Journal of Chromatography, 446 (1988) 103–108
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1356

GAS CHROMATOGRAPHY–MASS SPECTROMETRY OF C_1–C_{10} ALKYL BENZYL SUCCINATES

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SUMMARY

A mixture of ten synthesized C_1–C_{10} *n*-alkyl benzyl succinates (ABS) was separated using a gas chromatographic column packed with 3% OV-101 on Gas-Chrom Q. For all ABS, the programmed retention indices were determined and mass spectra were obtained by gas chromatography–mass spectrometry. The mass spectral fragmentation of this type of compound is discussed.

INTRODUCTION

Alkyl benzyl esters of dicarboxylic acids, such as alkyl benzyl phthalates, maleates and succinates, are employed as plasticizers for poly(vinyl chloride), poly(vinyl acetate) and poly(acrylic acid) esters. So far, some benzyl esters of aliphatic and aromatic acids have been analysed by gas chromatographic (GC)[1,2], electron-impact mass spectrometric (EI-MS)[3] and as chromatographic–electron-impact mass spectrometric (GC–EI-MS)[4,5] methods.

In previous papers[6,7], we reported the application of GC and GC–EI-MS methods to the separation and identification of *n*-alkyl benzyl phthalates and *n*-alkyl benzyl maleates. In this work, the GC–MS studies have been extended to *n*-alkyl benzyl succinates (ABS) in which the linear alkyl groups contain 1–10 carbon atoms. This paper reports the GC separation and MS behaviour of the ABS investigated.

EXPERIMENTAL

Preparation of esters

The C_1–C_{10} ABS were obtained by the reaction of succinic anhydride (Fluka, Buchs, Switzerland) with benzyl chloride (P.P.H. POCh, Gliwice, Poland) and the appropriate alcohols (C_1–C_5 aliphatic alcohols from P.P.H. POCh; C_6–C_{10} aliphatic alcohols from Fluka) in the presence of triethylamine (Loba Chemie, Vienna, Austria) as catalyst[8].

Gas chromatography

The mixture of ten ABS, dissolved in acetone, was separated on a Model 900 gas chromatograph (Perkin-Elmer, Norwalk, CT, U.S.A.). The chromatographic conditions were as follows: column, 0.8 m × 3 mm I.D. stainless steel; packing, 3% OV-101 (Applied Science Labs., State College, PA, U.S.A.) on Gas-Chrom Q (80–100 mesh); carrier gas (nitrogen) flow-rate, 20 ml/min; injector temperature, 350°C; and column temperature, programmed from 150 to 300°C at 12°C/min.

Gas chromatography–electron-impact mass spectrometry

The EI mass spectra of all ABS were recorded on a Model 2091 gas chromatograph–electron-impact mass spectrometer system (LKB, Bromma, Sweden). The same GC conditions for the separation of esters was used as above, but with helium as the carrier gas. The EI mass spectra were obtained under the following conditions: electron beam energy, 70 eV; accelerating voltage, 3.5 kV; trap current, 50 μA; temperature of ion source, 250°C; and temperature of Becker–Ryhage separator, 280°C. Scanning was performed from m/z 15 to 350 at 3 s per decade with a resolution of 1000.

RESULTS AND DISCUSSION

Fig. 1 shows a typical chromatogram of the separated mixture of ten ABS. The programmed retention indices, I_p, for individual ABS were calculated from the equation of Van den Dool and Kratz[9]:

$$I_p = 100 \frac{T_i - T_z}{T_{z+1} - T_z} + 100z$$

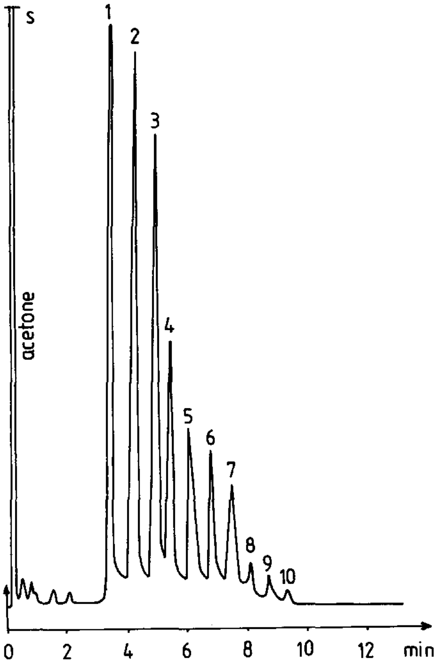

Fig. 1. Gas chromatogram of C_1–C_{10} ABS. Peak numbers 1–10 correspond to the carbon number of the n-alkyl group; s = solvent (acetone).

TABLE I

PROGRAMMED RETENTION INDICES I_p OF *n*-ALKYL BENZYL SUCCINATES

Peak numbers refer to Fig. 1.

Peak No.	*Compound*	I_p
1	Methyl benzyl succinate	1636
2	Ethyl benzyl succinate	1740
3	*n*-Propyl benzyl succinate	1842
4	*n*-Butyl benzyl succinate	1941
5	*n*-Pentyl benzyl succinate	2045
6	*n*-Hexyl benzyl succinate	2143
7	*n*-Heptyl benzyl succinate	2246
8	*n*-Octyl benzyl succinate	2344
9	*n*-Nonyl benzyl succnate	2448
10	*n*-Decyl benzyl succinate	2550

where $T_z < T_i < T_{z+1}$ are the retention times of component *i* and of the bracketing *n*-alkanes with *z* and *z* + 1 carbon atoms, respectively. The I_p values of the investigated ABS obtained in this way are given in Table I.

The normalized mass spectra of all ABS investigated are tabulated in Table II. As can be seen, in all instances the peaks of the molecular ions $M^{+\cdot}$ with low intensities are present and they give good molecular weight information. On the basis of the mass spectra and the results of metastable peak and high-resolution mass measurements[10], it was possible to determine the mass fragmentation behaviour of this type of

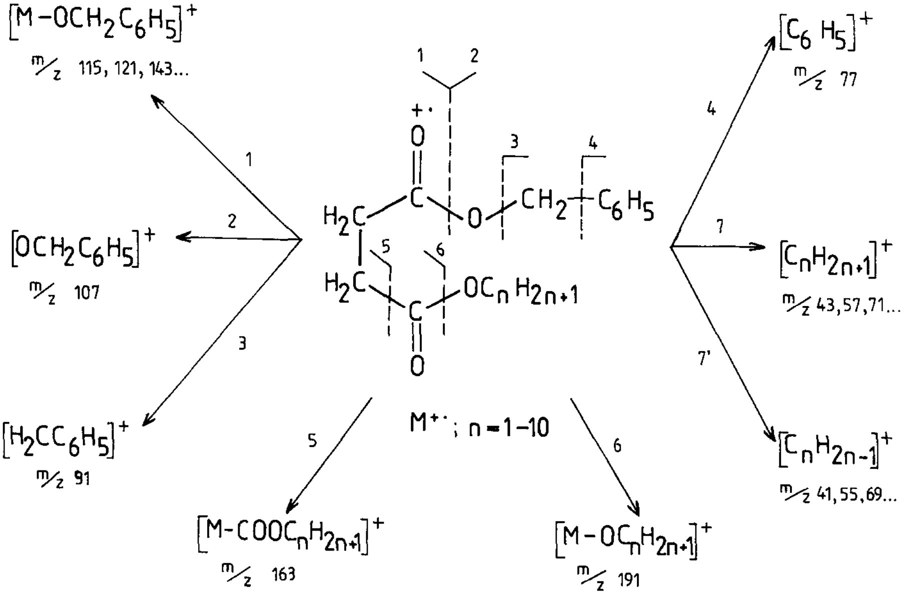

Fig. 2. Mass fragmentation pathways of $M^{+\cdot}$ of ABS, leading to the formation of the characteristic ions.

TABLE II

MASS SPECTRA OF C_1–C_{10} *n*-ALKYL BENZYL SUCCINATES

Compound	*m/z (relative intensity)*
Methyl benzyl succinate	222(2), 194(4), 191(1), 190(1), 177(1), 163(3), 162(3), 148(2), 122(1), 121(1), 116(3), 115(5), 108(5), 107(40), 92(20), 91(100), 90(7), 89(5), 88(7), 87(4), 79(7), 78(6), 77(7), 65(14), 63(3). 59(8), 57(3), 56(9), 55(20), 51(4), 50(2), 41(3), 39(7)
Ethyl benzyl succinate	236(4), 208(4), 191(1), 190(3), 162(6), 130(4), 129(42), 121(1), 108(7), 107(35), 105(7), 102(17), 101(48), 92(11), 91(100), 90(9), 89(5), 79(8), 77(7), 74(8), 73(7), 65(12), 63(3), 56(16), 55(9), 51(5), 41(3), 39(4)
n-Propyl benzyl succinate	250(5), 222(5), 191(2), 190(4), 162(8), 144(4), 143(26), 116(8), 108(10), 107(39), 106(3), 105(5), 102(3), 101(61), 92(10), 91(100), 90(8), 89(5), 79(6), 77(6), 75(11), 74(12), 65(12), 63(2), 56(13), 55(7), 51(5), 43(15), 42(3), 41(10), 39(5)
n-Butyl benzyl succinate	264(3), 236(2), 191(1), 190(3), 162(10), 158(2), 157(16), 130(9), 108(15), 107(47), 105(6), 102(5), 101(73), 92(12), 91(100), 90(8), 89(5), 79(9), 77(6), 75(9), 74(15), 73(6), 65(13), 63(2), 57(20), 56(23), 55(9), 51(6), 43(20), 42(2), 41(15), 39(7)
n-Pentyl benzyl succinate	278(5), 250(4), 191(1), 190(5), 172(2), 171(15), 163(2), 162(12), 144(6), 118(3), 108(20), 107(57), 105(5), 102(4), 101(73), 92(11), 91(100), 90(6), 89(4), 79(8), 77(6), 75(8), 74(14), 73(4), 71(15), 70(8), 65(11), 63(2), 57(2), 56(13), 55(11), 51(4), 43(35), 42(6), 41(13), 39(7)
n-Hexyl benzyl succinate	292(1), 264(1), 191(1), 190(2), 186(1), 185(4), 163(1), 162(5), 158(2), 141(2), 135(2), 121(2), 120(2), 118(2), 108(20), 107(40), 106(5), 105(5), 102(3), 101(56), 92(16), 91(100), 90(5), 89(4), 86(2), 85(20), 84(8), 83(4), 79(8), 78(3), 77(16), 75(12), 74(16), 73(4), 65(16), 63(2), 58(4), 57(40), 56(28), 55(24), 51(8), 43(38), 42(12), 41(32), 39(16)
n-Heptyl benzyl succinate	306(5), 278(4), 200(2), 199(11), 191(2), 190(7), 172(5), 163(2), 162(14), 121(2), 118(2), 108(23), 107(61), 102(3), 101(65), 99(8), 98(6), 97(5), 92(11), 91(100), 90(5), 89(4), 79(7), 78(2), 77(5), 75(9), 74(12), 73(4), 71(2), 70(3), 69(4), 65(9), 63(3), 58(4), 57(60), 56(18), 55(21), 51(4), 43(22), 42(6), 41(20), 39(6)
n-Octyl benzyl succinate	320(2), 292(1), 214(1), 213(6), 191(1), 190(5), 186(3), 163(2), 162(10), 119(2), 118(2), 113(10), 112(5), 108(24), 107(53), 105(5), 102(4), 101(57), 92(12), 91(100), 90(6), 89(4), 84(3), 83(4), 82(2), 79(7), 78(3), 77(6), 75(9), 74(12), 73(4), 71(35), 70(6), 69(16), 65(10), 63(2), 58(3), 57(47), 56(20), 55(21), 51(4), 43(35), 42(9), 41(26), 39(8)
n-Nonyl benzyl succinate	334(1), 306(1), 228(1), 227(3), 200(1), 191(1), 190(2), 162(5), 127(9), 119(12), 108(13), 107(38), 102(4), 101(63), 92(13), 91(100), 90(9), 89(4), 85(21), 83(13), 79(13), 77(13), 71(34), 70(13), 69(25), 63(4), 57(59), 56(50), 55((42), 51(9), 43(56), 42(9), 41(50), 39(12)
n-Decyl benzyl succinate	348(2), 320(1), 242(1), 241(8), 214(2), 191(1), 190(5), 180(1), 162(14), 156(4), 155(4), 154(4), 141(20), 140(4), 134(4), 120(2), 119(30), 108(20), 107(47), 102(7), 101(77), 99(10), 98(7), 97(13), 92(17), 91(100), 90(4), 89(3), 85(40), 84(10(10), 83(24), 82(7), 81(4), 79(7), 77(7), 75(10), 74(10), 72(7), 71(44), 70(17), 69(27), 67(7), 65(14), 63(2), 58(10), 57(74), 56(37), 55(50), 51(4), 43(79), 42(17), 41(47), 39(13)

compound. It was demonstrated that the ABS, under EI, have many common features. One of them, similarly to typical saturated carboxylic acid esters, is the formation of the most abundant ions as a result of the simple bond cleavages of the molecular ions $M^{+\cdot}$ as shown in Fig. 2.

Among the ions formed in this way, the tropylium ion at *m/z* 91 (2) is the most prominent. Elimination of $^{\cdot}OCH_2C_6H_5$ radicals from $M^{+\cdot}$ ions of the ABS 1 leads to the cyclization of the ions $[OCCH_2CH_2COOC_nH_{2n+1}]^+$, followed by the loss of a

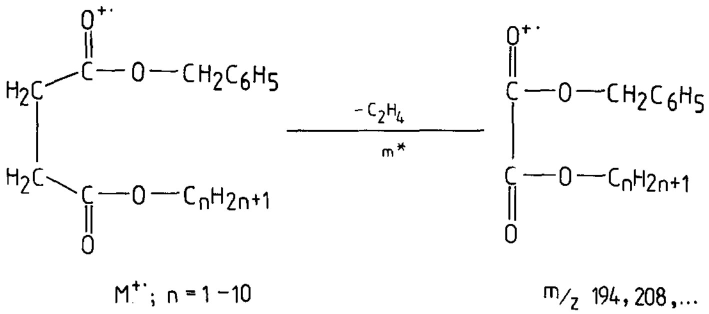

Fig. 3. Mass fragmentation pathway of $M^{+\cdot}$ of ABS connected with the formation of the series of the ions occuring at m/z 194, 208, etc.

C_nH_{2n} molecule, yielding the characteristic ions occuring at m/z 101 and containing the protonated succinic acid anhydride structure. The relative intensity of these ions decreases with increase in the alkyl chain length of the ABS. A very interesting aspect of ABS fragmentation is the elimination of C_2H_4 neutral molecules from their molecular ions $M^{+\cdot}$ (Fig. 3).

The ions obtained in this way are not stable and easily decompose with the expulsion of different neutral molecules, such as C_6H_5CHO, $C_nH_{2n+1}OH$ and C_nH_{2n}. Similarly, as with alkyl benzyl phthalates[6] and maleates[7], expulsion of the neutral molecules $C_nH_{2n+1}OH$ from the molecular ions $M^{+\cdot}$ of ABS takes place, giving rise to $[M - C_nH_{2n+1}OH]^{+\cdot}$ ions, which occur at m/z 190. Also, in the mass spectra of all ABS (Table II) the series of peaks corresponding to the ions obtained during the fragmentation of alkyl substituents (ions at m/z 41, 43, 55, 57, 69, 71, etc., with increasing intensity) and aromatic ring (ions at m/z 39, 51, 65 and 77) are observed. It should be noted that during the fragmentation processes of all the ABS investigated, in contrast to the alkyl benzyl phthalates and maleates, the ions that were formed as a result of hydrogen migration from the methylene group of the benzyl substituents to the carbonyl oxygens are almost insignificant.

CONCLUSION

The results presented here show that retention indices and the mass spectral data of the esters investigated can be used for the identification of ABS and alkyl monoesters of succinic acid (after the benzylation reaction), especially when they were present in complex mixtures, by GC, MS or GC–MS.

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