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Note

Gas chromatography-mass spectrometry of C₁-C₁₀ alkyl benzyl phthalates

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The identification of the long-chain dialkyl phthalates (alkyl chain length > C₅) by electron-impact mass spectrometry (EIMS) or gas chromatography-electron impact mass spectrometry (GC-EIMS) is very difficult because in the mass spectra, the molecular ions M^+ are not detectable¹⁻⁴. Better results can be obtained by the use of field-ionization mass spectrometry (FIMS)⁵ and chemical-ionization mass spectrometry (CIMS)^{6,7}.

The GC-EIMS method has been used, with good results, for the identification of some *n*-alkyl benzyl phthalates (ABP) occurring in technical-grade *n*-benzyl butyl phthalate, which is employed as a plasticizer for poly(vinyl chloride), poly(vinyl acetate) and poly(acrylic acid) esters⁸. However, the mass fragmentation patterns of these esters have not been discussed. So far, only the mass spectrum of *n*-benzyl butyl phthalate appears to have been reported⁹.

In this paper, a GC method for separating mixtures of ten ABP on a conventional packed column is presented and the basic mass spectrometric behaviour of these esters is discussed.

EXPERIMENTAL

Preparation of esters

C₁-C₁₀ ABP and dibenzyl phthalate (internal standard) were obtained by the reaction of phthalic anhydride with benzyl chloride (both reagents were obtained from P.P.H. POCh, Gliwice, Poland) with the appropriate alcohols (benzyl alcohol and C₁-C₅ aliphatic alcohols from P.P.H. POCh; C₆-C₁₀ aliphatic alcohols from Fluka, Buchs, Switzerland) in the presence of triethylamine (Loba-Chemie, Vienna, Austria) as catalyst, according to the literature⁸.

Gas chromatography

The GC separation of a mixture of ten ABP, dissolved in acetone, was carried out with a Perkin-Elmer Model 3920 gas chromatograph. Prior to GC analysis, dibenzyl phthalate (internal standard) was added. The chromatographic conditions were as follows: column, 2 m × 2.7 mm I.D. Stainless steel; packing, 3% OV-17 (Applied Science Labs., State College, PA, U.S.A.) on Chromosorb G (80-100 mesh); carrier gas, helium at 20 cm³/min; injector temperature, 320°C; column temperature, 280°C; flame-ionization detector temperature, 320°C.

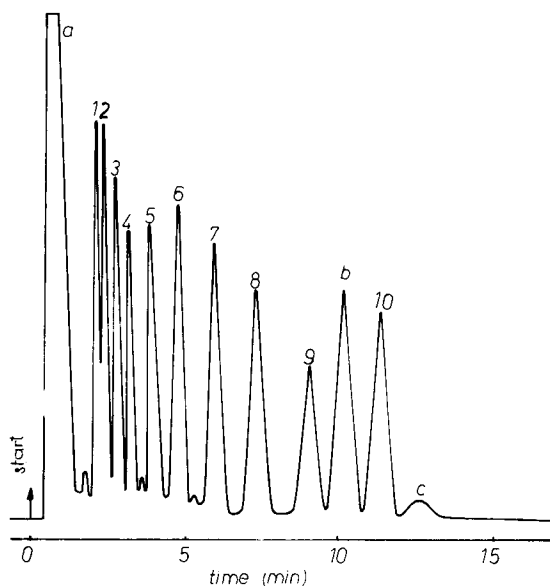


Fig. 1. Chromatogram of ten C_1 - C_{10} *n*-alkyl benzyl phthalates (peaks 1-10). Other peaks: a = acetone (solvent); b = dibenzyl phthalate (internal standard); c = unknown impurity. Stationary phase: 3% OV-17 on Chromosorb G. Column temperature: 280°C.

Gas chromatography-mass spectrometry

The mass spectra of all ABP were recorded on an LKB 2091 instrument (GC-EIMS) equipped with the OV-17 column specified above. The EI mass spectra were obtained under the following conditions: electron beam energy, 70 eV; accel-

TABLE I

RELATIVE RETENTION VALUES OF *n*-ALKYL BENZYL PHTHALATES

Peak numbers refer to Fig. 1.

Peak No.	Compound	Relative retention
1	Methyl benzyl phthalate	0.17
2	Ethyl benzyl phthalate	0.20
3	<i>n</i> -Propyl benzyl phthalate	0.24
4	<i>n</i> -Butyl benzyl phthalate	0.29
5	<i>n</i> -Pentyl benzyl phthalate	0.36
6	<i>n</i> -Hexyl benzyl phthalate	0.45
7	<i>n</i> -Heptyl benzyl phthalate	0.57
8	<i>n</i> -Octyl benzyl phthalate	0.72
9	<i>n</i> -Nonyl benzyl phthalate	0.80
b	Dibenzyl phthalate*	1.00
10	<i>n</i> -Decyl benzyl phthalate	1.11

* Internal standard.

erating voltage, 3.5 kV; trap current, 50 μ A; temperature of ion source, 250°C; and temperature of Becker-Ryhage separator, 280°C. Mass numbers from m/z 15 to 400 were recorded at a scan speed of 3 sec per decade with a resolution of 1000.

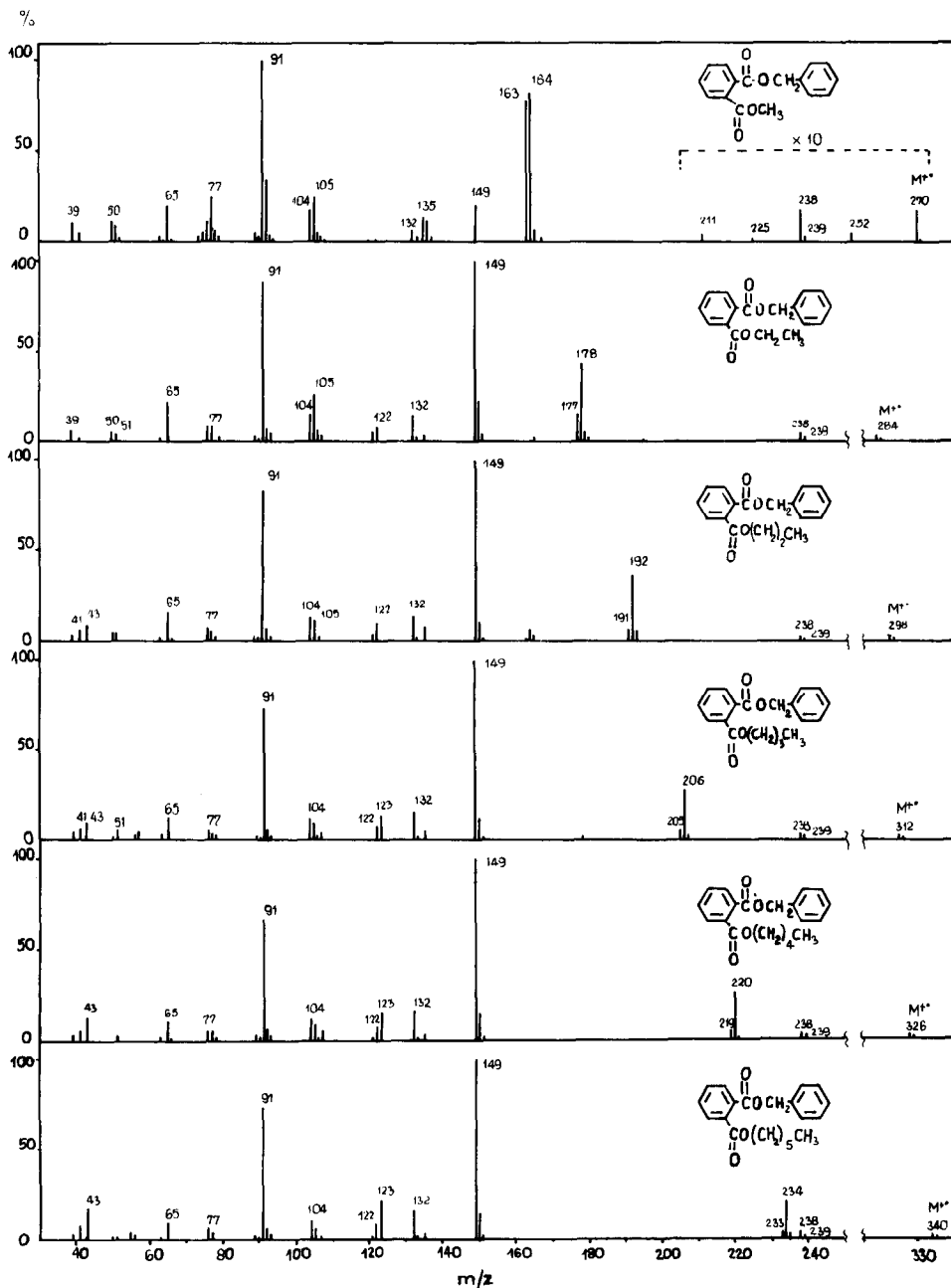


Fig. 2.

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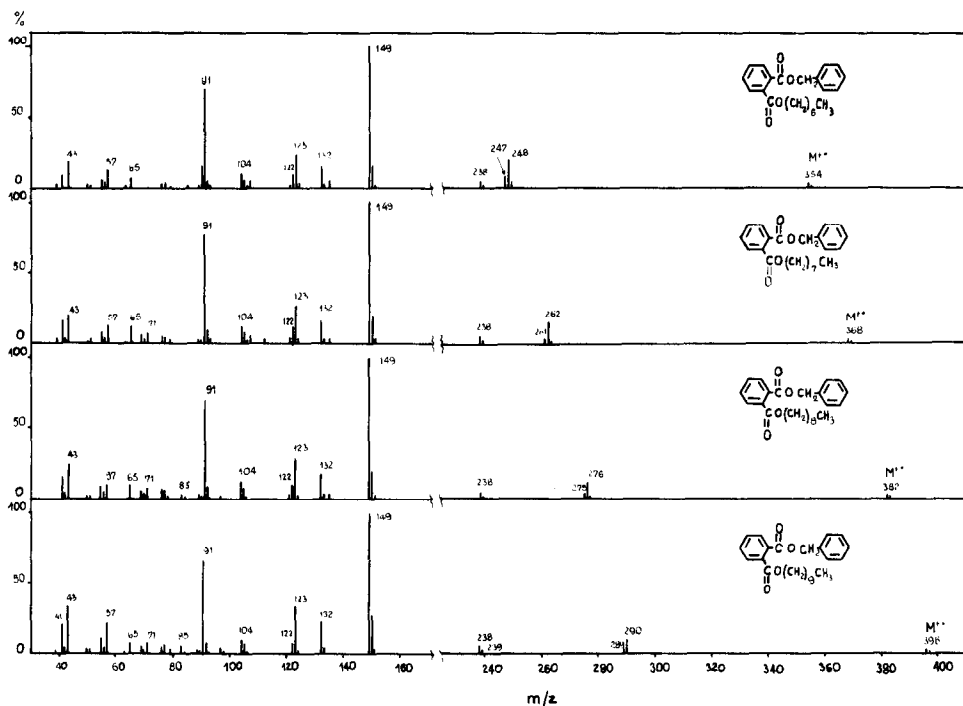


Fig. 2. Mass spectra of C_{1-10} *n*-alkyl benzyl phthalates.

RESULTS AND DISCUSSION

The chromatographic separation of the mixture of ten ABP is shown in Fig. 1. Dibenzyl phthalate was used as the internal standard to determine the relative retention values of the compounds investigated. These values are given in Table I.

The mass spectra of the separated ABP were recorded with the GC-EIMS system when the total ion current (TIC) values were at a maximum. The normalized mass spectra (*e.g.*, the intensities of all fragment ions were related to the peak with the greatest intensity) of these components are presented in Fig. 2. As can be seen, the mass spectra of all ABP investigated, as distinct from dialkyl phthalates, contain the molecular ions $M^{+\bullet}$ with 1–2.5% relative intensity. Similarly, as for dialkyl phthalates with a C_2 alkyl chain, the base peak with the protonated phthalic acid anhydride structure occurs at m/z 149 (except for methyl benzyl phthalate, with the base peak at m/z 91). As a result of the cleavage of ester bonds of all ABP molecular ions $M^{+\bullet}$, the tropylium ion at m/z 91 and $[M-OCH_2C_6H_5]^+$, $[M-O-alkyl]^+$ ions with a high relative intensity are produced. Further, mass spectrometric investigations of some deuterated analogue of ABP showed that during their fragmentation process migration of a hydrogen atom from the methylene group of the benzyl substituent to the neighbouring carbonyl group occurs and, in consequence, the ion with the $[C_6H_4(COH)COO-alkyl]^+$ structure is formed¹⁰. At a low ionizing energy (12 eV) this ion becomes the base peak. Also, for the ABP (with a C_2 alkyl chain),

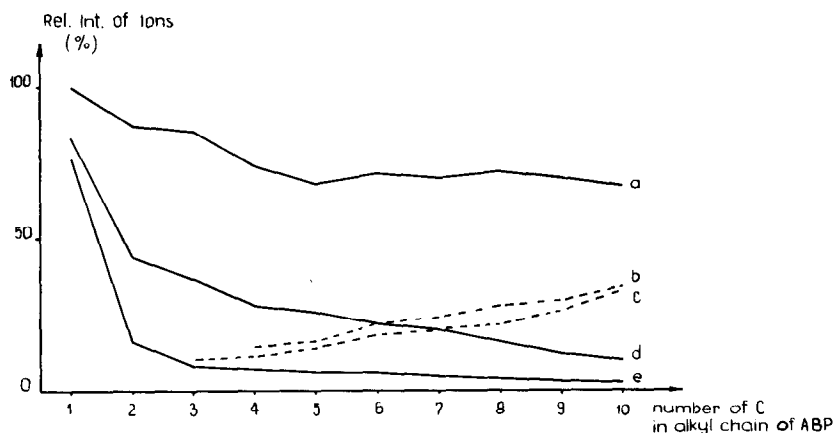


Fig. 3. Changes in relative intensities of the characteristic ions occurring in the mass spectra of *n*-alkyl benzyl phthalates at *m/z* (a) 91, (b) 123, (c) 43, (d) $[C_6H_4(COH)COOC_nH_{2n+1}]^+$; (e) $[M-OCH_2C_6H_5]^+$ with the increase in the alkyl chain length.

similarly to the case with alkyl benzoates^{1,2}, transfer of one or two hydrogen atoms from the alkyl chain to the neighbouring carboxyl group is observed. As result, ions at *m/z* 122 and 123 with the benzoic acid and protonated benzoic acid structures, respectively, are formed. In the mass spectra of all ABP (Fig. 2), the series of peaks corresponding to the ions obtained from the fragmentation of alkyl substituents (ions at *m/z* 41, 43, 55, 57, 69 and 71) and aromatic rings (ions at *m/z* 39, 51, 65 and 77) are observed. The changes in of the relative intensities of the most characteristic ions with increase in the alkyl chain length are shown in Fig. 3. Another common feature of the fragmentation process of all ABP investigated is the elimination of the neutral molecules of ROH (where R = alkyl group) from their molecular ions M^+ and the formation of $[M-ROH]^+$ ions at *m/z* 238. The loss of a benzoic aldehyde molecule from $[M-ROH]^+$ gives rise to an *m/z* 132 ion, which further decomposes with eliminaton of a CO molecule to an *m/z* 104 ion.

The molecular ion M^+ of methyl benzyl phthalate, as distinct from other ABP molecular ions, undergoes a similar rearrangement to that with benzyl benzoate and benzyl toluates^{11,12}. In this rearrangement, elimination of a water molecule and a carboxyl radical takes place and $[M-H_2O]^+$, $[M-COOH]^+$ ions at *m/z* 252 and 225, respectively, are formed.

The mass fragmentation of the ABP includes the fragmentation of benzyl benzoate and alkyl benzoates molecules. The results presented here shows that both relative retention values and the mass spectra of the esters investigated can be used to the identification not only alkyl benzyl phthalates but also of alkyl monoesters of phthalic acid after the benzylation reaction.

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