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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XXI*. CAPILLARY COLUMN STUDIES OF TRIHALOGENATED METHYL PROPANOATES AND BUTANOATES FORMED IN THE HALOGENATIONS OF MONOCHLORINATED METHYL PROPENOATES AND 2-BUTENOATES

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SUMMARY

The methyl esters of monochlorinated propenoic and 2-butenoic acids and their Cl_2, BrCl and Br_2 reaction products were separated on an OV-101 capillary column with temperature programming. The unsaturated esters are eluted in the order 2-Cl-C_3 $\leqslant$ *trans*-3-Cl-C_3 < *cis*-3-Cl-C_3 < *cis*-3-Cl-C_4 < *trans*-2-Cl-C_4 < *trans*-3-Cl-C_4 < *trans*-4-Cl-C_4, and their halogenated products in the order of increasing molecular weights. The BrCl compounds with geminal dichloro substitution have lower retention than their regioisomers with geminal bromochloro substitution. As a consequence of the relatively higher retention times of the 2,3,4-trihalo isomers, some geminal $BrCl_2$ and Br_2Cl homologues have lower retention than the vicinal Cl_3 and $BrCl_2$ isomers, respectively.

INTRODUCTION

Recently, a series of studies[1] to optimize the gas chromatographic (GC) separation of complex mixtures of various chlorinated esters with substitution in both the acyl and alkyl chains have been reported, using temperature programming and non-polar and polar capillary columns. The separation of the methyl esters of chlorinated propenoic acids has been examined, together with the effect of structure and of retention increments[2,3]. Komárek *et al.*[4–6] have described the GC separation of homologous series of halogenated esters containing fluorine, chlorine, bromine and iodine atoms in either the alcohol or the acid moiety of the ester, on packed columns with different polar stationary phases, *i.e.*, Apiezon L, silicone grease, silicone oil QF-1, XE-60 and butanediol succinate, and on a glass capillary column coated with non-polar OV-101 silicone phase. However, the GC of esters containing different halogen atoms has not been extensively studied. The separation of methyl esters of

* For Part XX, see ref. 1.

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some bromochlorinated butanoic, 2-methylbutanoic and 3-methylbutanoic acids has been reported and the effect of the position of both a substituent methyl group and the halogen atoms in the acyl chain elucidated, together with the behaviour of *erythro* and *threo* stereoisomers[7,8]. The presence of two asymmetric centres allows the formation of a diastereomeric pair, and the GC separation of the stereoisomers occurs better on polar than on non-polar stationary phases due to the presence of increased steric effects[7–15].

This paper extends the earlier studies and describes the retention behaviour of the methyl esters of α,β-unsaturated acids, *i.e.*, 2-chloropropenoic acid, *cis*- and *trans*-3-chloropropenoic acids, *trans*-2-chloro-2-butenoic acid, *cis*- and *trans*-3-chloro-2-butenoic acids and *trans*-4-chloro-2-butenoic acid, and particularly of all their dichloro, bromochloro and dibromo reaction products, *i.e.*, methyl esters of the trihalogenated propanoic and butanoic acids. The analyses were carried out on an OV-101 quartz capillary column with temperature programming. The elution orders are discussed with respect to the structures of the compounds.

EXPERIMENTAL

Gas chromatography

Analyses were performed on a Perkin-Elmer Sigma 3 gas chromatograph under the following operating conditions: injector and flame-ionization detector temperatures, 275°C (hydrogen and air flow-rates, 40 and 300 ml min^{-1}); carrier gas (nitrogen) flow-rate, 1 ml min^{-1}; splitting ratio, 1:25; chart speed, 10 mm min^{-1}. The column used was a vitreous silica OV-101 wall-coated open-tubular (WCOT) column (25 m × 0.30 mm I.D.), supplied by SGE (North Melbourne, Australia). The column temperature was programmed from 50°C at 6°C min^{-1} until elution of peaks had ceased.

The chromatographic data were analysed with a Hewlett-Packard Model 3390A reporting integrator using standard programs.

Samples

The monochlorinated α,β-unsaturated methyl esters (1, 6, 7, 14, 21, 22 and 29) and their halogenated products (2–5, 8–13, 15–20, 23–28 and 30–37) (see Tables I and II) were prepared in this laboratory as described earlier[16,17]. The esters (1–37) were verified by GC, ^1H nuclear magnetic resonance (NMR) and particularly by GC–mass spectrometry (MS)[17,18]. The diastereomers were identified on the basis of their nearly identical mass spectral fragmentation patterns[18].

RESULTS AND DISCUSSION

Fig. 1 gives the structures and the retention behaviours of the α,β-unsaturated methyl esters studied. Chromatograms of mixtures of the parent esters and all their dichloro, bromochloro and dibromo reaction products are illustrated in Figs. 2, 3 and 5–7. Tables I and II give the chromatographic data of the compounds, the retention times being relative to the parent, unsaturated esters and relative to the trichloro isomers. The retention behaviour of the trihalo derivatives, relative to the position of substitution, is shown in Figs. 4 and 8.

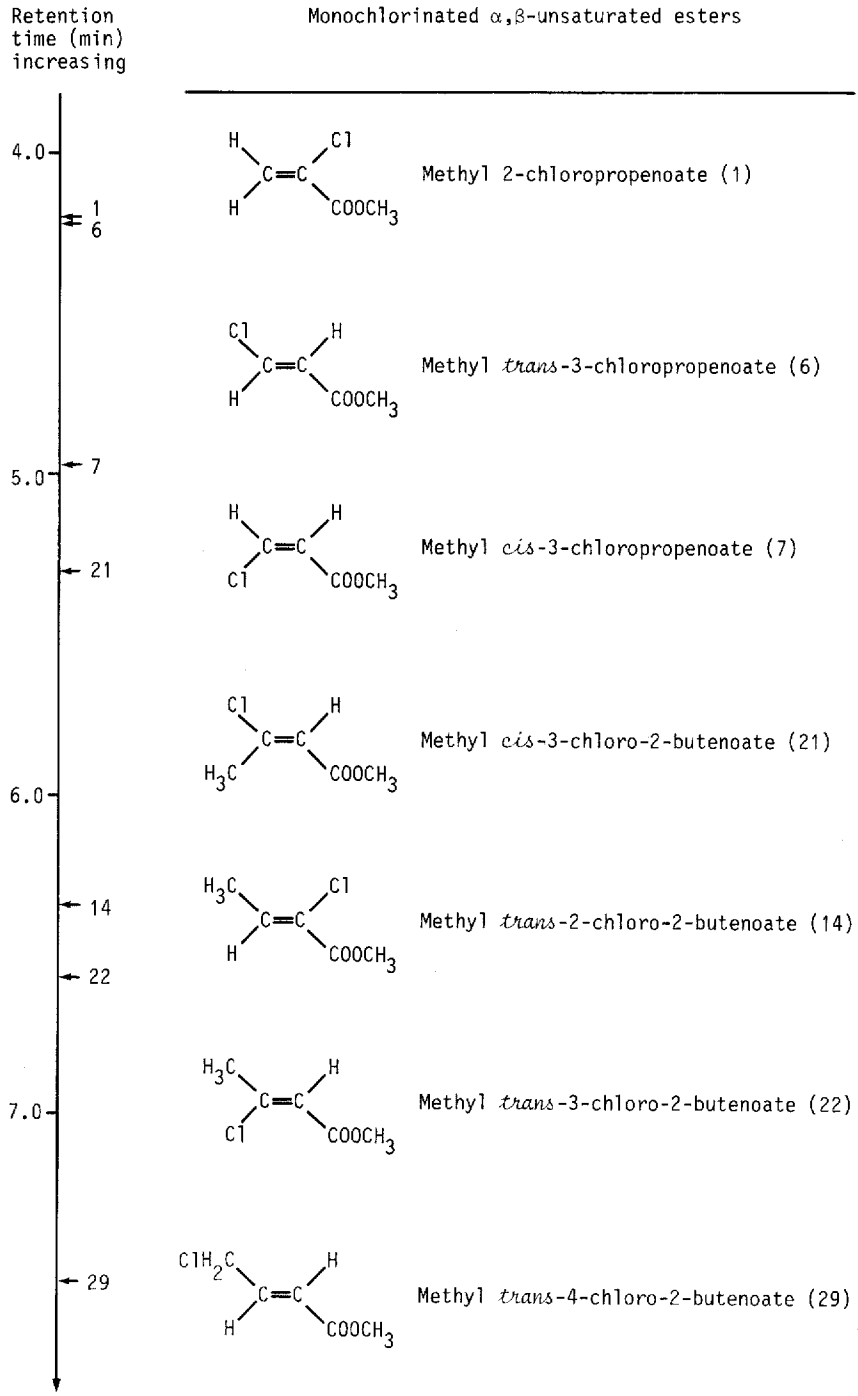

Fig. 1. Structures and retention behaviours of the α,β-unsaturated methyl esters of monochlorinated propenoic and 2-butenoic acids.

TABLE I

RETENTION DATA FOR MONOCHLORINATED METHYL PROPENOATES AND THEIR HALOGENATED PRODUCTS ANALYSED ON AN OV-101 QUARTZ CAPILLARY COLUMN

Conditions as shown in Figs. 2 and 3.

Peak No.	*Compound*	*ART**	*RRT***		*RRT****
1	Methyl 2-chloropropenoate	4.20	1.00		0.46
2	Methyl 2,2,3-trichloropropanoate	9.20	2.19		1.00
3	Methyl 2-bromo-2,3-dichloropropanoate	11.19	2.66		1.22
4	Methyl 3-bromo-2,2-dichloropropanoate	11.09	2.64		1.21
5	Methyl 2-chloro-2,3-dibromopropanoate	13.14	3.13		1.43
6	Methyl *trans*-3-chloropropenoate	4.21	1.00	0.85	0.46
7	Methyl *cis*-3-chloropropenoate	4.98	1.18	1.00	0.54
8	Methyl 2,3,3-trichloropropanoate	9.18	2.18	1.84	1.00
9	Methyl 2-bromo-3,3-dichloropropanoate	11.02	2.62	2.21	1.20
10	Methyl *erythro*-3-bromo-2,3-dichloropropanoate	11.20	2.66	2.25	1.22
11	Methyl *threo*-3-bromo-2,3-dichloropropanoate	11.39	2.71	2.29	1.24
12	Methyl *erythro*-3-chloro-2,3-dibromopropanoate	13.15	3.12	2.64	1.43
13	Methyl *threo*-3-chloro-2,3-dibromopropanoate	13.29	3.16	2.67	1.45

* Absolute retention times (min) were measured from sample injection (Figs. 2 and 3).
** Relative retention times for the parent esters (1,6 and 7) taken as 1.00.
*** Relative retention times for the trichloro isomers (2 and 8) taken as 1.00.

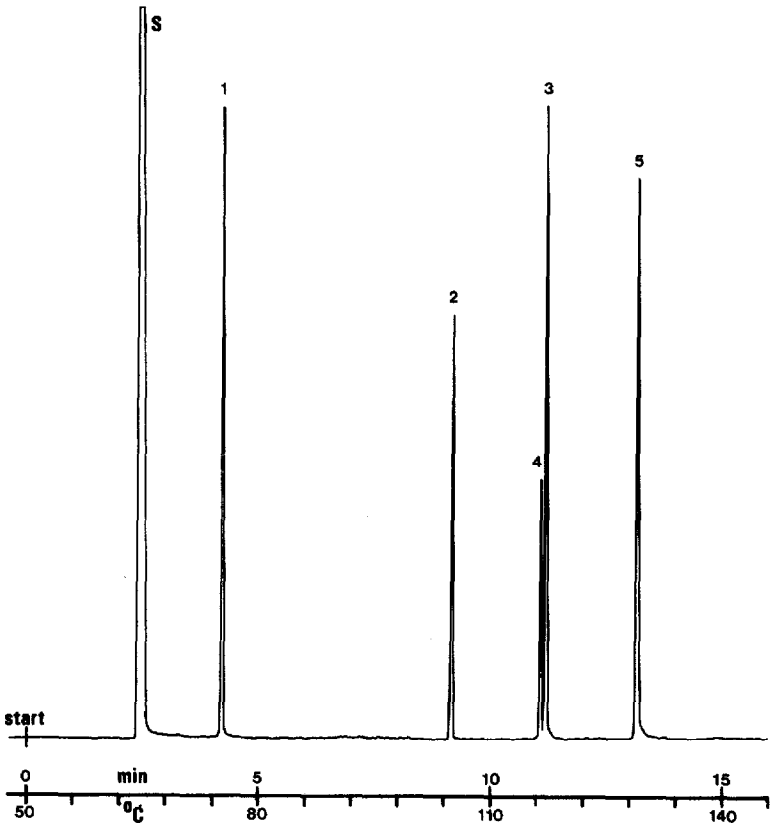

Fig. 2. Chromatogram of a mixture of methyl 2-chloropropenoate (1) and its halogenated products (2–5). S = Solvent; for peak identification see Table I.

TABLE II

RETENTION DATA FOR MONOCHLORINATED METHYL 2-BUTENOATES AND THEIR HALOGENATED PRODUCTS ANALYSED ON AN OV-101 QUARTZ CAPILLARY COLUMN

Conditions as shown in Figs. 5–7.

Peak No.	*Compound**	*ART***	*RRT****	*RRT*§
14	Methyl *trans*-2-chloro-2-butenoate	6.35	1.00	0.59
15	Methyl 2,2,3-trichlorobutanoate	10.77	1.70	1.00
16	Methyl (2*R*,3*S*)-, (2*S*,3*R*)-2-bromo-2,3-dichlorobutanoate	12.82	2.02	1.19
17	Methyl (2*R*,3*R*)-, (2*S*,3*S*)-2-bromo-2,3-dichlorobutanoate	12.91	2.03	1.20
18	Methyl 3-bromo-2,2-dichlorobutanoate	12.66	1.99	1.18
19	Methyl (2*R*,3*S*)-, (2*S*,3*R*)-2-chloro-2,3-dibromobutanoate	14.73	2.32	1.37
20	Methyl (2*R*,3*R*)-, (2*S*,3*S*)-2-chloro-2,3-dibromobutanoate	14.82	2.33	1.38
21	Methyl *cis*-3-chloro-2-butenoate	5.30	1.00 0.81	0.52
22	Methyl *trans*-3-chloro-2-butenoate	6.58	1.24 1.00	0.64
23	Methyl 2,3,3-trichlorobutanoate	10.29	1.94 1.56	1.00
24	Methyl 2-bromo-3,3-dichlorobutanoate	12.06	2.28 1.83	1.17
25	Methyl (2*R*,3*R*)-, (2*S*,3*S*)-3-bromo-2,3-dichlorobutanoate	12.13	2.29 1.84	1.18
26	Methyl (2*R*,3*S*)-, (2*S*,3*R*)-3-bromo-2,3-dichlorobutanoate	12.28	2.32 1.87	1.19
27	Methyl (2*R*,3*R*)-, (2*S*,3*S*)-3-chloro-2,3-dibromobutanoate	14.03	2.65 2.13	1.36
28	Methyl (2*R*,3*S*)-, (2*S*,3*R*)-3-chloro-2,3-dibromobutanoate	14.20	2.68 2.16	1.38
29	Methyl *trans*-4-chloro-2-butenoate	7.53	1.00	0.57 0.56
30	Methyl *erythro*-2,3,4-trichlorobutanoate	13.11	1.74	1.00 0.98
31	Methyl *threo*-2,3,4-trichlorobutanoate	13.34	1.77	1.02 1.00
32	Methyl *erythro*-2-bromo-3,4-dichlorobutanoate	14.83	1.97	1.13 1.11
33	Methyl *threo*-2-bromo-3,4-dichlorobutanoate	14.91	1.98	1.14 1.12
34	Methyl *erythro*-3-bromo-2,4-dichlorobutanoate	14.55	1.93	1.11 1.09
35	Methyl *threo*-3-bromo-2,4-dichlorobutanoate	14.63	1.94	1.12 1.10
36	Methyl *erythro*-4-chloro-2,3-dibromobutanoate	16.22	2.15	1.24 1.22
37	Methyl *threo*-4-chloro-2,3-dibromobutanoate	16.41	2.18	1.25 1.23

* Apparent *R,S*-configurations of the stereoisomers as a consequence of the *trans*-addition[17].
** Absolute retention times (min) were measured from sample injection (Figs. 5–7).
*** Relative retention times for the parent esters (14, 21, 22 and 29) taken as 1.00.
§ Relative retention times for the trichloro isomers (15, 23, 30 and 31) taken as 1.00.

It has been previously reported that the peaks of the methyl esters of 2-chloropropenoic (1) and *trans*-3-chloropropenoic (6) acids were overlapped on a SE-30 capillary column both when using temperature-programmed[2] and isothermal[3] operating conditions. With the polar column the elution order is greatly influenced by the structures of the compounds, the *trans* isomer (6) being less strongly retained than the 2-chloro isomer (1)[2,3]. Table I and Fig. 1 show that isomers 1 and 6 are coincident also on an OV-101 capillary column, the *trans* (6) and *cis* (7) isomers being eluted closer together than on SE-30[2].

The retention times of the methyl esters of the 2-butenoic acids increase in the order *cis*-3-chloro (21) < *trans*-2-chloro (14) < *trans*-3-chloro (22) < *trans*-4-chloro (29) as shown in Fig. 1. The *cis* isomer (21) is less strongly retained than the *trans* isomer (22), an elution order corresponding to that observed for the propenoic acid esters (6 and 7), *i.e.*, the chlorine substituents in 6 and 21 are at the *trans*-position with respect to the methoxyl group, but *cis* in 7 and 22. The 2-chloro isomer (14) is

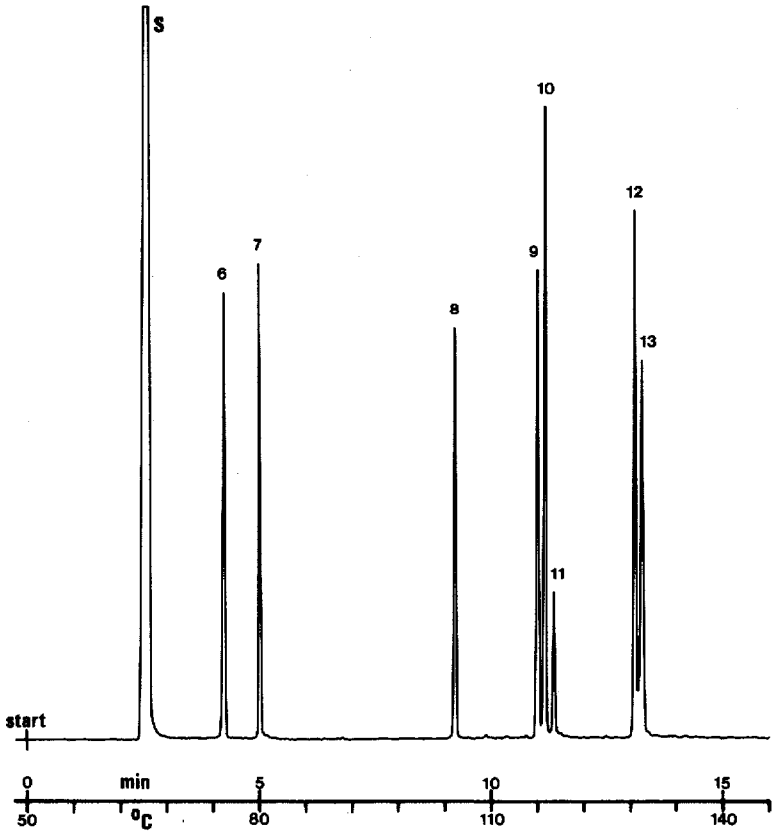

Fig. 3. Chromatogram of a mixture of methyl *trans*- and *cis*-3-chloropropenoates (6 and 7) and their halogenated products (8–13). S = Solvent; for peak identification see Table I.

eluted earlier than the *trans*-3-chloro isomer (22) and as expected, the *trans*-4-chloro isomer (29), owing to the ω-substitution[3], is of highest retention. Although (i) the retention behaviour of the *cis* isomers of the 2-chloro- and 4-chloro-2-butenoic acid esters has not been studied and (ii) the analyses have not been carried out on a polar column, it is apparent that for the monochlorinated 2-butenoic acid esters similar results and trends are evident to those previously reported for the methyl esters of the chlorinated propenoic acids[2,3].

The trihalo derivatives are eluted, as anticipated, in the order of increasing molecular weight, *i.e.*, Cl_3 isomer < $BrCl_2$ isomer < Br_2Cl isomer (Figs. 4 and 8). The retention behaviour of the pairs 2 and 8, 3 and 9, 4 and 10 and 5 and 12 shows that the propanoic acid derivatives are eluted close together, being unresolved on a non-polar column (Table I and Fig. 4). The compounds with the geminal dichloro substituents (4 and 9) are less strongly retained than their regioisomers (3 and 10) with geminal bromochloro substituents (Fig. 4). It is evident that a polar column would given a better separation of the isomers, as previously reported for the 2,2,3-trichloro (2) and 2,3,3-trichloro (8) isomers. The latter compound (8) was eluted on SE-30[15] somewhat earlier than the former (2), as occurred also in this work on

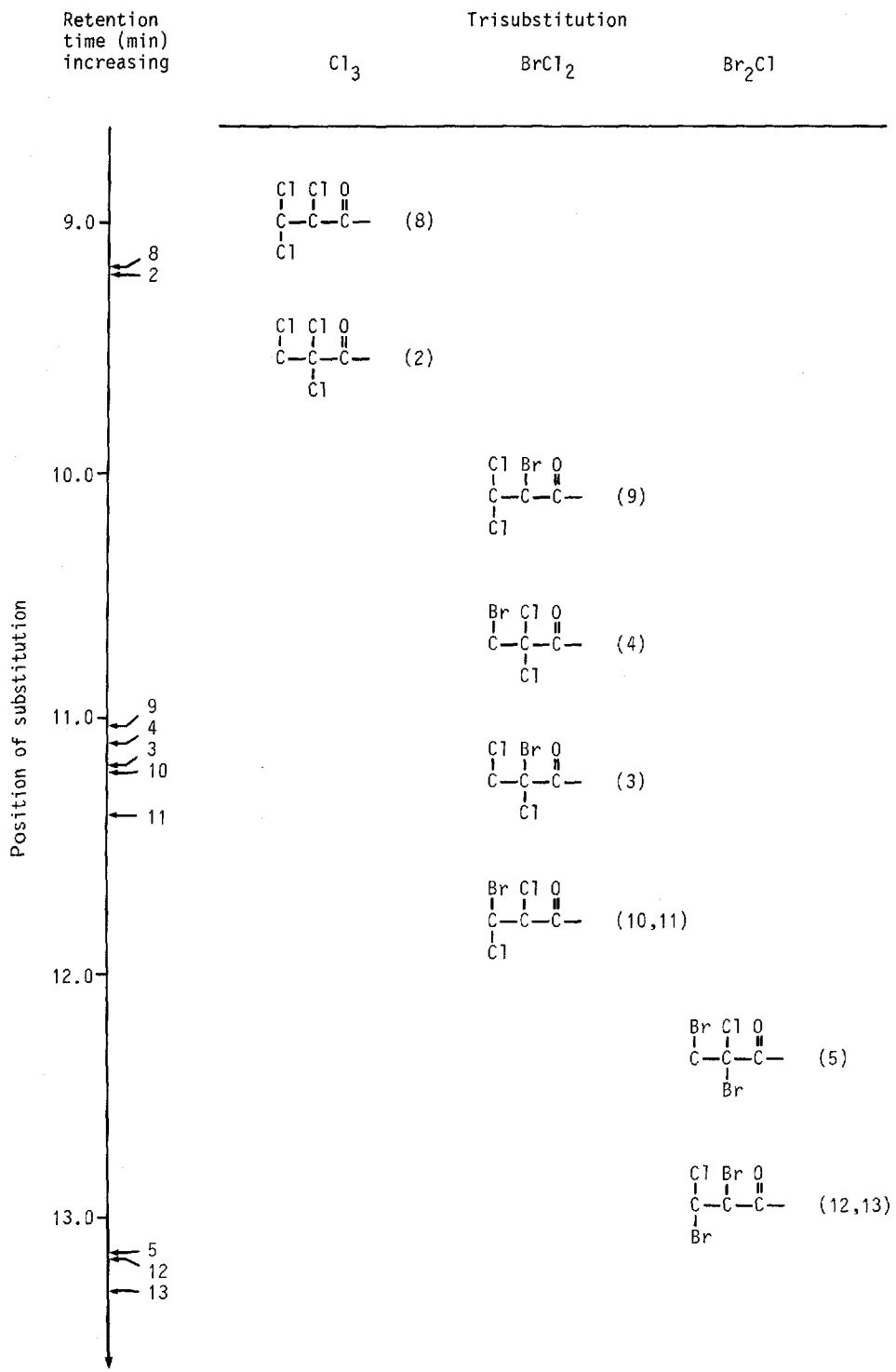

Fig. 4. Structures and retention behaviours of trihalogenated methyl propanoates.

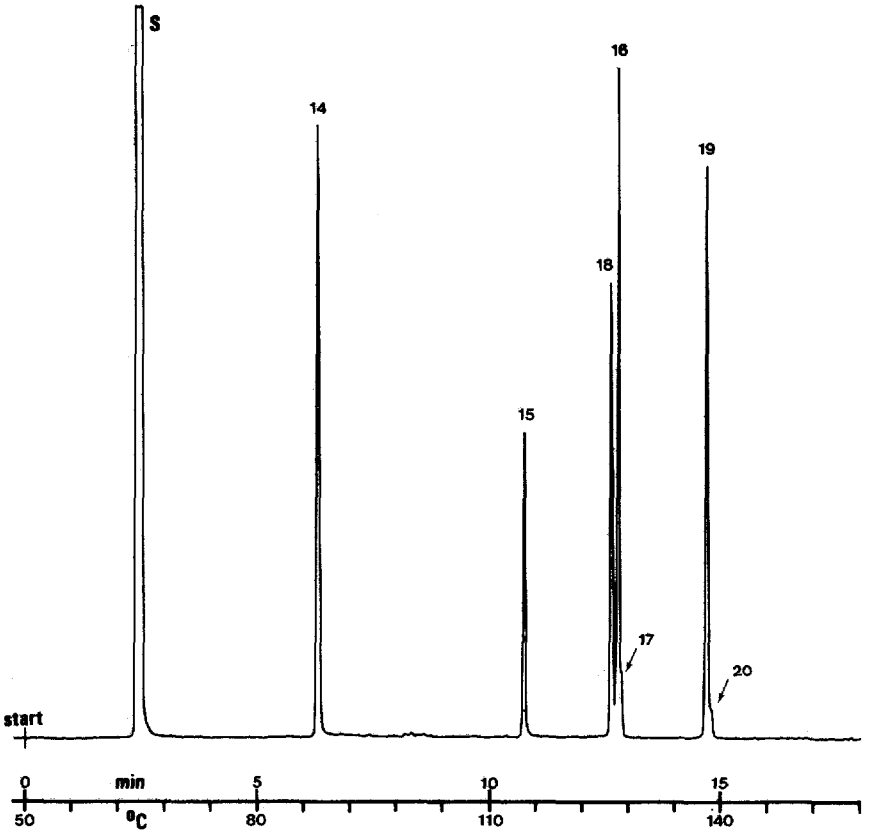

Fig. 5. Chromatogram of a mixture of methyl *trans*-2-chloro-2-butenoate (14) and its halogenated products (15–20). S = Solvent; for peak identification see Table II.

OV-101, whereas on Carbowax 20M[15,19] isomer 2 had clearly lower retention than 8. Figs. 2 and 3 show that both the regioisomers, 3 and 4 and 9 and 10, and the stereoisomers, 10 and 11 and 12 and 13, are sufficiently resolved.

Table II and Fig. 8 show that the retention times of the butanoic acid derivatives increase in the order 2,3,3-trihalo isomer < 2,2,3-trihalo isomer < 2,3,4-trihalo isomer. In contrast to the lower C_3 homologues, the isomers have now clearly different retention times, the compounds 15, 23 and 30, 16, 24 and 32, 18, 25 and 34 and 19, 27 and 36 being separable on a non-polar stationary phase. The geminal dichloro isomers (18 and 24) have lower retention than their regioisomers (16 and 25) as with trihalogenated methyl propanoates. The fact that the compounds having two geminal halo substituents at the $(\omega-1)$-position, *i.e.*, the 2,3,3-trihalo isomers, appeared always earlier than the 2,2,3-trihalo isomers (Fig. 8), is in accord with the elution behaviour of the lower homologues 4 and 10 and 5 and 12, the 2,2,3-trihalo isomers (4 and 5) being eluted first (Fig. 4). However, the disparities between the retention times are negligible relative to those of the butanoic acid derivatives.

As reported earlier[15], the retention times of the dihalogenated butanoic acid esters increase on SE-30 in the order 2,2- < 3,3- < 2,3- < 4,4- < 3,4- < 2,4-dichloro

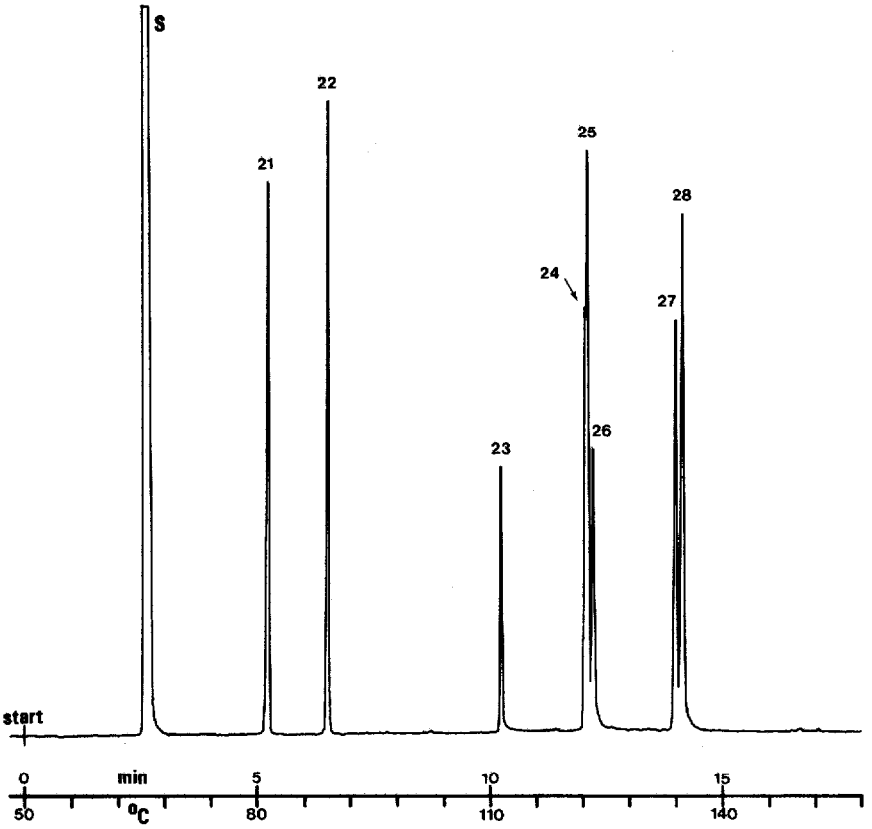

Fig. 6. Chromatogram of a mixture of methyl *cis*- and *trans*-3-chloro-2-butenoates (21 and 22) and their halogenated products (23–28). S = Solvent; for peak identification see Table II.

isomer. The polar effect of the two chlorine substituents is at a maximum when the two atoms are not attached to the same carbon atom[14]. Thus, the vicinal 2,3,4-trihalo isomers have highest retention. Fig. 8 shows that even the geminal $BrCl_2$ isomers (16–18 and 24–26) are eluted earlier than methyl 2,3,4-trichlorobutanoates (30 and 31), and the geminal Br_2Cl isomers (19, 20, 27 and 28) have lower retention than the vicinal 2-bromo-3,4-dichloro isomers (32 and 33). The 3-bromo-2,4-dichloro isomers (34 and 35) with the bromine substituent between the chlorine substituents are eluted earlier than the 2-bromo-3,4-dichloro isomers (32 and 33). As shown above, the corresponding 2,4- and 3,4-dichloro isomers are eluted in the reverse order on a non-polar stationary phase[15].

Figs. 5–7 show that the regioisomers are separated, except for the 2-bromo-3,3-dichloro isomer (24) and the 3-bromo-2,3-dichloro isomer (25). The stereoisomers 25 and 26, 27 and 28 (Fig. 6), 30 and 31 and 36 and 37 (Fig. 7) are separated, whereas the four other isomer pairs, *i.e.*, 16 and 17, 19 and 20 (Fig. 5), 32 and 33 and 34 and 35 (Fig. 7) overlap. As shown, the isomer of the higher retention time is always eluted as an unresolved shoulder with the other isomer.

The increases in retention relative to the parent esters (1 and 6) are as follows

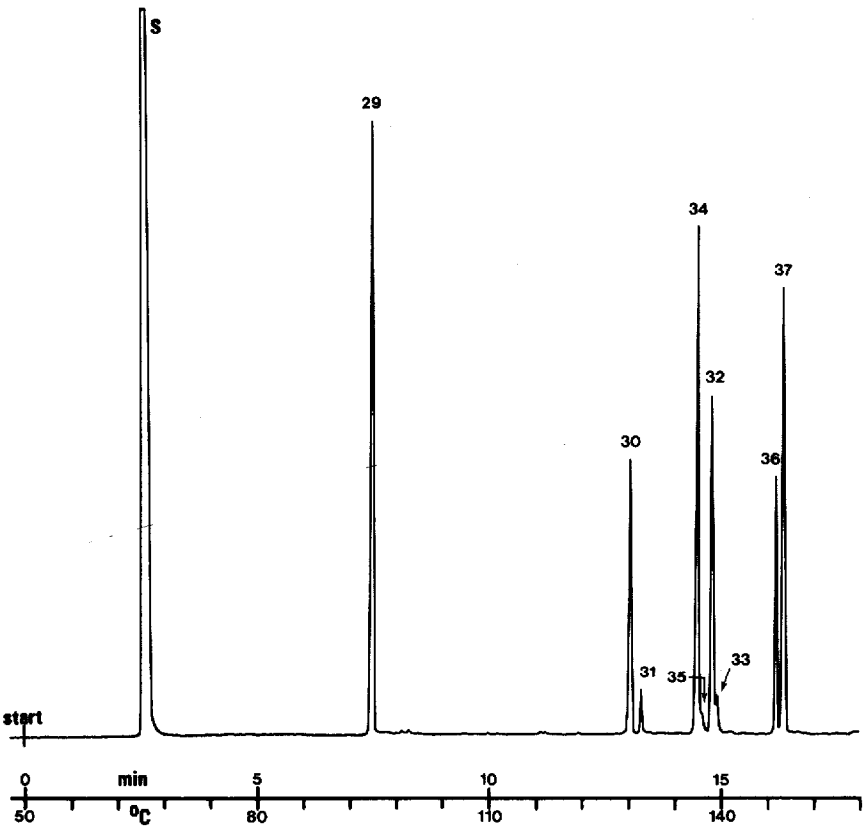

Fig. 7. Chromatogram of a mixture of methyl *trans*-4-chloro-2-butenoate (29) and its halogenated products (30–37). S = Solvent; for peak identification see Table II.

(Table I): for the Cl_3 isomers (2 and 8), 2.2; $BrCl_2$ isomers (3, 4 and 9–11), 2.7; Br_2Cl isomers (5, 12 and 13), 3.1. The corresponding increases for the derivatives of the *cis* isomer (7) are lower, *i.e.*, 1.8, 2.3 and 2.7, respectively. By assigning the retention time relative to the trichloro isomers (2 and 8), it can be seen that the retention increase for the $BrCl_2$ isomers is *ca.* 1.2 and for the Br_2Cl isomers is *ca.* 1.4. The corresponding retention increases with the higher homologues are lower (Table II).

The analyses carried out on a polar column would have given more information on the structures and retention behaviours of the trihalogenated esters studied. However, it is evident that similar trends are apparent to those previously reported for the methyl esters of chlorinated propanoic and butanoic acids[7,8,14,15,19,20], although the steric hindrance is assumed to increase due to the increased size of the bromine substituent(s).

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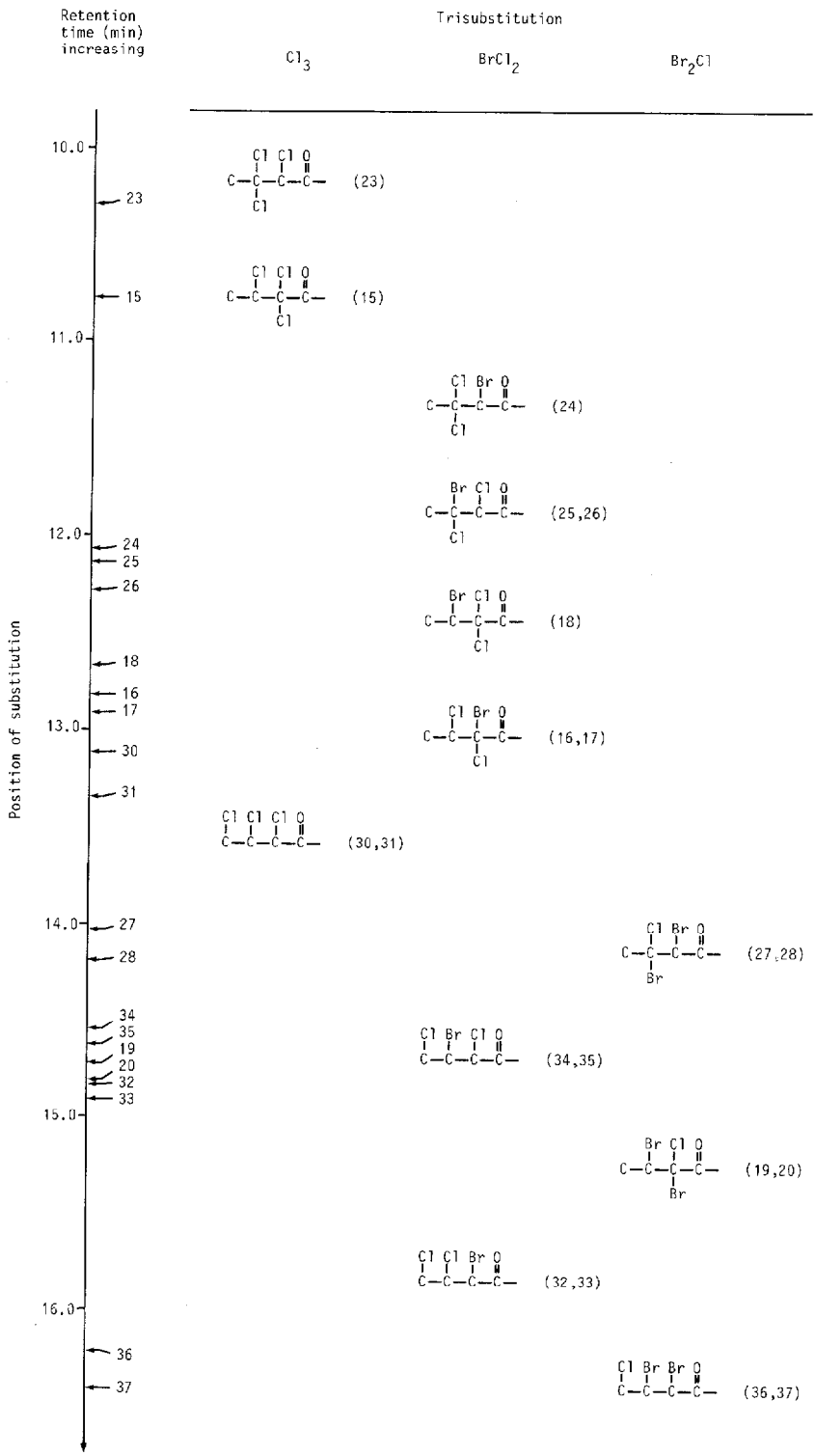

Fig. 8. Structures and retention behaviours of trihalogenated methyl butanoates.

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