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Note

Gas–liquid chromatographic analyses

V. Gas chromatographic separation of methyl esters of some dihalogenated butanoic, 2-methylbutanoic and 3-methylbutanoic acids on Carbowax 20M and SE-30 glass capillary columns

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Earlier studies[1–6] involved the gas chromatographic (GC) separations of mixtures of aliphatic methyl and chloromethyl monochloro esters with a wide range of chain lengths. This paper describes a GC study of methyl dichloro, bromochloro and dibromo esters of butanoic, 2-methylbutanoic and 3-methylbutanoic acids. The separation of an 18-component mixture containing three α,β-unsaturated methyl esters and their halogenated products was carried out on Carbowax 20M and SE-30 glass capillary columns under the same operating conditions. The relative retention times and the order of elution of the compounds are discussed.

EXPERIMENTAL

Samples

α,β-Unsaturated methyl esters (1–3)* were obtained from commercial acids (Merck, Darmstadt, G.F.R.) by treatment with thionyl chloride and methanol. 2,3-Dihalogeno methyl esters (4–18) were prepared in our laboratory by halogenation[7] of 1–3. The samples were purified, if necessary, by preparative GC and their structures were verified by ^{1}H nuclear magnetic resonance and mass spectrometry (MS) before GC analysis. *Threo* stereoisomers were identified in the halogenated mixtures by GC–MS, the mass spectra of the compounds being nearly identical with those of the *erythro* forms.

Apparatus

A Varian Model 2400 gas chromatograph, adapted for glass capillary work, and a Perkin-Elmer Model Sigma 3 instrument, equipped with flame-ionization detectors, were used for GC analyses. The instruments were fitted with a 50 m × 0.30 mm I.D. 3% Carbowax 20M glass capillary column and a 25 m × 0.22 mm I.D. vitreous silica SE-30 wall-coated open tubular (WCOT) column, respectively. Nitrogen was used as the carrier gas at a flow-rate of 1 ml/min. The column temperatures

* For numbering of compounds see Table I.

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were programmed from 50°C at 4°C/min. The splitting ratio was 1:20, the temperatures of the injector and detector were 230 and 250°C, respectively, and the chart speed was 10 mm/min.

The samples were purified using a Perkin-Elmer Model 800 instrument, adapted for preparative work, on a 6 m × 9.5 mm O.D. aluminium tube packed with 10% Carbowax 20M on Chromosorb W (60–80 mesh). Appropriate temperatures were used, with a flow-rate of nitrogen of 120 ml/min.

RESULTS AND DISCUSSION

The GC separation of a mixture of methyl butenoates and their halogenated products was studied on polar Carbowax 20M (Fig. 1a) and non-polar SE-30 (Fig. 1b) glass capillary columns under the same operating conditions. The absolute and relative retention times of the compounds are presented in Table I and tabulated relative to unsaturated methyl esters, relative to methyl *erythro*-2-bromo-3-chloro-(3-bromo-2-chloro)butanoate (6a, 6b) (Fig. 2), the retention times being similar on both columns, and relative to the compounds on Carbowax 20M.

The retention times of isomeric monochloro esters increase continuously as the chlorine substituent becomes more distant from the carbonyl group, 2-chloro isomers always being eluted first[1–5]. With separation of mixtures of higher halogenated compounds or closely related derivatives, the order of elution on a non-polar column is largely determined by the boiling point of the esters whereas on a polar column it is influenced by their structures[6,8–10].

A vitreous silica WCOT column proved to be more efficient than a glass capillary column. Table I shows that the retention times of the compounds are in general longer on SE-30 than on Carbowax 20M. The chromatograms show that the mixture can be completely separated on SE-30, whereas on Carbowax 20M the peaks of 17 and 11 partly overlapped. The separation of regioisomer pairs 6a, 6b; 7a, 7b; 12a, 12b; 13a, 13b; and 17a, 17b, however, could not be achieved (only a poor separation of 12a and 12b on Carbowax 20M was obtained).

In general the compounds were eluted according to their boiling points. The retention times of the unsaturated esters on both columns increase in the order 1 < 3 < 2 and, as expected, the retention times of their halogenated products increased in the order dichloro < bromochloro < dibromo esters. On SE-30 the order in which the same dihalogeno esters (*erythro* forms for methyl butanoates and 2-methylbutanoates) appear follows that of the substrates: 4 < 16 < 10, 6a, b < 17a, b < 12a, b and 8 < 18 < 14, whereas on Carbowax 20M the orders observed are 10 < 4 < 16, 12a, b < 6a, b < 17a, b and 14 < 8 < 18. The methyl substituent adjacent (C_2) to the carbonyl group has a stronger effect on the polarity of compounds than the substituent further away, giving rise to shorter elution times on a polar column.

Fig. 1a shows that dichloro (10,4,16), bromochloro (12a, b; 6a, b; 17a, b) and dibromo (14,8,18) compounds were eluted close to each other on Carbowax 20M. On SE-30 (Fig. 1b), however, the elution times of the halogenated products of 1 are shorter than those of 2 and 3 and even the dibromo compound 8 was eluted before the bromochloro ester (12).

The influence of structure on SE-30 is negligible, which can be seen from the retention times of *erythro* and *threo* stereoisomers (eluted close to each other). On Carbowax 20M, however, relatively long retention times are observed for the *threo* forms.

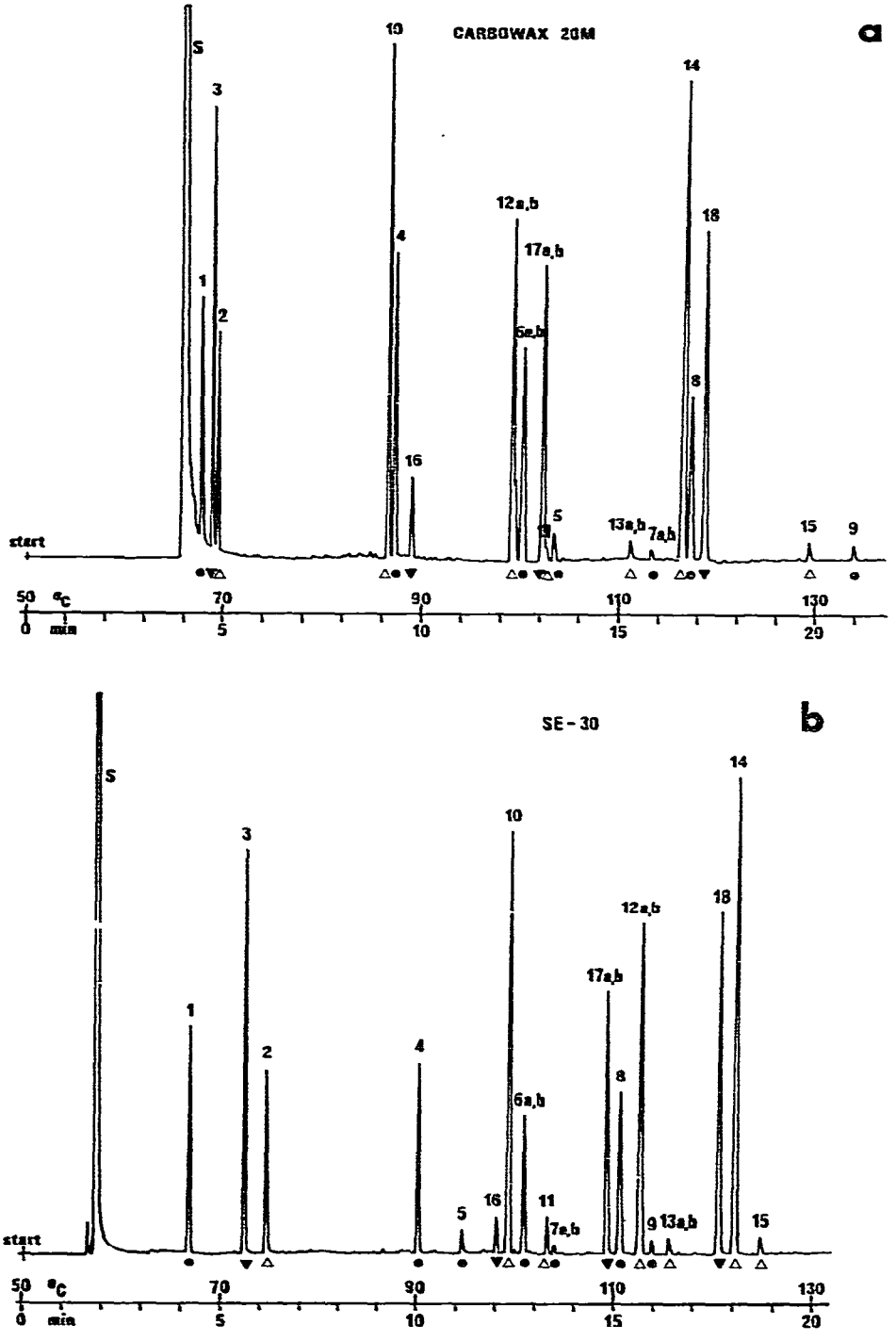

Fig. 1. Chromatogram of mixture of methyl butenoates and their halogenated products (a) on Carbowax 20M and (b) on SE-30. S = solvent; for peak identification see Table I.

TABLE I

ABSOLUTE AND RELATIVE RETENTION TIMES OF METHYL BUTENOATES AND THEIR HALOGENATED PRODUCTS ON CARBOWAX 20M AND SE-30 GLASS CAPILLARY COLUMNS

Peak	*Methyl ester*	*Carbowax 20M*			*SE-30*			
		*Retention time (min)**	*Relative retention time***		*Retention time (min)**	*Relative retention time***		
			A	*B*		*A*	*B*	*C*
1	*trans*-2-Butenoate	4.40	1.00	0.35	4.19	1.00	0.33	0.95
4	*erythro*-2,3-Dichlorobutanoate	9.31	2.12	0.74	10.05	2.40	0.79	1.08
5	*threo*-2,3-Dichlorobutanoate	13.38	3.04	1.07	11.14	2.66	0.88	0.83
6a	*erythro*-2-Bromo-3-chloro-butanoate	12.55	2.85	1.00	12.70	3.03	1.00	1.01
6b	*erythro*-3-Bromo-2-chlorobutanoate							
7a	*threo*-2-Bromo-3-chlorobutanoate	15.83	3.60	1.26	13.48	3.22	1.06	0.85
7b	*threo*-3-Bromo-2-chlorobutanoate							
8	*erythro*-2,3-Dibromobutanoate	16.84	3.83	1.34	15.12	3.61	1.19	0.90
9	*threo*-2,3-Dibromobutanoate	20.99	4.77	1.67	15.98	3.81	1.26	0.76
2	*trans*-2-Methyl-2-butenoate	4.80	1.00	0.38	6.15	1.00	0.48	1.28
10	*erythro*-2,3-Dichloro-2-methyl-butanoate	9.15	1.91	0.73	12.30	2.00	0.97	1.34
11	*threo*-2,3-Dichloro-2-methyl-butanoate	13.15	2.74	1.05	13.30	2.16	1.05	1.01
12a	*erythro*-2-Bromo-3-chloro-2-methyl-butanoate	12.30	2.56	0.98	15.63	2.54	1.23	1.27
12b	*erythro*-3-Bromo-2-chloro-2-methyl-butanoate							
13a	*threo*-2-Bromo-3-chloro-2-methyl-butanoate	15.30	3.19	1.22	16.40	2.67	1.29	1.07
13b	*threo*-3-Bromo-2-chloro-2-methyl-butanoate							
14	*erythro*-2,3-Dibromo-2-methyl-butanoate	16.61	3.46	1.32	18.05	2.93	1.42	1.09
15	*threo*-2,3-Dibromo-2-methyl-butanoate	19.80	4.13	1.58	18.71	3.04	1.47	0.94
3	3-Methyl-2-butenoate	4.70	1.00	0.37	5.59	1.00	0.44	1.19
16	2,3-Dichloro-3-methylbutanoate	9.77	2.08	0.78	12.02	2.15	0.95	1.23
17a	2-Bromo-3-chloro-3-methyl-butanoate	13.10	2.79	1.04	14.79	2.65	1.16	1.13
17b	3-Bromo-2-chloro-3-methyl-butanoate							
18	2,3-Dibromo-3-methylbutanoate	17.19	3.66	1.37	17.65	3.16	1.39	1.03

* Absolute retention times measured from sample injection (Fig. 1a and b).

** A, retention times relative to unsaturated methyl esters (1–3) taken as 1.00; B, retention times relative to methyl *erythro*-2-bromo-3-chloro-(3-bromo-2-chloro)butanoate (6a, 6b) taken as 1.00; C, retention times relative to compounds on Carbowax 20M taken as 1.00.

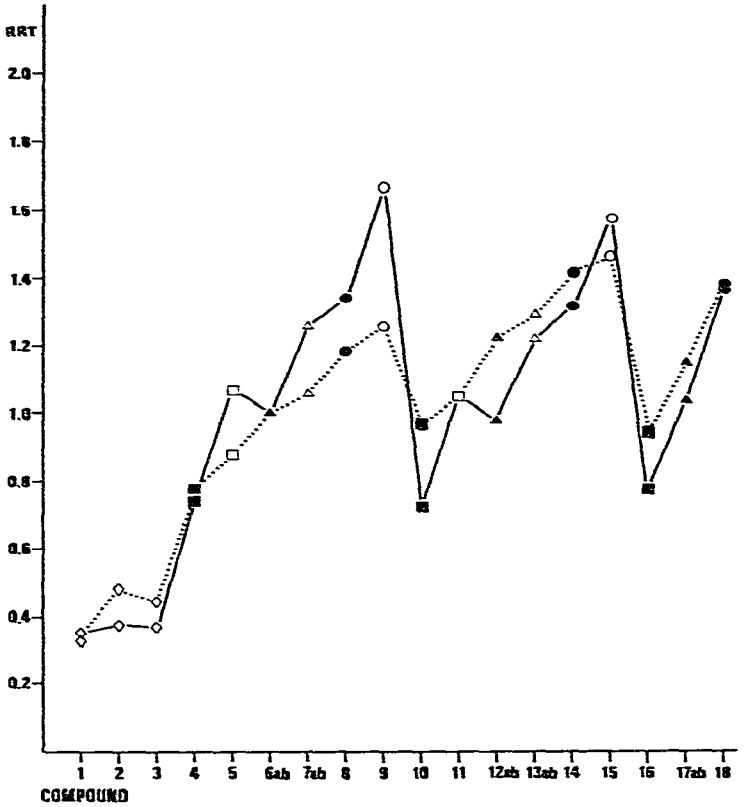

Fig. 2. Relative retention times (RRT) on Carbowax 20M (solid line) and SE-30 (broken line) relative to methyl *erythro*-2-bromo-3-chloro-(3-bromo-2-chloro)butanoate (6a, 6b). Numbering as in Table I. ◇, Unhalogenated esters. Dichloro esters: ■, *erythro*; □, *threo*. Bromochloro esters: ▲, *erythro*; △, *threo*. Dibromo esters: ●, *erythro*; ○, *threo*.

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REFERENCES

1 I. O. O. Korhonen, *J. Chromatogr.*, 209 (1981) 96.
2 I. O. O. Korhonen, *J. Chromatogr.*, 211 (1981) 267.
3 I. O. O. Korhonen, *J. Chromatogr.*, 219 (1981) 306.
4 I. O. O. Korhonen and J. N. J. Korvola, *Acta Chem. Scand., Ser. B*, 35 (1981) 139.
5 I. O. O. Korhonen and J. N. J. Korvola, *Acta Chem. Scand., Ser. B*, 35 (1981) 461.
6 I. O. O. Korhonen, *J. Chromatogr.*, 240 (1982) 377.
7 C. S. Marvel, J. Dec, H. G. Cooke and J. C. Cowan, *J. Amer. Chem. Soc.*, 62 (1940) 3495.
8 I. O. O. Korhonen, *J. Chromatogr.*, 213 (1981) 63.
9 I. O. O. Korhonen, *Acta Chem. Scand., Ser. B*, 35 (1981) 175.
10 M. T. Pitkänen, I. O. O. Korhonen and J. N. J. Korvola, *Tetrahedron*, 37 (1981) 3497.