CHROM. 11,070

ANALYSIS OF RESINS FROM HIGHER PHENOLS AND FORMALDEHYDE BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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(First received October 21st, 1977; revised manuscript received April 3rd, 1978)

SUMMARY

The reaction between dimethylphenols and formaldehyde in alkaline medium was studied by high-performance liquid chromatography and ^1H nuclear magnetic resonance spectroscopy. The course of the reaction between higher phenols and formaldehyde was established. The relative retention times of *ortho*- and *para*-substituted phenols produced by reaction with formaldehyde are given. Reactions via the *para* position of substituted phenols appear to be favoured.

INTRODUCTION

The formation of phenolic resins involves three reaction steps: the addition of formaldehyde to phenols to form hydroxymethylphenols, the condensation of hydroxymethylphenols to methylene ether bridged di- or high-molecular compounds and disproportionation of methylene ether bridge to methylene-bridged phenols and formaldehyde. The application of the highly selective high-performance liquid chromatography permits the separation of the products of the reaction between phenols and formaldehyde, which differ in the number of hydroxyl and methyl groups in the benzene ring and in the positions of the hydroxymethyl groups linked to the benzene ring[1,2].

In this paper, we report the results of studies of the separation and identification of the products of the reaction between higher phenols and formaldehyde in alkaline medium. The technique allows the rapid separation of the reaction products, which can be analysed by means of infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy.

EXPERIMENTAL

The phenols were products of Fluka (Buchs, Switzerland) and Ferak (Berlin, G.F.R.). These and all other reagents were of analytical-reagent grade.

A Perkin-Elmer 1220 analytical liquid chromatography was used; the columns were 0.5 m × 0.2 mm I.D. stainless-steel tubes filled with 5-μm LiChrosorb Si-60

using a high-pressure slurry-packing apparatus. For detection, a UV spectrophotometer monitoring at 254 nm was used.

The flow-rate was 0.75 ml/min and the solvent used for elution was dichloromethane–dioxane–methanol (250:8:8). The pressure necessary for maintaing constant a flow-rate was 1500 p.s.i. For injection of samples, an injector loop was used. The separations of resins were repeated 20 times and the products were collected manually at the detector outlet.

The compounds (1–10 mg) were identified by using a Perkin-Elmer 177 grating infrared spectrophotometer and a micro potassium bromide technique (2–13-mm diameter discs). Proton spectra were recorded using a Jeol JNC 60HL NMR spectrometer with a micro cell (0.05–0.1 ml of solution). The samples used in NMR measurements were dissolved in deuterated acetone or chloroform. Tetramethylsilane (TMS) was used as the internal standard. The reaction mixtures of phenols and formaldehyde (37% aqueous solution) prepared in the molar ratio 1:2 with the addition of 0.01 mole of sodium hydroxide as catalyst were studied in the temperature range 70–100°. The reaction time varied from 1 to 3 h.

RESULTS AND DISCUSSION

As described in previous papers[3,4], the separation of the products of reactions of phenols, cresols and dimethylphenols with formaldehyde can be achieved by using high-performance liquid chromatography. The products resulting from such reactions differ in both amounts and the positions of methyl and ethyl groups in the benzene ring. The amount of addition products formed in the reaction between dimethylphenols and formaldehyde depends on the amount of blocked *ortho-* and *para-*positions. The amounts of addition products obtained with *o-*, *m-* and *p-*ethylphenols correspond to the amounts found with cresols, whereas with trimethylphenols one, two or three addition products are formed.

Representative chromatograms of resins from higher phenols and formaldehyde are given in Figs. 1–4. In the reaction between 2,3,5-trimethylphenol and formaldehyde, three addition products are formed (Fig. 1). The first peak in the chromatogram is 2,3,5-trimethylphenol, the second, as inferred from IR and NMR spectra [$\tau_{CH_2OH_{(6)}} = 5.15$ (s)], is 2,3,5-trimethyl-6-hydroxymethylphenol. The third peak may be attributed, on the basis of vibration at 780 cm^{-1}, to a penta-substituted benzene ring. The chemical shift of the hydroxymethyl groups at $\tau = 5.35$ ppm can be ascribed to a *para*-substituted form, namely 2,3,5-trimethyl-4-hydroxymethylphenol. The fourth peak has no vibration due to out-of-plane C–H bonding. On the basis of its NMR [the ratio of area of $CH_2OH_{(2)}$ to area of $CH_2OH_{(4)}$ is 1:1] spectra, it is identified as 2,3,5-trimethyl-4,6-dihydroxydimethylphenol[5-7]. The ratio between the *ortho-* and *para*-substituted forms of 2,3,5-trimethylphenol is 0.4:1, which means that the reaction via the *para*-substituted form is favoured. The course of the reaction between 2,3,5-trimethylphenol and formaldehyde is similar to that of other bifunctional phenols.

From 2,3,6-trimethylphenol and formaldehyde, two peaks in addition to that of the starting phenol are obtained (Fig. 2), of which one represents the addition product and the other bimolecular condensation products. The first peak in the chromatogram is 2,3,6-trimethylphenol. The second peak is 2,3,6-trimethyl-4-
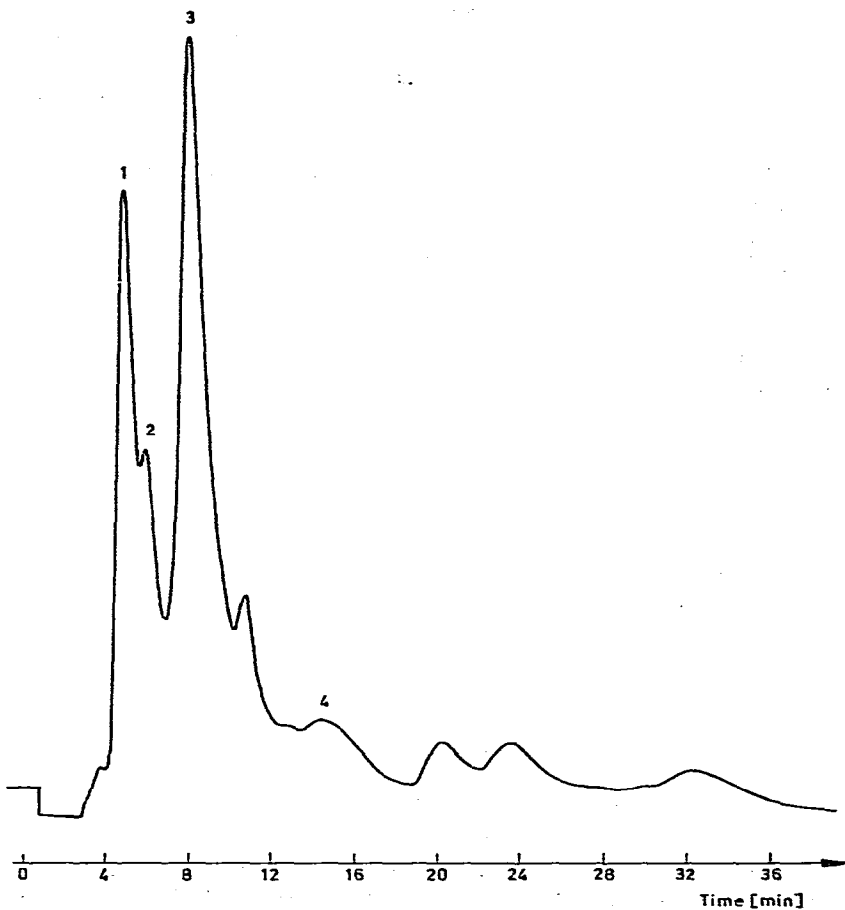
Fig. 1. Chromatogram of the mixture resulting from the reaction between 2,3,5-trimethylphenol and formaldehyde at 70°. Reaction time, 60 min; flow-rate 0.75 ml/min; solvent, dichloromethane–dioxane–methanol (250:8:8). Peaks: 1 = 2,3,5-trimethylphenol; 2 = 2,3,5-trimethyl-6-hydroxymethylphenol; 3 = 2,3,5-trimethyl-4-hydroxymethylphenol; 4 = 2,3,5-trimethyl-4,6-dihydroxydimethylphenol.

hydroxymethylphenol, the identification of which is based on a vibration at 870 cm^{-1} and a chemical shift $\tau_{CH_2OH_{(6)}}$ = 5.45 (s).

In the reaction between 2-ethylphenol and formaldehyde, three dominant components are obtained. The first component is 2-ethyl-6-hydroxymethylphenol, the second 2-ethyl-4-hydroxymethylphenol and the third 2-ethyl-4,6-dihydroxydimethylphenol (Fig. 3). Other peaks are bi- and high-molecular products. The ratio between the *ortho-* and *para*-substituted forms is 0.9:1.

4-Ethylphenol reacts with formaldehyde in a similar manner to *p*-cresol. 4-Ethyl-2-hydroxymethylphenol and 4-ethyl-2,6-dihydroxydimethyl phenol could be identified from the chromatogram.

Compounds of higher molecular weight result from the reaction between mono-, di- and trisubstituted products with a one-ring structure. In Fig. 4 a chro-
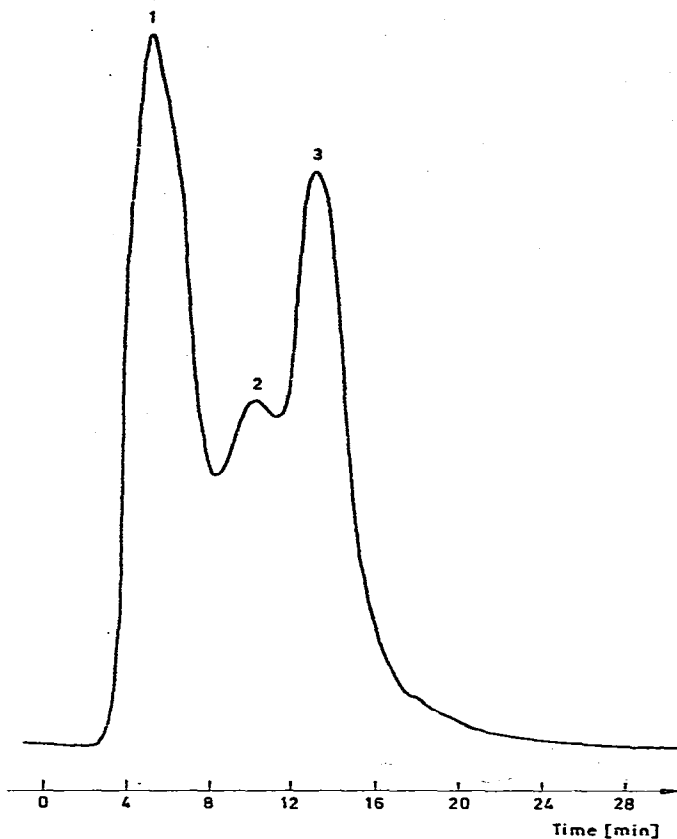
Fig. 2. Chromatogram of the mixture resulting from the reaction between 2,3,6-trimethylphenol and formaldehyde at 70°. Conditions as in Fig. 1. Peaks: 1 = 2,3,6-trimethylphenol; 2 = bimolecular products; 3 = 2,3,6-trimethyl-4-hydroxymethylphenol.

matogram is shown of the products resulting from the reaction between 2,3-dimethyl-phenol and formaldehyde at 70° for 30 min and at 100° for 1 h. In addition to addition products, molecules with two or more rings were also formed; these products have shorter retention times than trisubstituted single-ring compounds owing to the presence of hydroxyl groups, which determine the strength of the bond with the adsorbent.

The principle of separation in the high-performance liquid chromatography of phenolic resins is based on differences in intermolecular bonding between the surface of the silica gel and the hydroxyl groups on the benzene ring[8]. With increasing degree of addition of formaldehyde to phenols, the number of hydroxyl groups is increased. The sequence of appearance of components from the column is identical for all types of phenols, *i.e.*, the monomer is followed by the *ortho*- and *para*-substituted components. The retention times of single components also depend on the position and the number of methyl and ethyl groups linked to the ring (Table I).

Both hydroxymethyl and the hydroxyl groups are characterized by free rotation around the C–C and C–O bonds, so that they can assume various positions
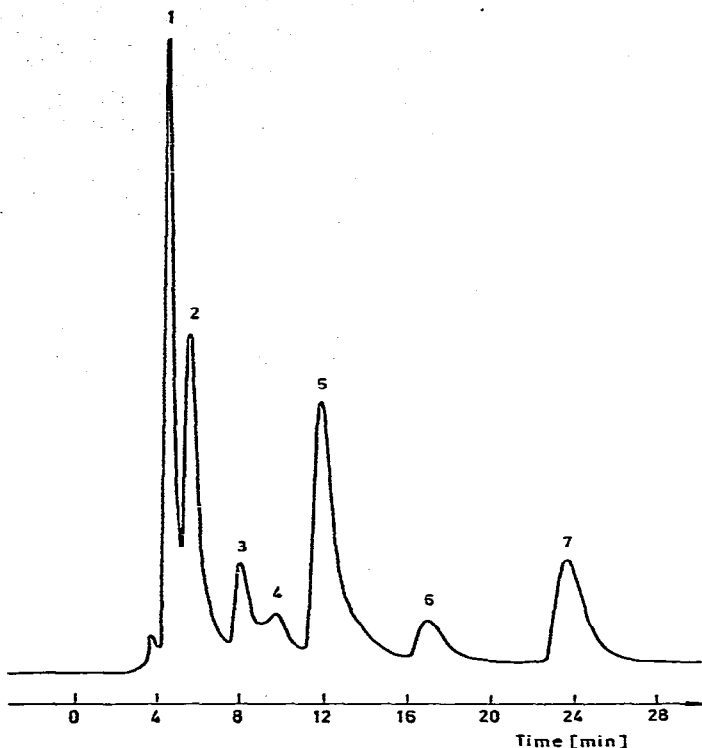
Fig. 3. Chromatogram of the mixture resulting from the reaction between 2-ethylphenol and formaldehyde at 70°. Conditions as in Fig. 1. Peaks: 1 = 2-ethylphenol; 2 = 2-ethyl-6-hydroxymethylphenol; 3, 4 and 6 = high-molecular-weight products; 5 = 2-ethyl-4-hydroxymethylphenol; 7 = 2-ethyl-4,6-dihydroxydimethylphenol.

reflecting both intra- and intermolecular forces. From investigations by Ackermark and other workers[10,11], it follows that the free rotation of hydroxymethyl and methyl groups around the C–C or C–O bond allows the formation of strong intramolecular hydrogen bonds between the hydroxymethyl and the hydroxyl group in the *ortho*-position, even in highly polar solvents; this was shown by the IR adsorption at 3420 cm^{-1} in 2-hydroxymethylphenol. Similar intramolecular bonds have also been observed in compounds obtained in the reaction of other *ortho*-substituted phenols with formaldehyde. Owing to the intramolecular bonds between the hydroxymethyl and the hydroxyl in the *ortho*-position, the intermolecular hydrogen bonds between the dissolved compound and the stationary phase become weakened, so that such a molecule has a weaker bond to the surface of silica gel.

In addition products of *para*-substituted phenols with formaldehyde, both the hydroxyl and hydroxymethyl groups are in different positions on the benzene ring and there is no possibility of the formation of intramolecular hydrogen bonds between the groups. The intermolecular hydrogen bonds formed between the hydroxyl groups of silica gel and the hydroxymethylene and hydroxyl groups linked to the benzene ring are stronger; the effect of this difference results in a longer retention time for *para*- than for *ortho*-substituted phenols with formaldehyde.
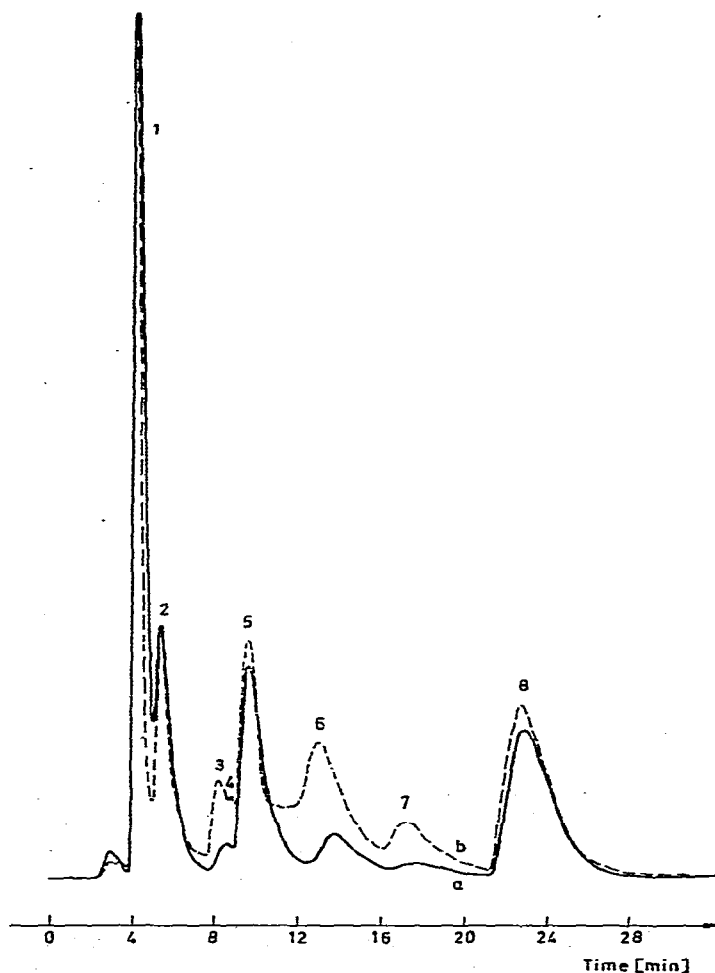
Fig. 4. Chromatogram of the mixture resulting from the reaction between 2,3-dimethylphenol and formaldehyde at (a) 70° and (b) 100°. Conditions as in Fig. 1. Peaks: 1 = 2,3-dimethylphenol; 2 = 2,3-dimethyl-6-hydroxymethylphenol; 3 and 4 = lower-molecular-weight products; 5 = 2,3-dimethyl-4-hydroxymethylphenol; 6 and 7 = high-molecular-weight products; 8 = 2,3-dimethyl-4,6-dihydroxydimethylphenol.

   There are two possible substitutions of formaldehyde on *m*-cresol in the *ortho*-positions, *i.e.*, in the 2- and 6-positions. Both of these forms can be separated into two components by chromatography.

   The hydroxymethyl group situated between the hydroxyl and methyl groups is sterically hindered and can form intramolecular bonds with both adjacent groups, so that the intermolecular forces with silica gel are lower than in 3-methyl-6-hydroxy-methylphenol, in which intramolecular bonds are formed only between the hydroxy-methyl and hydroxyl groups. The bond between 3-methyl-6-hydroxymethylphenol and silica gel is therefore stronger, resulting in a larger retention time. The *para*-substituted model of *m*-cresol has an intramolecular bond between the hydroxymethyl

TABLE I

RELATIVE RETENTION TIMES OF *ortho-* AND *para*-SUBSTITUTED PHENOLS PRODUCED BY REACTION WITH FORMALDEHYDE

Compound	Relative retention
Phenols (monomers)	1.00
2-Hydroxymethylphenol	1.25
4-Hydroxymethylphenol	1.69
2-Methyl-6-hydroxymethylphenol	1.18
2-Methyl-4-hydroxymethylphenol	2.11
3-Methyl-2-hydroxymethylphenol	1.15
3-Methyl-4-hydroxymethylphenol	1.45
3-Methyl-6-hydroxymethylphenol	1.45
4-Methyl-2-hydroxymethylphenol	1.30
2,3-Dimethyl-6-hydroxymethylphenol	1.16
2,3-Dimethyl-4-hydroxymethylphenol	1.72
2,4-Dimethyl-6-hydroxymethylphenol	1.14
2,5-Dimethyl-6-hydroxymethylphenol	1.13
2,5-Dimethyl-4-hydroxymethylphenol	1.74
2,6-Dimethyl-4-hydroxymethylphenol	1.60
3,4-Dimethyl-2-hydroxymethylphenol	1.40
3,4-Dimethyl-6-hydroxymethylphenol	1.40
3,5-Dimethyl-2-hydroxymethylphenol	1.16
3,5-Dimethyl-4-hydroxymethylphenol	1.31
2-Ethyl-6-hydroxymethylphenol	1.25
2-Ethyl-4-hydroxymethylphenol	2.50
4-Ethyl-2-hydroxymethylphenol	1.35

group in the *para*-position and the methyl group. The retention time corresponds to that of 3-methyl-6-hydroxymethylphenol.

The products of the reaction between 2,5- and 2,3-dimethylphenol and formaldehyde give a chromatogram similar to that observed with the products resulting from the reaction between 2,3,5-trimethylphenol and formaldehyde, and it may be supposed that the influence of the methyl group on the intramolecular bonds and steric hindrance in the 3- and 5-positions is the same. Comparison with the products of the reaction between *o*-cresol and formaldehyde indicates that for all *ortho*-substituted compounds retention times are similar, whereas 2-methyl-4-hydroxymethylphenol has a longer retention time than the *para*-substituted compound from 2,3- and 2,5-dimethylphenol and 2,3,5-trimethylphenol. This can be explained by the fact that the *para*-substituted compound from *o*-cresol does not possess an adjacent methyl group that could form intramolecular bonds and steric hindrance, thus reducing the bonding with the surface of the silica gel.

Similar results were obtained with products of the reaction between 3,4-dimethylphenol, 3,5-dimethylphenol and 2,3,6-trimethylphenol and formaldehyde.

The products of the reaction between ethylphenols and formaldehyde give similar chromatographic results to those obtained in the reaction of methylphenols with formaldehyde. The differences between the two groups of products are so slight that their chromatographic behaviour is virtually identical.

CONCLUSIONS

The use of high-performance liquid chromatography for the separation of phenolic resins combined with IR and NMR spectroscopy for identification of the products allows the course of the condensation of phenolic resins to be followed.

The number of hydroxyl groups introduced into the benzene ring and also their positions are of decisive importance for the retention times of products resulting from the reaction between phenols and formaldehyde. The formation of intramolecular bonds and steric hindrance between hydroxymethyl, hydroxyl and methyl groups result in a decrease in the intermolecular bonds formed with the stationary phase. Owing to stronger intermolecular forces caused by different positions of the hydroxymethyl group on the aromatic ring, the retention times of *ortho*-substituted phenols are lower than those of *para*-substituted phenols.

ACKNOWLEDGEMENTS

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