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Note

Gas chromatography of homologous esters

XIX*. Dihalogenated esters of butanoic and pentanoic acids

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Earlier studies^{1,2} have considered the retention behaviour of the methyl and chloromethyl esters of isomeric monochloro esters of C₂-C₁₈, of the corresponding monochloro esters of the isomeric C₅ aliphatic acids, of the mono- and dichloro esters of *n*-butyric acid and of all of the chlorinated esters of propionic acid. The effects of the position of the chlorine substituent and of branching in the acid or acyl chain on retention were discussed together with the results of other studies of aliphatic esters.

The present work extends the earlier studies to the retention behaviour of dichloro, bromochloro and dibromo reaction products of the methyl esters of the α,β -unsaturated acids, *trans*-2-butenic acid, *trans*-2-methyl-2-butenic acid and 3-methyl-2-butenic acid on capillary columns coated with SE-30 and Carbowax 20M. The effect of the position of both a substituent methyl group and halogen atoms in the acyl chain is elucidated, together with the behaviour of *erythro* and *threo* stereoisomers due to the presence of two chiral centres.

EXPERIMENTAL

The chromatography was carried out on a 50 m \times 0.30 mm I.D. 3% Carbowax 20M glass capillary column and a 25 m \times 0.22 mm I.D. vitreous-silica SE-30 WCOT column. The column temperatures were programmed from 50°C at 4°C/min. The data were not corrected for dead volume.

RESULTS AND DISCUSSION

Retention data of the halogenated derivatives of the three α,β -unsaturated acids from the work of Korhonen³ are shown in Table I. The elution behaviour of the α,β -unsaturated esters is such that the butenoic ester is eluted before the two branched-chain pentenoic esters on both the polar and non-polar phases. This is as expected⁴ as there are few circumstances where the position of unsaturation or of a substituent has a greater effect on retention than an additional substituent. The 2-methyl-2-butenate has a higher retention than the 3-methyl homologue.

The effect of the position of unsaturation and of various substituents including methyl groups has been studied with long chain fatty esters^{5,6}. With both unsatura-

* For Part XVIII, see ref. 2.

TABLE I

ABSOLUTE RETENTION TIMES FOR METHYL BUTENOATES AND THEIR HALOGENATION PRODUCTS ANALYSED ON CARBOWAX 20M AND SE-30 GLASS CAPILLARY COLUMNS

Methyl ester*	Retention time (min)	
	Carbowax 20M	SE-30
<i>trans</i> -2-Butenoate	4.40	4.19
E 2,3-Dichlorobutanoate	9.31	10.05
T 2,3-Dichlorobutanoate	13.38	11.14
E 2,-Bromo-3-chlorobutanoate	12.55	12.70
E 2-Chloro-3-bromobutanoate		
T 2-Bromo-3-chlorobutanoate	15.83	13.48
T 2-Chloro-3-bromobutanoate		
E 2,3-Dibromobutanoate	16.84	15.12
T 2,3-Dibromobutanoate	20.99	15.98
<i>trans</i> -2-Methyl-2-butenoate	4.80	6.15
E 2,3-Dichloro-2-methylbutanoate	9.15	12.30
T 2,3-Dichloro-2-methylbutanoate	13.15	13.30
E 2-Bromo-3-chloro-2-methylbutanoate	12.30	15.63
E 2-Chloro-3-bromo-2-methylbutanoate		
T 2-Bromo-3-chloro-2-methylbutanoate	15.30	16.40
T 2-Chloro-3-bromo-2-methylbutanoate		
E 2,3-Dibromo-2-methylbutanoate	16.61	18.05
T 2,3-Dibromo-2-methylbutanoate	19.80	18.71
3-Methyl-2-butenoate	4.70	5.59
2,3-Dichloro-3-methylbutanoate	9.77	12.02
2-Bromo-3-chloro-3-methylbutanoate	13.10	14.79
2-Chloro-3-bromo-3-methylbutanoate		
2,3-Dibromo-3-methylbutanoate	17.19	17.65

* E = *erythro*; T = *threo*.

tion and the position of the substituent, it has been shown that retention is maximized near the chain extremities, *i.e.*, near the carbonyl group and at the terminal position which has greatest retention. The largest retention occurs at the C-4 position, with the lowest retention at the C-2 position.

The shorter chain alkenoates do not follow this pattern, it having been shown that the 2-butenoates exhibit greater retention than the 3-butenoates on both polar and non-polar phases^{7,8}. The enhanced retention is attributed to conjugation with bonds in the carbonyl group.

Comparable data for branched chain methyl esters are not available, however some indication of the relative effect of methyl substitution may be obtained by a study of the effect on 2-propenoates of addition of a methyl group at the 2-position and on 2-butenoates of addition at the 3-position. With both non-polar, *i.e.*, SE-30, and polar, *i.e.*, SILAR-5CP, stationary phases substitution has a greater effect on retention at the 2-position, the relative effect being greater on the non-polar phase. A study of the individual contributions of polar and steric components to retention has recently been briefly reported⁹. The order of elution of the compounds was according to their boiling points, a factor previously shown to be of major importance with aliphatic esters on non-polar phases. The boiling point sequence is followed by the

present halogenated derivatives with, as anticipated, increasing retention of dichloro, bromochloro and dibromo esters. The 2-bromo-3-chloro and 2-bromo-3-bromo esters (both *erythro* and *threo* stereoisomers in two cases) appeared as a single peak on both columns. On the polar Carbowax 20M column the elution order of the halogenated products of the *trans*-2-butenolate and *trans*-2-methyl-2-butenolates is reversed, while the products of 3-methyl-2-butenolates were unaltered. The 2-methyl-2-halo isomers would be expected to be the most sterically hindered with reduced retention on the polar phase and lower than the compounds with straight (unbranched) alkyl chains. The 3-methyl-2,3-dihalo compounds show the highest retention as on the SE-30 column.

While the retention behaviour of geometric isomers particularly of fatty esters has been extensively studied and reviewed^{6,10}, stereoisomerism has not been extensively studied by gas chromatography. The presence of two asymmetric centres allows the formation of *erythro* and *threo* forms and the study of various regioisomer pairs is possible. On both the polar and non-polar stationary phase the *threo* isomer exhibits the highest retention, however it is evident that while on SE-30 the retention times are similar, a considerable difference in retention occurs the Carbowax 20M column due apparently to the presence of increased steric effects.

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