

Note

Separation and identification of phenol-formaldehyde condensates by gas chromatography-mass spectrometry

IV*. Application of a stationary phase of intermediate polarity to the analysis of methylolated dihydroxydiphenylmethanes

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Previous studies on the composition of the condensation products of phenol with formaldehyde have revealed that gas chromatography-mass spectrometry (GC-MS) using trimethylsilylation has considerable potential in the characterization of many low-molecular-weight compounds found in different resins¹⁻⁶. In investigations of the reaction mechanisms, several types of oligomeric species have received attention, especially those formed by the condensation of two or more phenolic nuclei. In certain instances not all the possible positional isomers of a given structure were detected. For instance, Lindner¹ identified 2,2'- and 4,4'-dihydroxydiphenylmethane in a product obtained under base-catalysed conditions and on applying an excess of formaldehyde the 2,4'-isomer was found to be absent.

The assignment of methylolated dihydroxydiphenylmethane positional isomers present in resol-type resins has been attempted based on the fact that the number of components separated by apolar stationary phases was less than the number of possible isomers and provided that complete separation has been achieved, the best matching was achieved by considering only two of the three possible types of connections of phenolic units via methylene bridges (*viz.*, 2,2'- and 4,4'-dihydroxy compounds).

Reversed-phase high-performance liquid chromatographic (HPLC) separation of the title compounds has been reported recently by Mechin *et al.*⁷. ¹H and ¹³C NMR spectrometric investigations revealed the predominant formation of 2,4'- and 4,4'-connections for the methylolated dimers.

This study was undertaken to reinvestigate the effectiveness of GC analyses in the field concerned.

EXPERIMENTAL

Gas chromatograms were recorded on a JGC-20K (JEOL, Tokyo, Japan) instrument equipped with a flame ionization detector and using an SP-4000 chromato-

* For Part III, see ref. 6.

graphy data system (Spectra-Physics, San Jose, CA, U.S.A.). The mass spectrometer interfaced to the gas chromatograph as described earlier^{4,5}. Borosilicate glass column of 30 m \times 0.25 mm I.D. coated with SP-2250 stationary phase of 0.20 μ m film thickness (Supelco, Bellefonte, PA, U.S.A.) was used. Helium was applied as the carrier gas with a linear velocity of 30 cm/min. The injection port and detector temperatures were maintained at 280°C. Split injection with a ratio of *ca.* 1:100 was used. The column oven was held at 120°C for 3 min, then programmed to 280°C at 12°C/min.

The preparation and trimethylsilylation of resol with N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) were carried out as described previously⁵.

RESULTS AND DISCUSSION

Using a stationary phase of intermediate polarity [SP-2250; methylsilicone-phenylsilicone (50:50)] in the analysis of trimethylsilylated resol obtained with a 1:1.5 phenol to formaldehyde molar ratio, in contrast with apolar stationary phases⁵, trinuclear phenols and methylolated trinuclear phenols were not present in the chromatogram under the conditions described above. Mononuclear methylolated phenols showed similar retention properties in both instances.

Further separation of the methylolated dihydroxydiphenylmethanes was achieved, however, as is shown by the relevant part of the chromatogram in Fig. 1. GC and GC-MS investigations of the unsubstituted dimers revealed that only 2,4'- and 4,4'-dihydroxydiphenylmethane were present. From a chemical point of view it

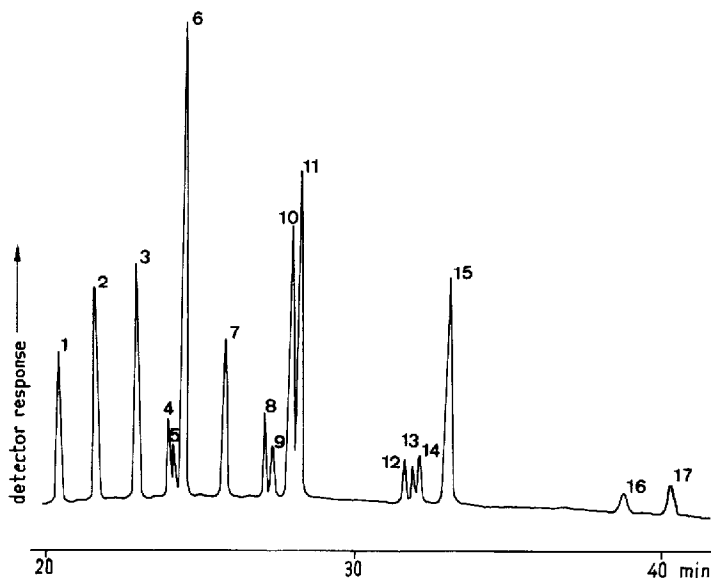


Fig. 1. Separation of trimethylsilylated dinuclear compounds present in phenol-formaldehyde resol. Column, 30 m \times 0.25 mm I.D. coated with 0.20 μ m SP-2250. Carrier gas, helium, linear velocity 30 cm/min. Split injection (1:100); port temperature, 280°C. Flame ionization detector; temperature, 280°C. GC oven, initial hold for 3 min at 120°C then programmed to 280°C at 12°C/min. For peak assignments, see in Table I.

TABLE I

IDENTIFICATION OF COMPONENTS HAVING THE DIHYDROXYDIPHENYLMETHANE SKELETON AS TRIMETHYLSILYL DERIVATIVES

Peak No.	Compound
1	2,4'-Dihydroxydiphenylmethane
2	4,4'-Dihydroxydiphenylmethane
3	3'-Methylol-2,4'-dihydroxydiphenylmethane
4	3-Methylol-2,4'-dihydroxydiphenylmethane
5	5-Methylol-2,4'-dihydroxydiphenylmethane
6	3-Methylol-4,4'-dihydroxydiphenylmethane
7	3',5'-Dimethylol-2,4'-dihydroxydiphenylmethane
8	3,3'-Dimethylol-2,4'-dihydroxydiphenylmethane
9	5,3'-Dimethylol-2,4'-dihydroxydiphenylmethane
10	3,3'-Dimethylol-4,4'-dihydroxydiphenylmethane
11	3,5-Dimethylol-4,4'-dihydroxydiphenylmethane
12	3,3',5'-Trimethylol-2,4'-dihydroxydiphenylmethane
13	5,3',5'-Trimethylol-2,4'-dihydroxydiphenylmethane
14	3,5,3'-Trimethylol-2,4'-dihydroxydiphenylmethane
15	3,5,3'-Trimethylol-4,4'-dihydroxydiphenylmethane
16	3,5,3',5'-Tetramethylol-2,4'-dihydroxydiphenylmethane
17	3,5,3',5'-Tetramethylol-4,4'-dihydroxydiphenylmethane

is obvious that these compounds can be accepted as skeletons of methylol-substituted components. This conclusion is confirmed by ^{13}C NMR spectrometric results. Based on mass spectra, the two distinct groups of isomers are readily distinguishable. The only problem is the assignment of components possessing the 2,4'-dihydroxydiphenylmethane skeleton but substituted by only one methylol in the ring having an *ortho*-hydroxy group relative to the methylene bridge in the parent compound (*i.e.*, for peaks 4 and 5, 8 and 9, 12 and 13). These pairs of isomer structures produce similar mass spectra as expected from the fragmentation pattern⁵.

Obviously, the position of the substituent introduced by the condensation with formaldehyde can be *ortho* or *para* as in mononuclear compounds where the order of retention for trimethylsilyl derivatives has been ascertained previously^{1,3,5}. Accepting the rule that *ortho* isomers precede *para* isomers in the present compounds also, the tentative identification of components containing two aromatic nuclei is made as listed in Table I. These assignments are in agreement with the results of HPLC separation followed by NMR spectroscopy⁷; hence GC can also be applied effectively for the characterization of dimer condensation products present in resol-type resins.

REFERENCES

- 1 W. Lindner, *J. Chromatogr.*, 151 (1978) 406.
- 2 R. Gnauck and D. Habisch, *Plaste Kautsch.*, 27 (1980) 485.
- 3 G. M. Anthony and G. Kemp, *Angew. Makromol. Chem.*, 115 (1983) 183.
- 4 L. Prókai, *J. Chromatogr.*, 329 (1985) 290.
- 5 L. Prókai, *J. Chromatogr.*, 331 (1985) 91.
- 6 L. Prókai, *J. Chromatogr.*, 333 (1985) 161.
- 7 B. Mechin, D. Hanton, J. Le Goff and J. P. Tanneur, *Eur. Polym. J.*, 20 (1984) 333.