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ANALYSIS OF 2,2-DI(*p*-OLIGOOXYETHYLENEPHENYL)PROPANE BY GAS CHROMATOGRAPHY AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

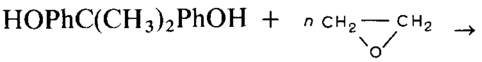
Gas chromatography and gas chromatography–mass spectrometry were used to analyse polydisperse mixtures of diols containing up to ten oxyethylene groups. The products were analysed as their trimethylsilyl derivatives. Arithmetic retention indices were determined for the diol homologues. The mass spectra of the trimethylsilyl derivatives of the compounds investigated are discussed.

INTRODUCTION

2,2-Di(*p*-oligooxyethylenephenyl)propane (dianol) is formed as a result of the reaction of 2,2-di(*p*-hydroxyphenyl)propane (bisphenol A, dian) with chlorhydrins, usually ethylene chlorhydrin, or in the addition reaction with ethylene oxide. The reactions in the synthesis of dianols can be described by

$$\mathrm{HOPhC(CH_3)_2PhOH + 2\ ClCH_2CH_2OH \rightarrow}$$
$$\mathrm{HOCH_2CH_2OPhC(CH_3)_2PhOCH_2CH_2OH + 2\ HCl}$$

where Ph is a phenylene group. The main product of this reaction is 2,2-di(*p*-2-hydroxyethoxyphenyl)propane



$$\mathrm{HOPhC(CH_3)_2PhOH} + n\ \mathrm{CH_2{-}CH_2}\ (\mathrm{{-}O{-}}) \rightarrow$$

$$\mathrm{H(OCH_2CH_2)_{\mathit{x}}OPhC(CH_3)_2PhO(CH_2CH_2O)_{\mathit{y}}H}$$

where $x + y = n$.

The addition reaction of ethylene oxide to 2,2-di(*p*-hydroxyphenyl)propane leads to the formation of a polydisperse mixture of the oxyethylated homologues of bisphenol A, having various numbers of oxyethylene groups. Dianols are bifunctional compounds. Their composition has an important influence on the quality of the final products, which are used in the production of epoxide resins, polycarbonates and polyurethanes. So far, only monofunctional compounds of this type, such as oxyethylated alkylphenols, have been analyzed by gas chromatography (GC)[1–3] and high-performance liquid chromatography (HPLC)[4,5].

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The aim of our work was the analysis of the dianol homologues by GC and gas chromatography–mass spectrometry (GC–MS).

EXPERIMENTAL

A gas chromatograph (Perkin-Elmer Model 900) with a flame ionization detector was used. The separation was carried out in a stainless-steel column (0.6 m × 2.7 mm I.D.) containing Chromosorb G AW DMCS (60–80 mesh) as the support and silicone resin OV-17 (1.0%) as the liquid phase. Argon was the carrier gas at a flow-rate of 15 ml/min. The temperature of both the injector and detector was 320°C. The column temperature was raised from 150 to 320°C at a rate of 4°C/min.

Trimethylsilyl derivatives of the dianols were prepared in a glass micro reaction vessel (capacity, 5 ml) with a PTFE-lined cap (Supelco, Bellefonte, PA, U.S.A.). A sample of *ca.* 0.01 g of the dianol and 0.2 ml of N,O-bis(trimethylsilyl)acetamide (BSA) (POCh, Gliwice, Poland) were added. The sealed reaction vessel containing dianol and BSA was maintained at 80°C for 30 min and shaken from time to time. The silylated product was then analysed.

Acetate derivatives were also prepared for the analysis of polyoxyethylene glycol. To a sample of 0.05–0.1 g of the dianol, 2 ml of acetyl chloride (AR grade; Fluka, Buchs, Switzerland) were added. The reaction mixture was then heated until it gently boiled and was kept in this state for about 1 min. After keeping the reaction mixture at room temperature for *ca.* 1 min, it was heated to 40–50°C, and the excess of acetyl chloride, acetic acid and hydrogen chloride which were formed during the reaction were evaporated by passing dried nitrogen over the surface of the reaction mixture. Then, a few drops of benzene were added and the product was analyzed.

The identification of the dianol homologues separated was carried out by means of a mass spectrometer, coupled through a Becker-Ryhage separator with a gas chromatograph (GC/MS 2091; LKB, Bromma, Sweden). The chromatographic column and conditions were the same as for the GC analysis. The mass spectra were taken at the tops of the chromatographic peaks. An ionization energy of 70 eV, an ion-source temperature of 250°C, an accelerating voltage of 3.5 kV and a sweep time of 9 s were employed. The products were analyzed in the form of their trimethylsilyl derivatives.

RESULTS AND DISCUSSION

The dianols obtained were examined in the form of their bis(trimethylsilyl) (TMS) derivatives. In order to confirm the occurrence of the polyoxyethylene glycols in the presence of dianols, the final products have also been analyzed as their diacetyl derivatives.

Fig. 1 shows a chromatogram of the products of the reaction of bisphenol A with ethylene chlorhydrin. Three main peaks were observed: the first one with an arithmetic retention index, I_A, of 2366 is the free bisphenol A; the other two are homologues of the dianols containing one or two oxyethylene groups.

The dianols obtained in the reaction of the oxyethylation of bisphenol A by ethylene oxide formed a more complex mixture of the dianol homologues differing in the number of oxyethylene groups. In this case, besides the main peaks which

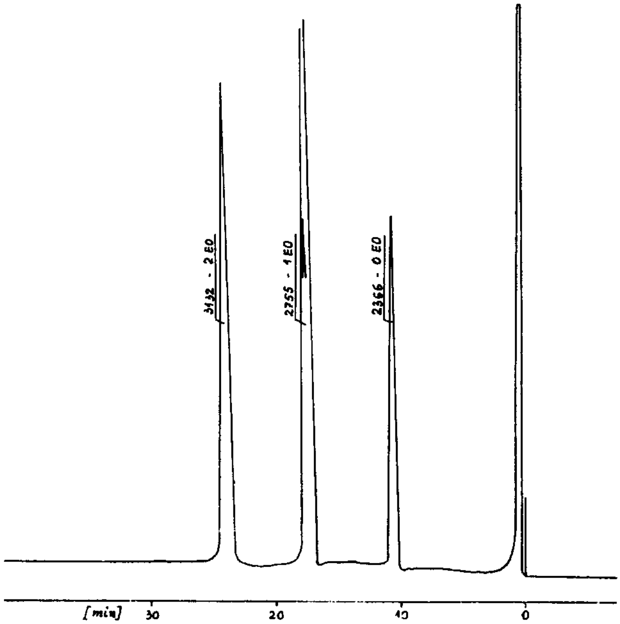

Fig. 1. Chromatogram of the dianols obtained in the reaction of bisphenol with ethylene chlorhydrin; EO = ethylene oxide group. Chromatographic conditions as in the Experimental.

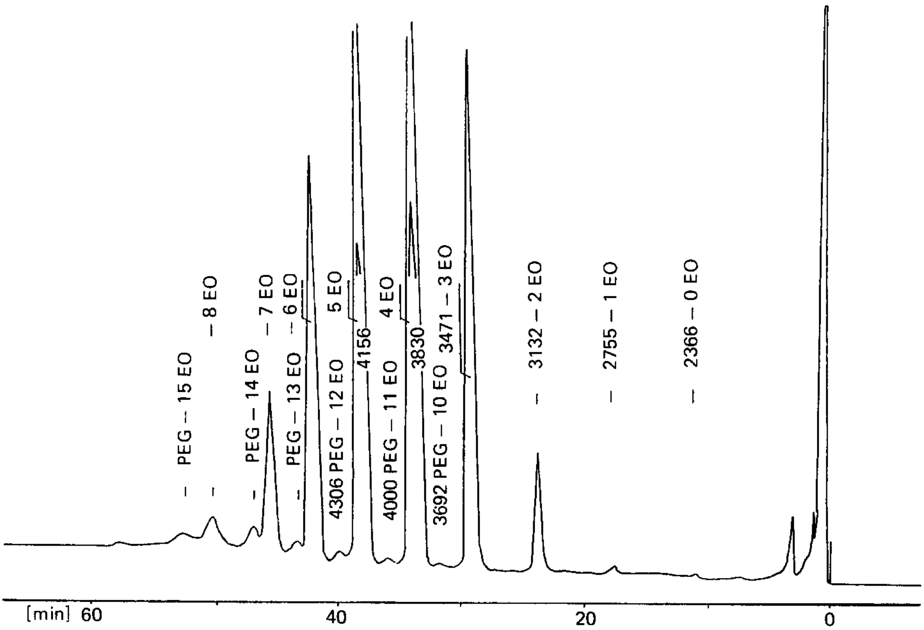

Fig. 2. Chromatogram of the dianols obtained in the reaction of bisphenol with ethylene oxide. Chromatographic conditions as in the Experimental.

TABLE I

POSITIONAL ISOMERS OF DIANOL HOMOLOGUES

x_1 and x_2 were not determined.

I_A	*Difference,* ΔI_A	*Molecular weight*	*Number of ethoxy groups*	*Number of isomers*	*m/z of characteristic ion*	*Distribution of ethoxy groups in the isomers*
2366		372	0	–	–	–
	389					
2755		416	1	1	207	0:1
	377					
3132		460	2	2	207	0:2
	359				251	1:1
3491		504	3	2	207	0:3
	339				251	1:2
3830		548	4	3	207	0:4
	326				251	1:3
					295	2:2
4156		592	5	3	207	0:5
					251	1:4
					295	2:3
x_1		636	6	4	207	0:6
					251	1:5
					295	2:4
					339	3:3
x_2		680	7	4	207	0:7
					251	1:6
					295	2:5
					339	3:4

correspond to the dianol homologues, there also appeared some small peaks of the polyoxyethylene glycols as by-products. Fig.2 shows a chromatogram of the final products of the oxyethylation reaction of bisphenol A (as TMS derivatives), containing 5 mol of the ethylene oxide. The values of I_A for the separated dianols were also determined. Thus, the peaks with $I_A = 2366, 2755, 3132, 3491, 3830$ and 4156 refer to the oxyethylated bisphenol A homologues having 0, 1, 2, 3, 4 and 5 oxyethylene groups, respectively. Among them, some small peaks of the polyoxyethylene glycols were observed. They contained 10, 11 and 12 oxyethylene groups, having I_A values of 3692, 4000 and 4306, respectively. The arithmetic retention indices for higher dianol homologues and glycols have not been determined.

We have stated that the difference between the I_A values of the successive dianol homologues is about 390 (see Table I). This value decreases with increasing length of the polyoxyethylene chain in dianol homologues and reaches a value of about 300. It seems to be connected with the decrease in the polar interaction of the oxyphenylene (–O–Ph–) groups with oxyethylene groups further away in the dianol molecules. The differences between the I_A values of the successive homologues of the polyoxyethylene glycols are lower than for the dianols, about 300.

To identify the individual dianol homologues (also as their TMS derivatives), GC–MS was used. Fig. 3 shows the mass spectra of TMS-bisphenol A and seven

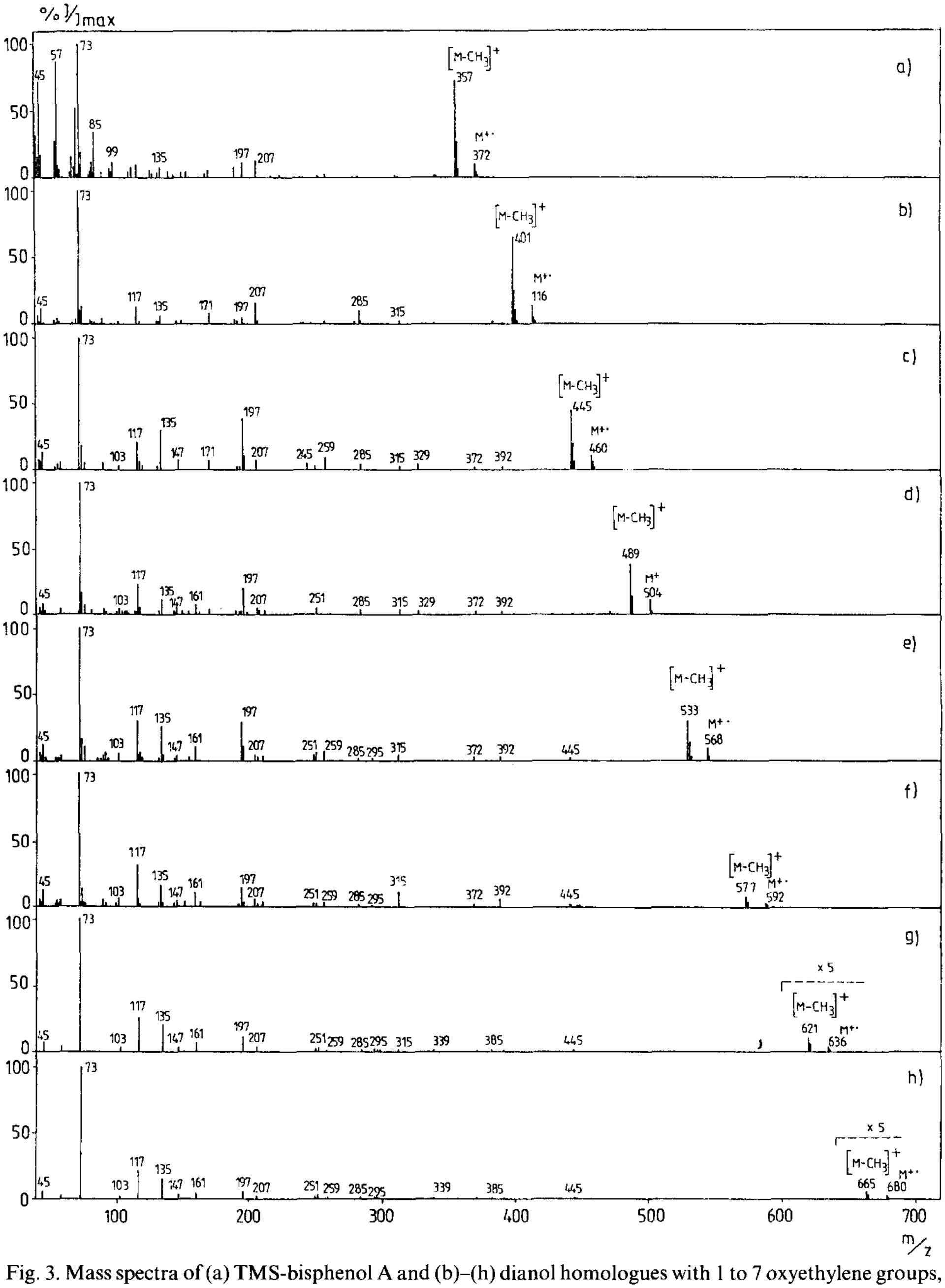

Fig. 3. Mass spectra of (a) TMS-bisphenol A and (b)–(h) dianol homologues with 1 to 7 oxyethylene groups, respectively.

TMS-dianols the chromatograms of which have been presented in Figs. 1 and 2. The mass fragmentation of this type of compounds, under electron impact (EI) conditions, showed many common features. The peaks of the molecular ions $M^{+\cdot}$ were present in

TABLE II

TYPICAL COMPOSITION OF SOME DIANOLS (%)

EO = Ethylene oxide; PG = polyoxyethylene glycol

Number of oxyethylene groups	*Dianol 4 EO*		*Dianol 6 EO*	
	PG	*Dianol homologues*	*PG*	*Dianol homologues*
0	–	–	–	–
1	–	0.9	–	–
2		14.3	–	1.7
3	–	24.3	–	9.9
4	–	24.2	–	22.0
5	–	16.8	–	25.6
6	–	9.0	–	18.8
7	–	5.3	–	11.8
8	–	2,2	–	6.0
9	–	1.1	–	2.1
10	–	0.1	–	0.9
11	0.1	–	–	–
12	0.1	–	0.1	–
13	0.3	–	0.2	–
14	0.4	–	0.3	–
15	0.3	–	0.2	–
16	0.1	–	0.1	–
Unidentified compounds		0.5		0.3

all mass spectra of the dianol homologues. The base peaks, specific to the trimethylsilyl derivatives, refer to the ions at *m/z* 73 with structure $[Si(CH_3)_3]^+$. Another very important mass fragmentation reaction of these compounds is the cleavage of the C–C and C–O bonds in the (poly)oxyethylene groups. In this way, some characteristic ions are formed, such as $[(CH_3)_3SiOCH_2]^+$ (*m/z* 103); $[(CH_3)_3SiOCH_2CH_2]^+$ (*m/z* 117); $[(CH_3)_3SiOCH_2CH_2O]^+$ (*m/z* 133 with a low intensity $< 0.5\%$); $[(CH_3)_3SiOCH_2CH_2OCH_2]^+$ (*m/z* 147) or $[(CH_3)_3SiO(CH_2CH_2O)_2]^+$ (*m/z* 161). More intense fragmentation ions are formed by the cleavage of the C–Ph bonds. The structure of these ions may be represented as $[(CH_3)_3Si(OCH_2CH_2)_nOC_6H_4C(CH_3)_2]^+$ where $n = 0, 1, 2, 3$, etc. The peaks of such ions were observed in the mass spectra of TMS-dianols at *m/z* 207, 251 or 295. Other fragments ions were probably formed after the rearrangement of their precursors.

As is seen from Fig. 3, the mass spectra of the TMS-dianols with two or more oxyethylene groups did not correspond to pure compounds but represented a mass fragmentation of a few isomers having the same molecular weight. On the basis of the occurrence in the mass spectra of the TMS-dianols of the characteristic fragmentation ions resulting from cleavage of the Ph–C bonds, it was possible to identify the presence of the positional isomers of the dianol homologues. These data are summarized in Table I. The isomers identified differ only in the number of oxyethylene groups in their polyoxyethylene chains. The products of the reaction of bisphenol A with ethylene oxide were also determined quantitatively by using an internal normalization method. The correction factor for each compound is 1. The composition of some typical dianol mixtures is given in Table II.

CONCLUSIONS

Dianols can be analyzed as their bis(trimethylsilyl) derivatives by means of GC. Using GC–MS, it was possible to identify individual homologues of the dianols having up to seven oxyethylene groups. A detailed interpretation of the mass spectra of the compounds investigated permitted the detection of isomers of dianol homologues containing two or more oxyethylene groups.

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