to use.

RESULTS AND DISCUSSION

A representative separation of a standard solution of di- to octanuclear P-F oligomers is illustrated in Figure 1. Optimum resolution of components and time of analysis were achieved on a μ-Bondapak C_{18} reverse-phase column employing isocratic ambient elution with a solvent mixture of methanol/water 80:20 (v/v) as described in the Experimental. In the range of 0.3 to 6.0 μg of injected sample the UV detector response at 280 nm was linear for all seven oligomers. The standard calibration curves showed excellent linearity with a correlation coefficient greater than 0.99.

The precision of the oligomer analysis is shown in Table 1. The average %RSD (relative std deviation) using peak area was 2.62% while no significant loss of precision was observed in the size ranging from 1.0 to 5.0 μg. The relative response factors were calculated using the mean peak area and were as follows: Di = 1.000, Tri = 1.009, Tetra = 0.998, Penta = 0.996, Hexa = 0.997, Hepta = 0.993, and Octa = 0.990.

There was an insignificant variation in response factors with a decrease of less than 0.01% for di- to octanuclear oligomers thus

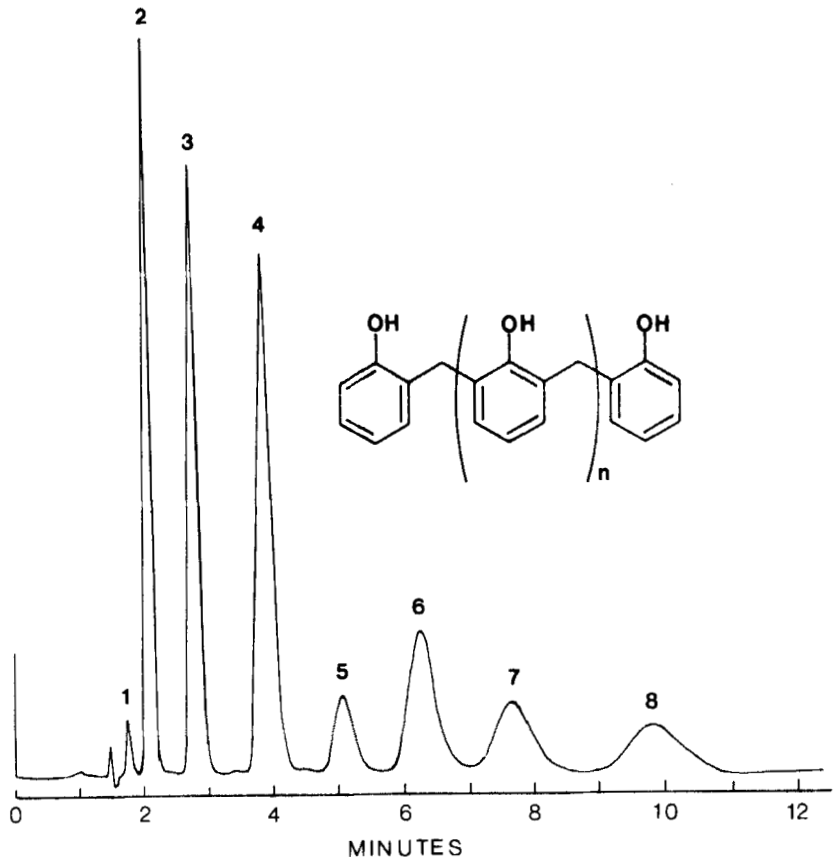

FIGURE 1

Chromatogram of a P-F oligomer reference mixture. Conditions: detector sensitivity 0.1 AUFS; back pressure 2800 psi; flow-rate 2.0 ml/min; chart speed 2.0 cm/min; peak identities: (1) phenol, (2) 1.01 µg Di (n = 0), (3) 1.25 µg Tri (n = 1), (4) 1.63 µg Tetra (n = 2), (5) 0.25 µg Penta (n = 3), (6) 1.00 µg Hexa (n = 4), (7) 0.54 µg Hepta (n = 5), and (8) 0.64 µg Octa (n = 6) in 12.5 µl methanol.

TABLE 1

Precision of Ortho P-F Oligomers

(3.66 μg sample)

Peak Areas (cm^2)

RUN NO.	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa
1	12.196	12.010	11.685	12.120	11.788	11.968	12.120
2	12.204	11.940	12.180	11.170	11.968	12.030	12.150
3	12.015	11.967	12.035	12.056	12.312	12.110	11.935
4	11.969	12.453	12.852	11.960	12.272	11.652	11.023
5	12.246	12.469	12.240	11.936	12.156	11.354	12.411
6	12.302	12.090	12.300	12.044	11.932	11.561	11.832
7	11.790	11.697	11.542	12.289	12.042	12.211	11.598
8	12.401	11.942	12.420	12.456	12.213	11.813	12.232
9	12.601	12.014	12.354	12.198	12.456	12.223	12.010
10	11.940	12.551	11.890	11.988	12.234	12.322	12.036
Mean	12.166	12.281	12.148	12.122	12.137	12.087	12.045
Standard Deviation	± .215	± .334	±.490	±.355	±.235	±.365	±.240
% RSD	1.77%	2.71%	4.03%	2.93%	1.93%	3.01%	1.99%

offering a fortunate circumstance for our quantitation. Thus, for routine analyses, peak area should be the method of choice with no necessity of response correction for di- to octanuclear oligomers.

The use of a common calibration plot (slope 3.23 $cm^2/\mu g$; intercept 0.43 cm^2; correlation coefficient 0.998) in Figure 2, possible because of the negligible variance in the calibration constants of individual curves, is the most attractive feature of this method in its application to the quantitation of ortho-linked P-F oligomers. The most likely explanation for the near coincidence of all calibration plots lies in the well-known linear dependence of the molar absorptivity upon the number of phenolic units in the polyphenol oligomer series (8, 9). Assuming that in all oligomers there is, on the average, the same number of phenolic units per unit of weight,

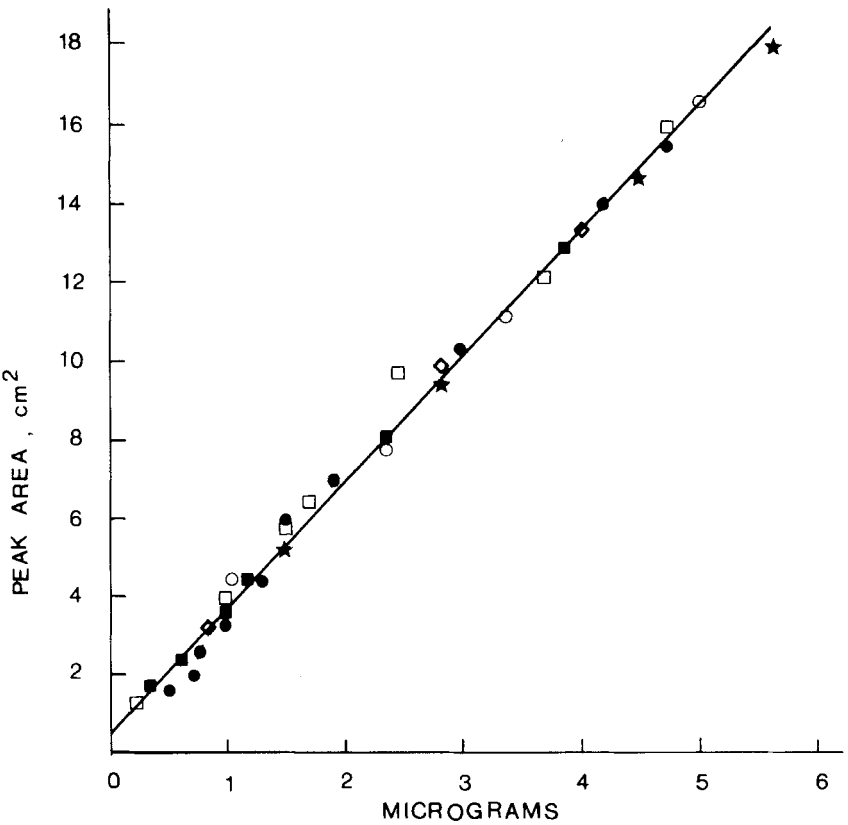

FIGURE 2

Load-response curve for di- to octanucelar P-F ortho-oligomers. ■Di; ● Tri;□ Tetra,○ Penta,★ Hexa;◇ Hepta; ⌀ Octa. Solid line is a linear least-squares fit to data from 0.29 to 5.65 µg.

the UV absorption at 280 nm (λ_{max} for all oligomers) gives the same integrated value for unit of weight for each component whatever its molecular weight.

Analysis of four mixtures of all-ortho P-F oligomers of known composition, as summarized in Table 2, shows an average relative error of 4.02%.

TABLE 2

P-F Oligomer Mixture Composition

(Weight %)

	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa
MIXTURE 1							
Certified	15.98	19.78	25.79	3.95	15.82	8.54	10.13
Experimental	16.27	20.57	26.63	3.82	15.31	8.34	9.41
Rel.Error (%)	1.81	3.99	3.26	3.29	3.22	2.34	7.11
MIXTURE 2							
Certified	14.36	16.52	23.34	4.49	14.36	16.16	10.77
Experimental	14.05	15.99	23.64	4.72	14.03	15.51	9.93
Rel.Error (%)	2.15	3.20	1.28	5.12	2.29	4.02	7.80
MIXTURE 3							
Certified	16.24	19.28	26.39	5.07	16.24	6.60	10.15
Experimental	16.08	20.10	27.39	5.27	16.83	6.28	9.04
Rel.Error (%)	0.98	4.25	3.78	3.94	3.63	4.84	10.93
MIXTURE 4							
Certified	18.31	18.31	32.04	1.33	18.31	4.94	6.77
Experimental	17.70	19.53	31.18	1.31	17.80	5.26	7.18
Rel.Error (%)	3.33	6.66	2.68	1.50	2.78	6.48	6.05

Average Relative Error, 4.02% (0.98% - 10.93%)

From the presented data it appears that the reverse-phase technique is especially appropriate for the analysis of identified components in novolac resins. The C_{18} column was able to separate all seven oligomers with both high speed and good resolution.

As an application of this procedure, analysis of two faster-curing novolac samples was carried out. Fingerprints obtained for NOVO-A and NOVO-B resins are compared in Figure 3. The compositions of the major oligomers are shown in Table 3.

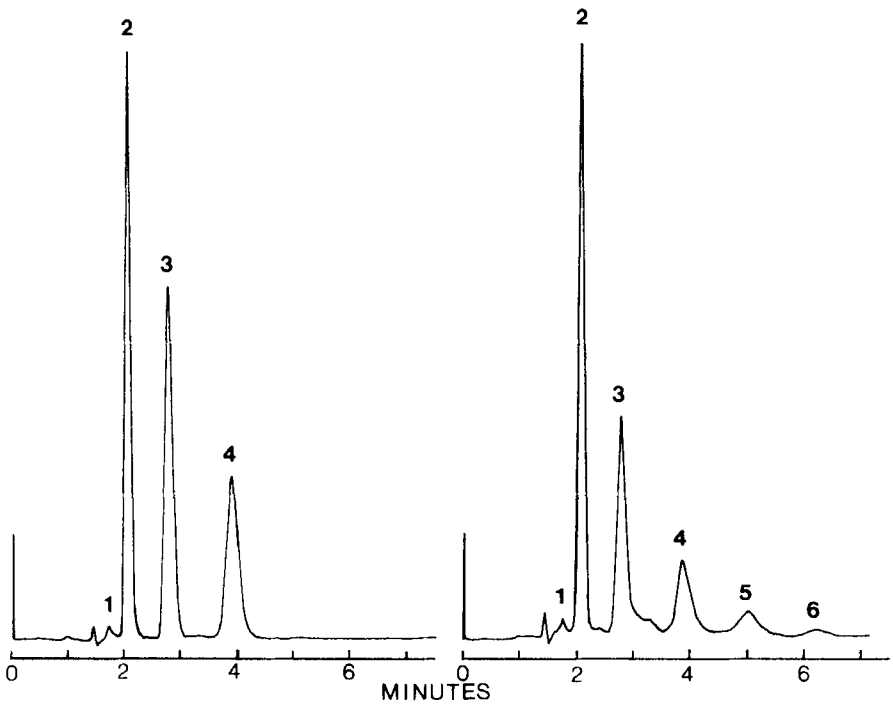

FIGURE 3

Separation of oligomers of all-ortho novolac resins. Resin NOVO-A (left), load 3 µg in 6 ml of methanol; resin NOVO-B (right), load 3 µg in 10 ml of methanol. Conditions and peak identities as in Figure 1.

The results of the HPLC runs for both samples agree,within the experimental error, with the values obtained by other techniques. From these and the above data it is clear that the application of this method to the isolation and quantitation of various polyphenol components is quite facile.

CONCLUSIONS

We have found a suitable HPLC procedure for the identification, separation, and quantitation of methylene-bridged polyphenol com-

TABLE 3
Major Oligomer Composition of
All-ortho Novolac Resins
(Weight %)

	Di	Tri	Tetra	Penta	Hexa
RESIN NOVO-A					
Composition %	39.84	33.53	26.06		
$\bar{M}n$(HPLC)	289.64				
$\bar{M}n$(^{1}H NMR)	280.60				
$\bar{M}n$(^{13}C NMR)	286.51				
$\bar{M}n$(Osmometry)	294.00				
RESIN NOVO-B					
Composition %	53.30	26.89	13.21	4.72	1.89
$\bar{M}n$(HPLC)	279.55				
$\bar{M}n$(^{1}H NMR)	271.40				
$\bar{M}n$ (^{13}C NMR)	275.60				
$\bar{M}n$(Osmometry)	283.00				

pounds occurring in all-ortho P-F novolac resins. Although only seven oligomers (di- to octanuclear) were considered, this was sufficient for the analysis of commercial resins with an average molecular weight ranging from 200 to 600 max. The technique had %RSD from 1.77% for di- to 4.03 for tetranuclear oligomer and the analysis had an average relative error less than 4.05% for analysis of known mixtures. The methodology reportedhere could be useful for the investigation of faster-curing P-F resins in which ortho-ortho methylenes are the sole or the largely predominant bridges.

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