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SEPARATION AND IDENTIFICATION OF PHENOL–FORMALDEHYDE CONDENSATES BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY

II*. BASE-CATALYSED CONDENSATION PRODUCTS

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SUMMARY

The characterization of phenol–formaldehyde condensates obtained by base catalysis is described. Trimethylsilyl derivatives of the components were prepared and analysed by gas chromatography–mass spectrometry. Electron impact ionization mass spectra of methylolated dihydroxydiphenylmethane positional isomers are discussed. Prominent differences in ion abundances facilitate the identification of the compounds. Substituted trinuclear phenols among the reaction products are also described.

INTRODUCTION

Bakelite, the first plastic produced and commercially applied, is prepared by condensation of the prepolymer, the so-called resol, which is obtained by base-catalysed condensation of phenol with a molar excess of formaldehyde[1]. The condensation itself is complex and not completely understood in every detail. Diverse analytical methods have been used for the determination of the molecular species and the chemical composition of different resins of the resol type in order to obtain information on the mechanism of the reactions. These methods have been reviewed[2].

Numerous types of reaction may occur[3] and a multitude of mono- and polynuclear phenols (with both methylene and dimethylene ether linkages) and their mono- and polyhemiformals have been identified as reaction products. However, the complete characterization of the individual compounds is not exhaustive. The complexity of the resol requires the application of high-performance separation techniques (*e.g.*, liquid chromatography, gas chromatography). In this paper, emphasis is placed on the investigation of a resol similar to those which are produced on a large scale in the chemical industry as commodities. Gas chromatography (GC) was chosen to resolve the components prior to mass spectrometric analysis.

The direct gas–liquid chromatography of resols has failed because of the in-

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* For Part I, see ref. 9.

volatility and thermal instability of the compounds. Derivative formation by blocking off the hydroxy groups, however, has been successfully applied to surmount these difficulties. Mononuclear phenols were converted into acetyl derivatives and analysed by GC[4]. Trimethylsilylation was found to be more effective and improved the resolution and allowed the characterization of high-molecular-weight polynuclear methylol phenols[5]. GC coupled with mass spectrometry (GC–MS) was used to identify the trimethylsilylated resol components[3,6,7].

The exploitation of the above technique, however, is far from complete; in particular, the identification of positional isomers has been lacking. This paper attempts to clarify this aspect.

EXPERIMENTAL

Resol was prepared from phenol and formaldehyde [in 37% (w/w) aqueous solution] using a 1:1.5 molar ratio and sodium hydroxide (0.02 mole) as a catalyst. The stirred reaction mixture was maintained under reflux. After 2 h, the liquid was allowed to cool and the resinous layer was separated, washed with water and the residual moisture was removed by means of a vacuum evaporator at ambient temperature[8].

Trimethylsilylation was carried out with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) as described previously[9].

Low- and high-resolution mass spectra were recorded on a Jeol JMS-01SG-2 double focusing instrument at 75 or 15 eV ionizing electron energy, 200 μA trap current, 250°C ion source temperature and 10 kV accelerating voltage. Accurate mass measurements were carried out at resolution of $\geqslant 10\ 000$ (10% valley definition) using perfluorokerosene as an internal mass standard. The GC instrumentation described previously[9] (Jeol JGC-20K, jet separator, etc.) was used.

Separations were performed using 40 m × 0.5 mm I.D. SP-2100 support-coated open-tubular (SCOT) and 50 m × 0.33 mm I.D. BP-1 bonded-phase fused-silica columns with a 1.0-μm film thickness (Scientific Glass Engineering, North Melbourne, Australia). Split injection with a ratio of 1:20 was used. The GC oven temperatures were programmed from 120 to 275°C at 3°C/min (SCOT column) and from 150 to 300°C at 5°C/min (fused-silica capillary column).

RESULTS AND DISCUSSION

The total ion current chromatogram of trimethylsilylated resol obtained with the SCOT column is presented in Fig. 1. Peaks are numbered consecutively. Structure-type assignments (Table I) were made according to the mass-to-charge (m/z) value of the molecular ions. Schematic representations are shown in Fig. 2. The formulae enclosed in square brackets denote the aromatic nuclei, namely phenol or two or three phenols connected to each other by methylene linkages. These can be further substituted with the given number of methylol groups that are enclosed in parentheses. Considering *ortho* and *para* substitution, the number of possible isomers exceeds the number of components separated by GC under the chromatographic conditions used [number of effective plates for peak 4 ($k' = 8.45$), $N_{eff} = 62\ 000$]. For instance, three and four components were separated instead of six and ten in the
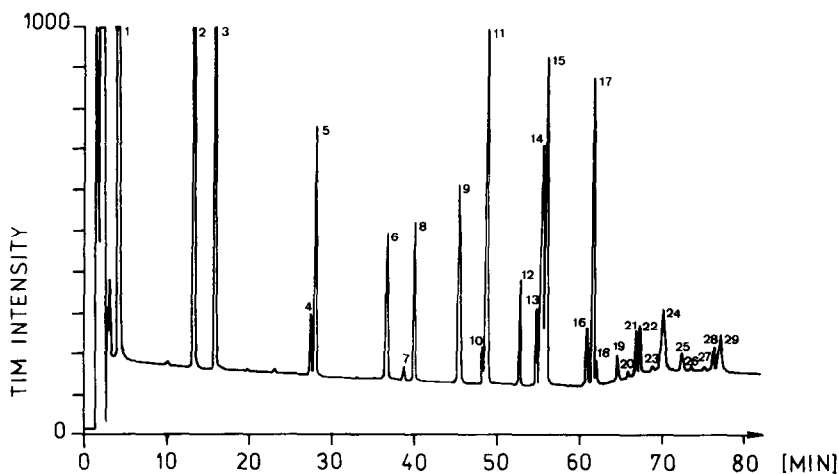
Fig. 1. Total ion chromatogram of trimethylsilylated resol. Column: 40 m × 0.5 mm I.D. SP-2100 SCOT capillary. Carrier gas, helium; flow-rate, 2 ml/min; injection port temperature, 280°C; GC oven, programmed from 120 to 275°C at 3°C/min.

case of V and VI, respectively. The fused-silica capillary column was used to achieve a better resolution (N_{eff} = 135 000 for peak 4).

Selected ion monitoring of m/z = 446 + 548 was applied to ensure the rapid recording of the molecular ion intensities. The chromatogram is displayed in Fig. 3, and shows the presence only of those compounds that had been separated formerly. Therefore, it was concluded that no other isomers were present in a single GC peak at a concentration comparable to the amount of the main component. Similar results have been obtained by other workers[3] and some of the isomers were identified using authentic compounds, but generally the appearances of the mass spectra and the

TABLE I

STRUCTURE-TYPE IDENTIFICATION OF RESOL COMPONENTS BY GC–MS

Peak No.	$M^{+\cdot}$ of trimethylsilyl derivative*	Structure type
1	166	Phenol
2–3	268	I
4–5	370	II
6	344	IV
7	472	III
8	344	IV
9–11	446	V
12–15	548	VI
16–18	650	VII
19	522	IX
20–21	752	VIII
22–24	624	X
25–29	726	XI

* $M^{+\cdot}$, m/z of molecular ion.

$$\left[\begin{array}{c}OH\\ \bigcirc \end{array}\right](CH_2OH) \qquad \left[\begin{array}{c}OH\\ \bigcirc \end{array}\right](CH_2OH)_2 \qquad \left[\begin{array}{c}OH\\ \bigcirc \end{array}\right](CH_2OH)_3$$

$$\text{I} \hspace{3cm} \text{II} \hspace{3cm} \text{III}$$

$$\left[\begin{array}{c}OH \qquad OH\\ \bigcirc\!-\!CH_2\!-\!\bigcirc \end{array}\right] \qquad \left[\begin{array}{c}OH \qquad OH\\ \bigcirc\!-\!CH_2\!-\!\bigcirc \end{array}\right](CH_2OH)$$

$$\text{IV} \hspace{4cm} \text{V}$$

$$\left[\begin{array}{c}OH \qquad OH\\ \bigcirc\!-\!CH_2\!-\!\bigcirc \end{array}\right](CH_2OH)_2 \qquad \left[\begin{array}{c}OH \qquad OH\\ \bigcirc\!-\!CH_2\!-\!\bigcirc \end{array}\right](CH_2OH)_3$$

$$\text{VI} \hspace{4cm} \text{VII}$$

$$\left[\begin{array}{c}OH \qquad OH\\ \bigcirc\!-\!CH_2\!-\!\bigcirc \end{array}\right](CH_2OH)_4 \qquad \left[\begin{array}{c}OH \qquad OH \qquad OH\\ \bigcirc\!-\!CH_2\!-\!\bigcirc\!-\!CH_2\!-\!\bigcirc \end{array}\right]$$

$$\text{VIII} \hspace{4cm} \text{IX}$$

$$\left[\begin{array}{c}OH \quad OH \quad OH\\ \bigcirc\!-\!CH_2\!-\!\bigcirc\!-\!CH_2\!-\!\bigcirc \end{array}\right](CH_2OH) \qquad \left[\begin{array}{c}OH \quad OH \quad OH\\ \bigcirc\!-\!CH_2\!-\!\bigcirc\!-\!CH_2\!-\!\bigcirc \end{array}\right](CH_2OH)_2$$

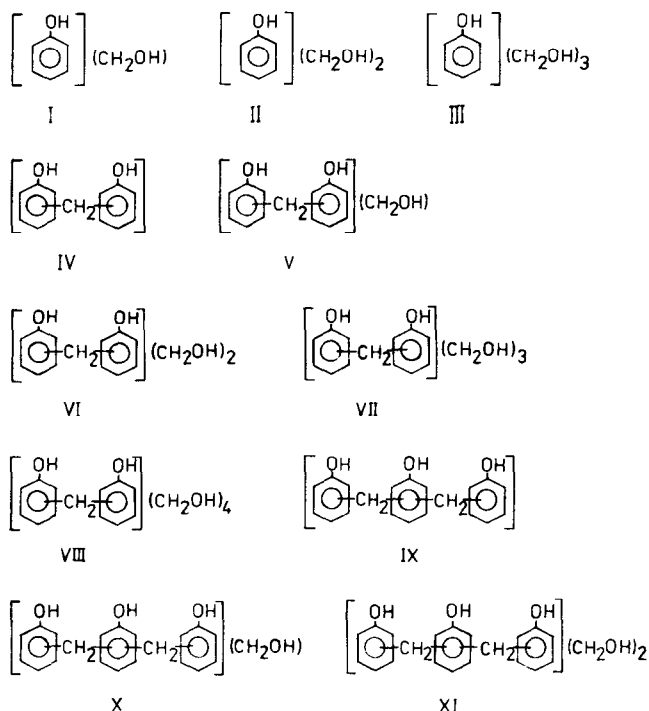$$\text{X} \hspace{4cm} \text{XI}$$

Fig. 2. Schematic representation of compound types identified in resol. Formulae enclosed in square brackets denote the aromatic nuclei, which are substituted by the given number of methylol groups shown in parentheses.

fragmentation patterns have not been considered extensively. It was shown that the *ortho* isomer of I preceded the *para* isomer[3]. Comparing their mass spectra, it can be stated that the latter has a more abundant molecular ion than the former. In an analogous way, the identification of 2,6- and 2,4-dimethylolphenol is obvious.

All of the positional isomers of IV and IX were found among the acid-catalysed condensation products and, therefore, the assignment of the above-mentioned components was apparent[9]. Their methylol-substituted analogues require further considerations based on mass spectra. Structure-type VI is chosen as a representative. In Fig. 4 the 75 eV mass spectra of peaks 12–15 are shown. These components can be
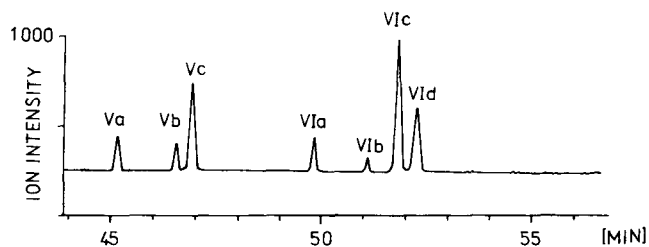

Fig. 3. Ion chromatogram of molecular ions of structure types V and VI. Selected ion monitoring, $m/z = 446 + 548$. Chromatographic conditions: 50 m × 0.33 mm I.D. BP-1 bonded-phase fused-silica column; GC oven, programmed from 150 to 300°C at 5°C/min; other conditions in Fig. 1.
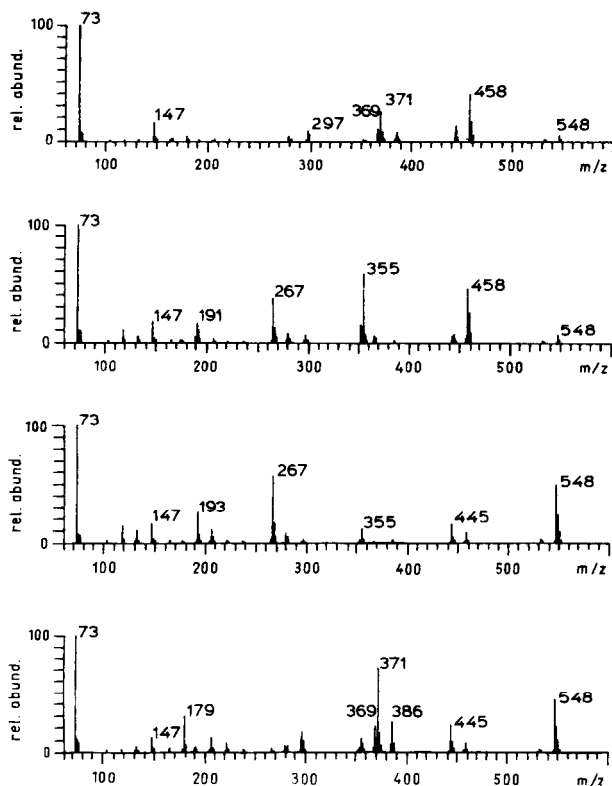
Fig. 4. Mass spectra of structure-type VI isomers (trimethylsilyl derivatives). (a) Tetrakis(trimethylsilyl)-3,5-dimethylol-2,2'-dihydroxydiphenylmethane;   (b)   tetrakis(trimethylsilyl)-3,5'-dimethylol-2,2'-dihydroxydiphenylmethane; (c) tetrakis(trimethylsilyl)-3,3'-dimethylol-4,4'-dihydroxydiphenylmethane; (d) tetrakis(trimethylsilyl)-3,5-dimethylol-4,4'-dihydroxydiphenylmethane. Recorded at electron energy 75 eV and source temperature 250°C.

divided into two groups according to the molecular ion abundances. Within these groups the variation of the parent peak intensities is much less than the difference between them. As a consequence, it can be concluded that the relative position of the trimethylsiloxy groups directly attached to the aromatic rings has a definitive effect on the relative abundance of the molecular ion and the substitution mode of trimethylsilylated methylol groups is of secondary importance, although the substitution itself causes an overall decrease in the abundance of the parent ion. Thus, 12 and 13 are assigned to 2,2'- and 14 and 15 to 4,4'-dihydroxydiphenylmethane derivatives.

The elemental composition of characteristic fragments inferred from accurate mass measurements is given in Table II. A common feature of the mass spectra is the extensive loss of silicon-containing functionalities in the form of neutral molecules, such as trimethylsilanol from the molecular ion giving $m/z = 458$, or in form of radicals, such as the loss of $.CH_2OSi(CH_3)_3$ from the molecular ion or $m/z = 458$ giving $m/z = 445$ and $m/z = 355$, respectively.

TABLE II

ELEMENTAL COMPOSITION OF CHARACTERISTIC FRAGMENTS PRESENT IN THE MASS SPECTRA OF VIa–d

m/z	Elemental composition	Parity*
267	$C_{13}H_{23}O_2Si_2$	EE^+
297	$C_{14}H_{25}O_3Si_2$	EE^+
355	$C_{20}H_{27}O_2Si_2$	EE^+
369	$C_{17}H_{33}O_3Si_3$	EE^+
371	$C_{20}H_{27}O_3Si_2$	EE^+
386	$C_{21}H_{30}O_3Si_2$	$OE^{+\cdot}$
445	$C_{23}H_{37}O_3Si_3$	EE^+
458	$C_{24}H_{38}O_3Si_3$	$OE^{+\cdot}$

* EE^+ = even-electron ion; $OE^{+\cdot}$ = odd-electron ion.

A structurally informative ion at $m/z = 267$ is obtained in the case of VIb and VIc (Fig. 4b and c), which is explained by

$$\left[\begin{array}{c} OSi(CH_3)_3 \\ \bigcirc -CH_2OSi(CH_3)_3 \end{array} \right]^+$$
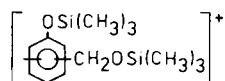
resulting from the cleavage of the methylene bridge between the aromatic rings. This peak is not present in the mass spectra shown in Fig. 4a and d, but the latter exhibit $m/z = 369$, which can be assigned to

$$\left[(CH_3)_3SiOCH_2 - \bigcirc \begin{array}{c} OSi(CH_3)_3 \\ -CH_2OSi(CH_3)_3 \end{array} \right]^+$$
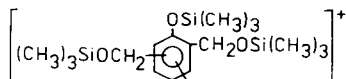
The loss of bis(trimethylsilyl) ether ($m/z = 386$) and the consecutive loss of a methyl radical ($m/z\ 371$) and then trimethylsilane ($m/z = 297$) are caused by silicon-containing substituents that are attached to the same aromatic ring. Although these could be treated as rearrangements due to the functionalities, especially to the tri-methylsiloxy groups, they are useful in the identification of the particular isomer structure. The ion genetic information is supported by the accurate mass measurements and partly by the fact that in the low ionizing voltage mass spectra (at 15 eV) the consecutive steps in the fragmentation are greatly reduced and rearrangements leading to odd-electron ions are favoured[10]. Thus, e.g., in the case of VId, $m/z = 458$ and 386 are more prominent than their daughter ions, i.e., $m/z = 355$ and 371, as well as $m/z = 297$, respectively. To summarize, the precursors of the fully trimeth-ylsilylated derivatives described above were the following: VIa = 3,5-dimethylol-2,2'-dihydroxydiphenylmethane, VIb = 3,5'-dimethylol-2,2'-dihydroxydiphenyl-methane, VIc = 3,3'-dimethylol-4,4'-dihydroxydiphenylmethane and VId = 3,5-di-methylol-4,4'-dihydroxydiphenylmethane.

Applying the fragmentation rules elucidated previously, the components containing two phenolic nuclei could be identified easily. There were no striking differences, however, in the mass spectra of trinuclear isomer compounds. On the other hand, only one isomer of structure-type IX was found [19 = 5-(4-hydroxybenzyl)-2,2'-dihydroxydiphenylmethane] in the resol. Their methylolated analogues were assigned assuming this type of connection of aromatic rings to be present alone.

The compounds identified in resol are listed in Table III.

TABLE III

IDENTIFICATION OF PRECURSOR COMPONENTS IN RESOL FOLLOWING TRIMETHYL-SILYLATION AND GC–MS ANALYSIS

Peak no.	Compound
1	Phenol
2 (Ia)	2-Methylolphenol
3 (Ib)	4-Methylolphenol
4 (IIa)	2,6-Dimethylolphenol
5 (IIb)	2,4-Dimethylolphenol
6 (IVa)	2,2'-Dihydroxyphenylmethane
7 (III)	2,4,6-Trimethylolphenyl
8 (IVb)	4,4'-Dihydroxydiphenylmethane
9 (Va)	3-Methylol-2,2'-dihydroxydiphenylmethane
10 (Vb)	5-Methylol-2,2'-dihydroxydiphenylmethane
11 (Vc)	3-Methylol-4,4'-dihydroxydiphenylmethane
12 (VIa)	3,5-Dimethylol-2,2'-dihydroxydiphenylmethane
13 (VIb)	3,5'-Dimethylol-2,2'-dihydroxydiphenylmethane
14 (VIc)	3,3'-Dimethylol-4,4'-dihydroxydiphenylmethane
15 (VId)	3,5-Dimethylol-4,4'-dihydroxydiphenylmethane
16 (VIIa)	3,3',5-Trimethylol-2,2'-dihydroxydiphenylmethane
17 (VIIb)	3,3',5-Trimethylol-4,4'-dihydroxydiphenylmethane
18 (VIIc)	3,5,5'-Trimethylol-2,2'-dihydroxydiphenylmethane
18 (IX)	5-(4-Hydroxybenzyl)-2,2'-dihydroxydiphenylmethane
20 (VIIIa)	3,3',5,5'-Tetramethylol-2,2'-dihydroxydiphenylmethane
21 (VIIIb)	3,3',5,5'-Tetramethylol-4,4'-dihydroxydiphenylmethane
22 (Xa)	3'-Methylol-5-(4-hydroxybenzyl)-2,2'-dihydroxydiphenylmethane
23 (Xb)*	3- or 5'-methylol-5-(4-hydroxybenzyl)-2,2'-dihydroxydiphenylmethane
24 (Xc)	5-(3-Methylol-4-hydroxybenzyl)-2,2'-dihydroxydiphenylmethane
25 (XIa)	3',5'-Dimethylol-5-(4-hydroxybenzyl)-2,2'-dihydroxydiphenylmethane
26 (XIb)*	3,3'- or 3,5'-dimethylol-5-(4-hydroxybenzyl)-2,2'-dihydroxydiphenylmethane
27 (XIc)*	3'- or 5'-methylol-5-(3-methylol-4-hydroxybenzyl)-2,2'-dihydroxydiphenylmethane
28 (XId)	3-Methylol-5-(3-methylol-4-hydroxybenzyl)-2,2'-dihydroxydiphenylmethane
29 (XIe)	5-(3,5-Dimethylol-4-hydroxybenzyl)-2,2'-dihydroxydiphenylmethane

    * Present only in low concentration; the positions of substituents are estimates.

CONCLUSIONS

Trimethylsilylation has facilitated GLC analysis of components obtained by base-catalysed condensation of phenol and formaldehyde which are otherwise thermally unstable. In this work compound types of higher molecular weight (over 600, in the trimethylsilylated form) were found for the first time. Capillary columns were applied to achieve the separation of positional isomers.

By means of detailed electron impact ionization (EI) mass spectrometric investigations, the general rules of the fragmentation of methylolated polynuclear phenols were elucidated and characteristic ions for the identification of the particular structures were determined. These results offer great prospects for the detailed characterization of phenolic condensates, so that GC–MS might become an invaluable technique in the analysis of the molecular species.

REFERENCES

1 R. Wegler and H. Herlinger, *Houben-Weyl, Methoden der organischen Chemie*, Band XIV, Teil 2, Georg Thieme Verlag, Stuttgart, 1963, p. 193.
2 M. Tsuge, *Prog. Org. Coat.*, 9 (1981) 107.
3 G. M. Anthony and G. Kemp, *Angew. Makromol. Chem.*, 115 (1983) 183.
4 H. P. Higginbottom, H. M. Culbertson and J. C. Woodbrey, *Anal. Chem.*, 37 (1965) 1021.
5 G. E. Throughton and L. Rozon, *Wood Sci.*, 4 (1972) 219.
6 W. Lindner, *J. Chromatogr.*, 151 (1978) 406.
7 R. Gnauck and D. Habisch, *Plaste Kautsch.*, 27 (1980) 485.
8 G. F. D'Alelio, *Experimental Plastics and Synthetic Resins*, Wiley, New York, 1948, p. 8.
9 L. Prókai, *J. Chromatogr.*, 329 (1985) 290.
10 F. W. McLafferty, *Interpretation of Mass Spectra*, University Science Books, Mill Valley, CA, 3rd ed., 1980.