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Note

Gas–liquid chromatographic analyses

XXIII*. Separation of primary C_1–C_{12} straight-chain alkanols and C_1–C_{12} *n*-alkyl acetates, monobromoacetates, dibromoacetates and tribromoacetates

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Recent papers have described the retention behaviour of homologous series of esters containing chlorine atoms in either the acid or the alkanol moiety of the ester[1,2]. However, the gas chromatography (GC) of esters containing other halogen atoms has not been so extensively studied[3]. Separations of a series of *n*-alkyl and isoalkyl esters of monobromoacetic, monoiodoacetic and trifluoroacetic acids[3], 2-bromopropanoic and 2-bromobutanoic acids[4] and 2-bromoethyl and 2-iodoethyl esters of aliphatic monocarboxylic acids[5] on a non-polar OV-101 capillary column have been reported by Komárek and co-workers. The GC of the methyl esters of brominated and bromochlorinated butanoic and methylbutanoic acids[6,7] and trihalogenated propanoic and butanoic acids containing chlorine and bromine atoms has also been investigated[8].

As previously shown with halogenated acetates, a significant reduction in retention occurs on introduction of fluorine atoms[3]. As expected, different behaviour with other halogen substituents is observed, the esters being eluted on an OV-101 capillary column in the sequence trifluoroacetate < acetate < monochloroacetate < monobromoacetate ⩽ dichloroacetate < trichloroacetate ⩽ monoiodoacetate[3]. The enhancement of retention is due to the increased molecular weight, *i.e.*, increased boiling point, leading to a decreased sensitivity of the flame-ionization detector. This is also partly due to the fact that instability of the compounds increases with increasing the size of the halogen substituent, obtained previously by analysing brominated esters particularly on a polar column[6]. As packed columns are less suitable than capillary columns, the GC of the bromo and iodo esters has received little attention. By using electron-capture detection (ECD) and suitable fluorinated derivatives, the mobility of the compounds and the sensitivity of the detector can be increased. This is particularly useful in the GC analysis of environmental samples[9].

This paper extends the earlier studies[1,3,10] by reporting the retention behaviour of primary C_1–C_{12} straight-chain alkanols and the corresponding *n*-alkyl acetates, monobromoacetates, dibromoacetates and tribromoacetates. The separation of mix-

* For Part XXII, see ref. 1.

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tures was carried out on non-polar (SE-30) and highly polar (OV-351) capillary columns with temperature programming. The retention data are given, relative to *n*-tetradecane, *n*-alkanols, *n*-alkyl acetates and the compounds analysed on SE-30. The retention order of the compounds is discussed.

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, 250°C; carrier gas (nitrogen) flow-rate, 1 ml min^{-1}; splitting ratio, 1:50; and chart speed, 10 mm min^{-1}. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.30 mm I.D.), supplied by SGE (North Melbourne, Australia), and a fused silica OV-351 WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). 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 C_1–C_{12} *n*-alkanols (1–12) were commercial products (Fluka, Buchs, Switzerland). *n*-Alkyl acetates (a1–a12) were prepared from the corresponding alkanols and commercial acetyl chloride (Fluka). *n*-Alkyl monobromoacetates (m1–m12), dibromoacetates (d1–d12) and tribromoacetates (t1–t12) were obtained by the usual

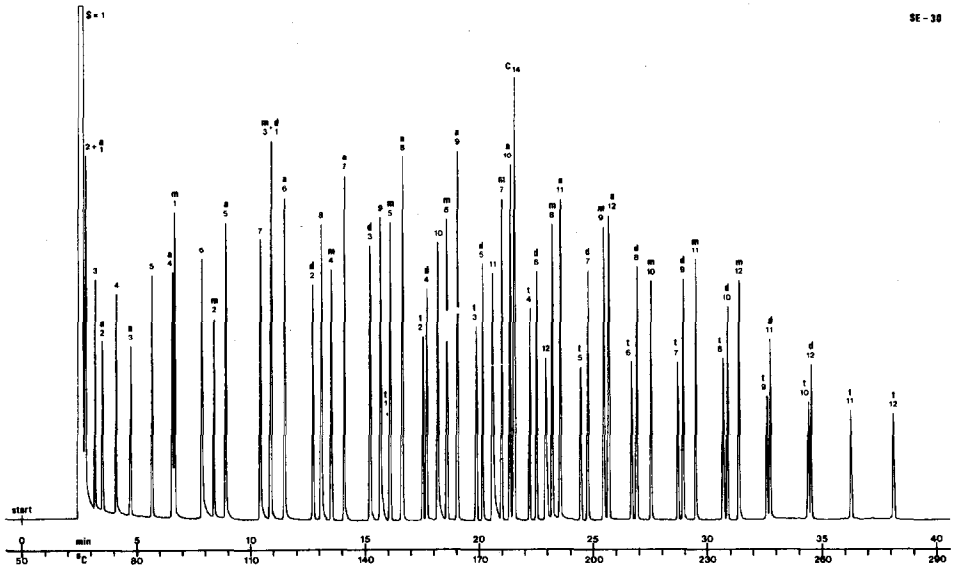

Fig. 1. Chromatogram of a mixture of primary C_1–C_{12} straight-chain alkanols (1–12) and the corresponding *n*-alkyl acetates (a1–a12), monobromoacetates (m1–m12), dibromoacetates (d1–d12) and tribromoacetates (t1–t12), separated on SE-30. S = Solvent; C_{14} = *n*-tetradecane.

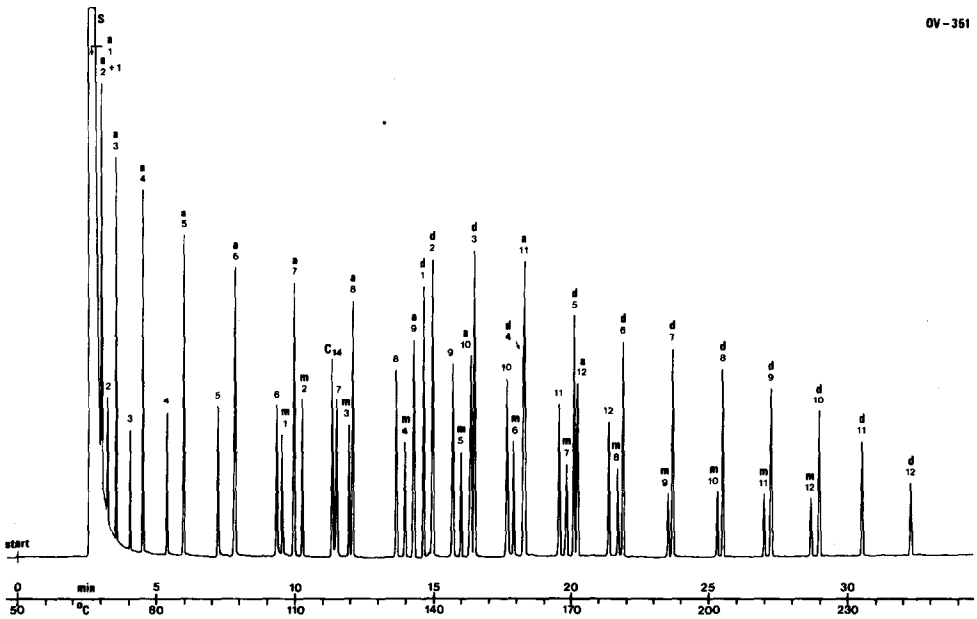

Fig. 2. Chromatogram of the mixture as in Fig. 1, without the tribromo isomers (t1–t12), separated on OV-351.

sulphuric acid-catalysed esterification of commercial monobromoacetic acid (Merck-Schuchardt, F.R.G.), dibromoacetic acid (Fluka) and tribromoacetic acid (Fluka). *n*-Tetradecane was obtained from Merck (Darmstadt, F.R.G.).

A mixture of GC-pure components was used for the GC analyses.

RESULTS AND DISCUSSION

The separation of a mixture of the compounds obtained on SE-30 and OV-351 is illustrated in Figs. 1 and 2, respectively. The retention data, relative to *n*-tetradecane, *n*-alkanols, *n*-alkyl acetates and the compounds on SE-30 are presented in Table I. Plots of the retention are shown in Figs. 3 and 4.

Fig. 1 shows that the individual components are generally eluted from SE-30 in the order C_n-alkanol < C_{n-4}-alkyl monobromoacetate < C_{n-1}-alkyl acetate < C_{n-7}-alkyl tribromoacetate < C_{n-5}-alkyl dibromoacetate. However, the methyl esters of the mono-, di- and tribromoacetic acids (m1, d1 and t1) constituted exceptions from the retention order, *i.e.*, m1 was eluted after butyl acetate (a4), d1 after 1-heptanol (7) and t1 after propyl dibromoacetate (d3) and 1-nonanol (9). Methyl acetate (a1) and ethanol (2), propyl monobromoacetate (m3) and methyl dibromoacetate (d1), and methyl tribromoacetate (t1) and pentyl monobromoacetate (m5) overlapped (Fig. 1), so that complete resolution of the mixture was not achieved. The sensitivity of the flame-ionization detector towards the brominated esters decreased strongly with increasing degree of bromination and therefore the mixture used contained greater amounts of the higher brominated isomers. An increased chain length in the alkanol moiety seems to have a smaller effect to the flame-ionization detector response.

TABLE I

RETENTION DATA FOR PRIMARY STRAIGHT-CHAIN C_1–C_{12} ALKANOLS AND C_1–C_{12} *n*-ALKYL ESTERS OF ACETIC, MONOBROMOACETIC, DIBROMOACETIC AND TRIBROMOACETIC ACIDS, ANALYSED ON SE-30 AND OV-351

Conditions as in Figs. 1 and 2.

Peak No.	*Compound*	*Column*								
		SE-30				*OV-351*				
		*ART**	*RRT***	*RRT****	*RRT§*	*ART**	*RRT***	*RRT****	*RRT§*	*RRT§§*
1	Methanol	2.44	0.11	1.00	0.89	3.05	0.27	1.00	1.13	1.25
2	Ethanol	2.72	0.13	1.00	0.78	3.27	0.29	1.00	1.07	1.20
3	1-Propanol	3.18	0.15	1.00	0.67	4.09	0.36	1.00	1.14	1.29
4	1-Butanol	4.09	0.19	1.00	0.62	5.41	0.48	1.00	1.19	1.32
5	1-Pentanol	5.66	0.26	1.00	0.64	7.23	0.64	1.00	1.20	1.28
6	1-Hexanol	7.84	0.36	1.00	0.68	9.38	0.83	1.00	1.19	1.20
7	1-Heptanol	10.43	0.48	1.00	0.74	11.53	1.01	1.00	1.15	1.11
8	1-Octanol	13.09	0.61	1.00	0.79	13.69	1.21	1.00	1.13	1.05
9	1-Nonanol	15.69	0.73	1.00	0.82	15.72	1.38	1.00	1.10	1.00
10	1-Decanol	18.19	0.84	1.00	0.85	17.68	1.56	1.00	1.08	0.97
11	1-Undecanol	20.59	0.95	1.00	0.87	19.57	1.72	1.00	1.07	0.95
12	1-Dodecanol	22.92	1.06	1.00	0.89	21.37	1.88	1.00	1.06	0.93
a1	Methyl acetate	2.73	0.13	1.12	1.00	2.69	0.24	0.88	1.00	0.99
a2	Ethyl acetate	3.49	0.16	1.28	1.00	3.05	0.27	0.93	1.00	0.87
a3	Propyl acetate	4.72	0.22	1.48	1.00	3.59	0.32	0.88	1.00	0.76
a4	Butyl acetate	6.57	0.30	1.61	1.00	4.55	0.40	0.84	1.00	0.69
a5	Pentyl acetate	8.90	0.41	1.57	1.00	6.02	0.53	0.83	1.00	0.68
a6	Hexyl acetate	11.50	0.53	1.47	1.00	7.89	0.69	0.84	1.00	0.69
a7	Heptyl acetate	14.11	0.65	1.35	1.00	10.02	0.88	0.87	1.00	0.71
a8	Octyl acetate	16.64	0.77	1.27	1.00	12.12	1.07	0.89	1.00	0.73
a9	Nonyl acetate	19.05	0.88	1.21	1.00	14.32	1.26	0.91	1.00	0.75
a10	Decyl acetate	21.39	0.99	1.18	1.00	16.39	1.44	0.93	1.00	0.77
a11	Undecyl acetate	23.59	1.09	1.15	1.00	18.32	1.61	0.94	1.00	0.78
a12	Dodecyl acetate	25.70	1.19	1.12	1.00	20.22	1.78	0.95	1.00	0.79
m1	Methyl monobromoacetate	6.65	0.31	2.73	2.44	9.56	0.84	3.13	3.55	1.44
m2	Ethyl monobromoacetate	8.40	0.39	3.09	2.41	10.27	0.90	3.14	3.37	1.22
m3	Propyl monobromoacetate	10.91	0.51	3.43	2.31	11.96	1.05	2.92	3.33	1.10
m4	Butyl monobromoacetate	13.53	0.63	3.31	2.06	13.97	1.23	2.58	3.07	1.03

m5	Pentyl monobromoacetate	16.10	0.75	2.84	1.81	15.99	1.41	2.21	2.66	0.99
m6	Hexyl monobromoacetate	18.59	0.86	2.37	1.62	17.91	1.58	1.91	2.27	0.96
m7	Heptyl monobromoacetate	20.98	0.97	2.01	1.49	19.81	1.74	1.72	1.98	0.94
m8	Octyl monobromoacetate	23.28	1.08	1.78	1.40	21.68	1.91	1.58	1.79	0.93
m9	Nonyl monobromoacetate	25.48	1.18	1.62	1.34	23.51	2.07	1.50	1.64	0.92
m10	Decyl monobromoacetate	27.55	1.28	1.51	1.29	25.29	2.23	1.43	1.54	0.92
m11	Undecyl monobromoacetate	29.51	1.37	1.43	1.25	27.00	2.38	1.38	1.47	0.91
m12	Dodecyl monobromoacetate	31.40	1.46	1.37	1.22	28.70	2.53	1.34	1.42	0.91
d1	Methyl dibromoacetate	10.91	0.51	4.47	4.00	14.66	1.29	4.81	5.45	1.34
d2	Ethyl dibromoacetate	12.72	0.59	4.68	3.64	15.00	1.32	4.59	4.92	1.18
d3	Propyl dibromoacetate	15.23	0.71	4.79	3.23	16.51	1.45	4.04	4.60	1.08
d4	Butyl dibromoacetate	17.72	0.82	4.33	2.70	18.27	1.61	3.38	4.02	1.03
d5	Pentyl dibromoacetate	20.17	0.94	3.56	2.27	20.05	1.76	2.77	3.33	0.99
d6	Hexyl dibromoacetate	22.52	1.04	2.87	1.96	21.89	1.93	2.33	2.77	0.97
d7	Heptyl dibromoacetate	24.78	1.15	2.38	1.76	23.70	2.09	2.06	2.37	0.96
d8	Octyl dibromoacetate	26.92	1.25	2.06	1.62	25.50	2.24	1.86	2.10	0.95
d9	Nonyl dibromoacetate	28.96	1.34	1.85	1.52	27.22	2.40	1.73	1.90	0.94
d10	Decyl dibromoacetate	30.90	1.43	1.70	1.44	28.98	2.55	1.64	1.77	0.94
d11	Undecyl dibromoacetate	32.77	1.52	1.59	1.39	30.59	2.69	1.56	1.67	0.93
d12	Dodecyl dibromoacetate	34.53	1.60	1.51	1.34	32.31	2.84	1.51	1.60	0.94
t1	Methyl tribromoacetate	16.05	0.74	6.58	5.88					
t2	Ethyl tribromoacetate	17.52	0.81	6.44	5.02					
t3	Propyl tribromoacetate	19.90	0.92	6.26	4.22					
t4	Butyl tribromoacetate	22.23	1.03	5.44	3.38					
t5	Pentyl tribromoacetate	24.49	1.14	4.33	2.75					
t6	Hexyl tribromoacetate	26.70	1.24	3.40	2.32					
t7	Heptyl tribromoacetate	28.75	1.33	2.76	2.04					
t8	Octyl tribromoacetate	30.70	1.42	2.35	1.84					
t9	Nonyl tribromoacetate	32.60	1.51	2.08	1.71					
t10	Decyl tribromoacetate	34.41	1.60	1.89	1.61					
t11	Undecyl tribromoacetate	36.30	1.68	1.76	1.54					
t12	Dodecyl tribromoacetate	38.16	1.77	1.66	1.48					
C_{14}	*n*-Tetradecane	21.57	1.00			11.36	1.00			0.53

* Absolute retention times (min) were measured from sample injection (Figs. 1 and 2).
** Relative retention time for *n*-tetradecane (C_{14}) taken as 1.00.
*** Relative retention time for the corresponding alkanol (1–12) taken as 1.00.
§ Relative retention time for the corresponding *n*-alkyl acetate (a1–a12) taken as 1.00.
§§ Relative retention time for the corresponding compound on SE-30 taken as 1.00.

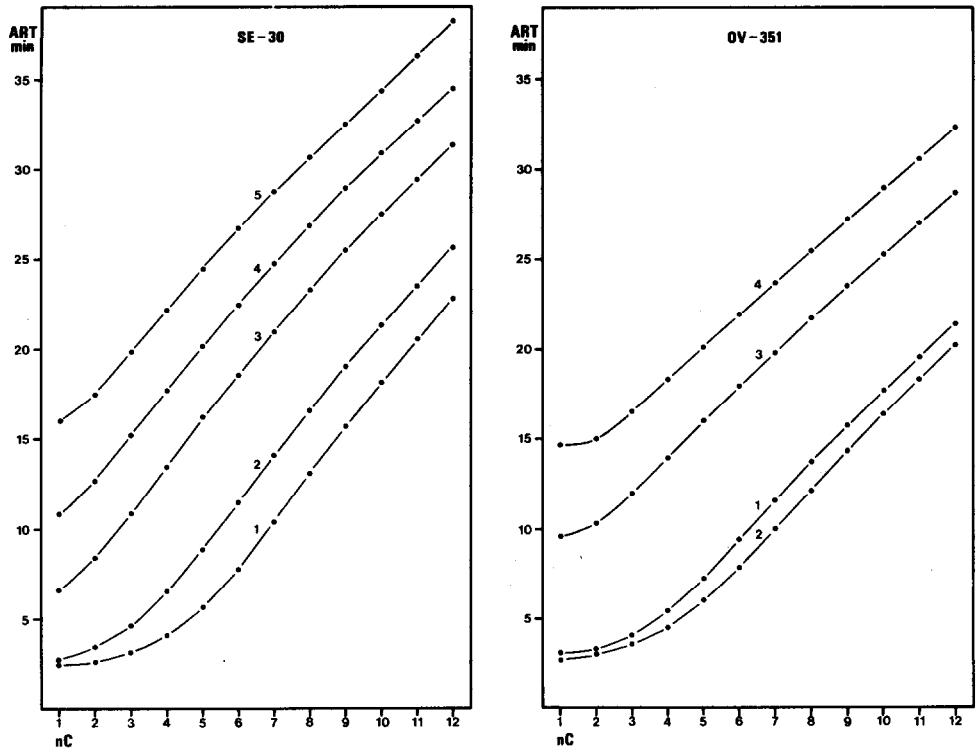

Fig. 3. Plot showing retention of C_1–C_{12} *n*-alkanols (curve 1), *n*-alkyl acetates (curve 2), *n*-alkyl monobromoacetates (curve 3), *n*-alkyl dibromoacetates (curve 4) and *n*-alkyl tribromoacetates (curve 5), obtained on SE-30 and OV-351. ART = Absolute retention time, measured from sample injection; *n*C = carbon number of the alkanol moiety.

Fig. 3 shows plots of the retention times for the five series. Based on earlier studies with halogenated acetic acid esters[3,10,11], it is evident that the monobromo isomer is eluted on a non-polar column nearly at the same time as the dichloro isomer and the dibromo isomer has a higher retention than the trichloro and the monoiodo isomers. As expected, a greater enhancement of retention compared with the chlorinated esters[1,10] is indicated by the addition of the bulky bromine atom(s) (curves 3–5) to the simple ester (curve 2). The alkanols (curve 1) always have a lower retention than the corresponding *n*-alkyl acetates (curve 2).

The polar OV-351 capillary column gave no peaks for the tribromo isomers (only small peaks indicating the formation of the dibromo isomers were obtained). The polar stationary phase also seems to be unsuitable for the monobromo isomers, giving broad, tailing peaks. However, by using very dilute samples the monobromo isomers are eluted sharply, as are the dibromo isomers. Generally the following retention order is observed: C_n-alkyl acetate < C_n-alkanol < C_{n-4}-alkyl monobromoacetate < C_{n-6}-alkyl dibromoacetate ($n \geqslant 11$). With chain lengths of $5 \leqslant n < 11$ the following exceptions in the retention order are observed: (i) methyl monobromoacetate (m1) is eluted after hexyl acetate (a6) and 1-hexanol (6), (ii) ethyl monobromoacetate (m2) after heptyl acetate (a7), (iii) methyl dibromoacetate (d1)

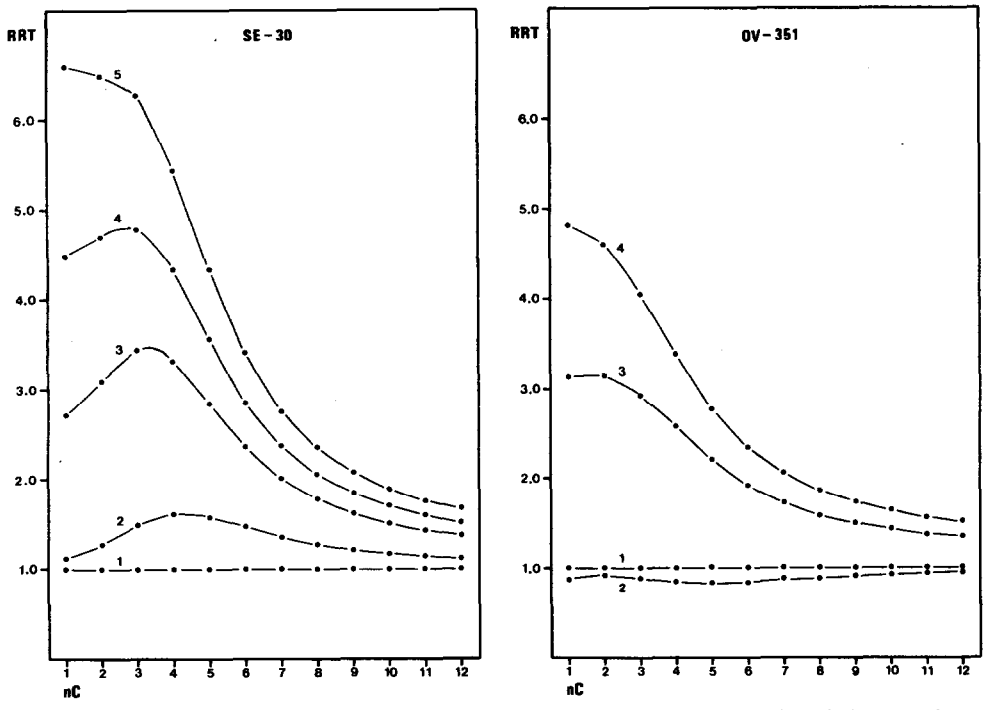

Fig. 4. Plot showing retention of the five homologous series as in Fig. 3 (curves 1–5). Relative retention time (RRT) for the *n*-alkanols (1–8) taken as 1.00.

after octyl acetate (a8), 1-octanol (8), butyl monobromoacetate (m4) and nonyl acetate (a9), (iv) ethyl dibromoacetate (d2) after nonyl acetate (a9) and (v) propyl dibromoacetate (d3) after decyl acetate (a10). As shown in Fig. 2, two compound pairs overlapped, *viz.*, ethyl acetate (a2) with methanol (1) and butyl dibromoacetate (d4) with undecyl acetate (a11).

Judging from the earlier studies[1,10,11], on OV-351 the monobromo isomer has a higher retention than the last eluted chloro, *i.e.*, dichloro, isomer. Plots of the retentions of the four series show (Fig. 3) that the alkyl acetates (curve 2) have lower retentions than the corresponding alkanols (curve 1). The increased retention of the monobromo isomers (curve 3) and the dibromo isomers (curve 4) is greater than on SE-30 owing to the influence of the polar esters with the more polar stationary phase[12].

By expressing the retention time relative to the alkanols (Fig. 4), it becomes apparent that on SE-30 the retention is maximized with butyl acetate (curve 2), propyl monobromoacetate (curve 3), propyl dibromoacetate (curve 4) and methyl tribromoacetate (curve 5). On OV-351 the retention is minimized for pentyl acetate (curve 2) and maximized for the ethyl monobromo isomer (curve 3) and the methyl dibromo isomer (curve 4). The last column in Table I shows that the greatest disparities between the retention behaviour of the compounds on the columns used are observed with 1-butanol (4), pentyl acetate (a5) and the monobromo (m1) and dibromo (d1) isomers.

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REFERENCES

1 I. O. O. Korhonen, *J. Chromatogr.*, 285 (1984) 443, and earlier parts of the series cited therein.
2 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 284 (1984) 474, and earlier parts of the series cited therein.
3 K. Komárek, L. Hornová and J. Churáček, *J. Chromatogr.*, 244 (1982) 142, and references cited therein.
4 K. Komárek, L. Hornová, A. Horna and J. Churáček, *J. Chromatogr.*, 262 (1983) 316.
5 K. Komárek, L. Hornová and J. Churáček, *J. Chromatogr.*, 252 (1982) 293.
6 I. O. O. Korhonen, *J. Chromatogr.*, 244 (1982) 137.
7 J. K. Haken, *J. Chromatogr.*, 253 (1982) 264.
8 I. O. O. Korhonen, *J. Chromatogr.*, 285 (1984) 115.
9 A. B. McKague, *J. Chromatogr.*, 208 (1981) 287.
10 I. O. O. Korhonen, *Chromatographia*, 15 (1982) 635.
11 I. O. O. Korhonen, *J. Chromatogr.*, 248 (1982) 69.
12 J. K. Haken, B. G. Madden and I. O. O. Korhonen, *J. Chromatogr.*, 256 (1983) 221.