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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XXV*. BRANCHED-CHAIN C_3–C_5 ALKYL ESTERS OF HALOGENATED ACETIC ACIDS

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SUMMARY

The temperature-programmed capillary gas chromatography of branched-chain C_3–C_5 alkyl esters of acetic and mono-, di- and tri-chloro- and -bromoacetic acids was studied on low-polarity (SE-30) and highly polar (OV-351) columns. The retention behaviour of the esters was compared with that of the corresponding alcohols, the retention indices and the retention index increments for the methylene units and the various halogen substituents were determined and the retention order of the individual components in the eight homologous series is discussed.

INTRODUCTION

The gas chromatographic (GC) retention behaviour of some isoalkyl esters, *viz.*, methylethyl, 2-methylpropyl and 3-methylbutyl esters, of aliphatic C_1–C_6 carboxylic acids has been previously extensively studied[1]. Komárek and co-workers[2–4] dealt with the GC separation of the C_3–C_6 isoalkyl esters of lower (C_2–C_4) carboxylic acids and their halogenated derivatives on non-polar OV-101 as the stationary phase.

Recently, eight lower (C_3–C_5) branched-chain alcohols and their propanoyl, 2- and 3-chloropropanoyl, butanoyl and 2-, 3- and 4-chlorobutanoyl derivatives have been separated by GC on SE-30 and OV-351 capillary columns with temperature programming[1]. In this paper, the retention behaviour of the same series of alcohols and the corresponding alkyl esters of acetic and mono-, di- and tri-chloro- and -bromoacetic acids is reported, this work extending previous studies with esters of acetic acid derivatives[1,2,5,6]. The separations were carried out on SE-30 and OV-351 quartz capillary columns with temperature programming. The relative retentions and Kováts retention indices for all 64 individual components in the eight homologous series were determined, and also the effects of the chain branching and the retention index increments of the various halogen substituents. The results are compared with those reported earlier[1,2].

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EXPERIMENTAL

Materials

Branched-chain alcohols (1–8) were commercial products (Fluka, Buchs, Switzerland). The corresponding alkyl esters of acetic acid (9–16 = A1–A8), monochloroacetic acid (17–24 = MCl1–MCl8), dichloroacetic acid (25–32 = DCl1–DCl8), trichloroacetic acid (33–40 = TCl1–TCl8), monobromoacetic acid (41–48 = MBr1–MBr8), dibromoacetic acid (49–56 = DBr1–DBr8) and tribromoacetic acid (57–64 = TBr1–TBr8) were synthesized from the corresponding alcohols and acid chlorides as described earlier[7]. Acetyl chloride (Fluka) and trichloroacetyl chloride (Merck-Schuchardt, Darmstadt, F.R.G.) were commercial products; the other halogenated acetyl chlorides were prepared by the reaction of thionyl chloride (Fluka) with the commercial acids (Fluka and Merck-Schuchardt)[5,6]. Compounds 1–64 are listed in Table I.

Commercial mixtures of *n*-alkanes were obtained from different sources.

Methods

GC analyses were performed on a Perkin-Elmer Sigma 3 gas chromatograph on SE-30 and OV-351 quartz capillary columns under the operating conditions reported previously[6]. The column temperature was programmed from 50°C at 6°C min^{-1} until the elution of peaks had ceased. The retention data were analysed with a Hewlett-Packard Model 3390A reporting integrator using standard programs. Retention times were measured from the time of sample injection and the mixtures of the compounds and *n*-alkanes were chromatographed immediately one after the other to allow identical operating conditions.

The Kováts retention indices for the components were calculated[8] by using two appropriate adjacent *n*-alkanes. The value of the dead volume time has no effect on the Kováts retention indices in temperature-programmed GC and it was not determined.

RESULTS AND DISCUSSION

Chromatograms of a mixture of the branched-chain alcohols and their acetyl and chloroacetyl derivatives, analysed on SE-30 and OV-351, are illustrated in Figs. 1 and 2, and the GC separations of a mixture containing the brominated esters are shown in Figs. 3 and 4. Table I gives the retention data, relative to alcohols, alkyl acetates, *n*-tetradecane and the compounds analysed on SE-30. The plots of the retention are shown in Figs. 5 and 6.

As previously reported[1], the branched-chain alcohols are eluted on SE-30, except for the compound pair 2-methyl-1-propanol (4) and 2-methyl-2-butanol (5), in order of increasing boiling point, the retention order of the esters of branched-chain alcohols remaining unaltered. As is evident from Table II, the alkyl acetates (9–16) are eluted on a non-polar column in the sequence according to their boiling points, methyl and ethyl esters being eluted earlier than the methylethyl ester (9), *n*-propyl acetate between dimethylethyl (10) and 1-methylpropyl (11) esters, *n*-butyl acetate with 1,1-dimethylpropyl acetate (13) and *n*-pentyl acetate having the highest retention[6].

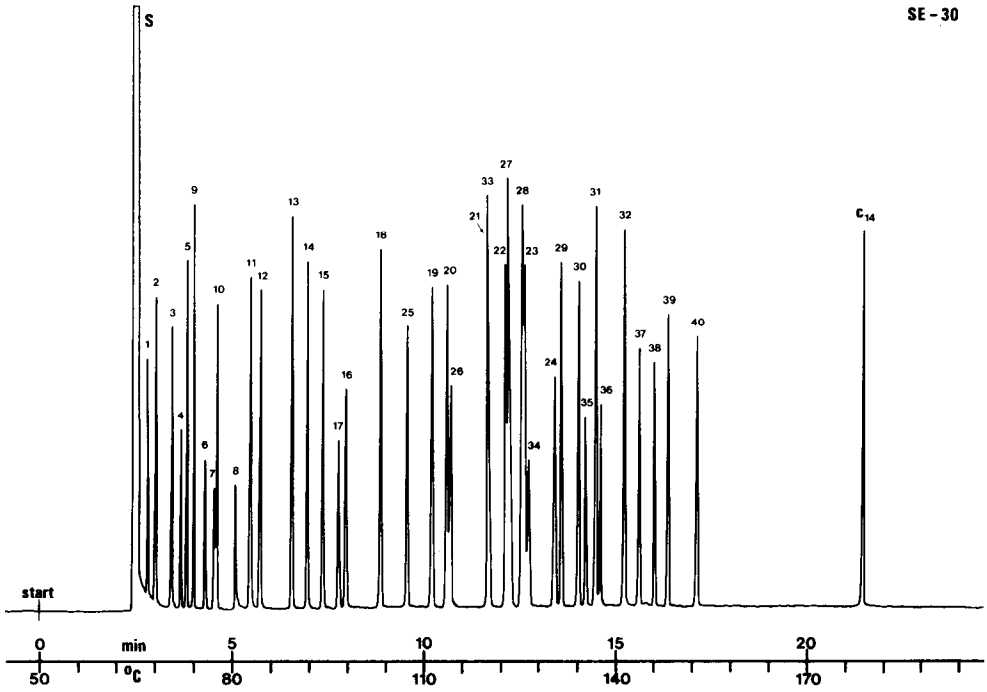


Fig. 1. Chromatogram of a mixture of branched-chain alcohols (1–8) and the corresponding alkyl esters of acetic acid (9–16) and chlorinated acetic acids (17–40), analysed on SE-30. S = Solvent; C_{14} = *n*-tetradecane; peaks are identified in Table I.

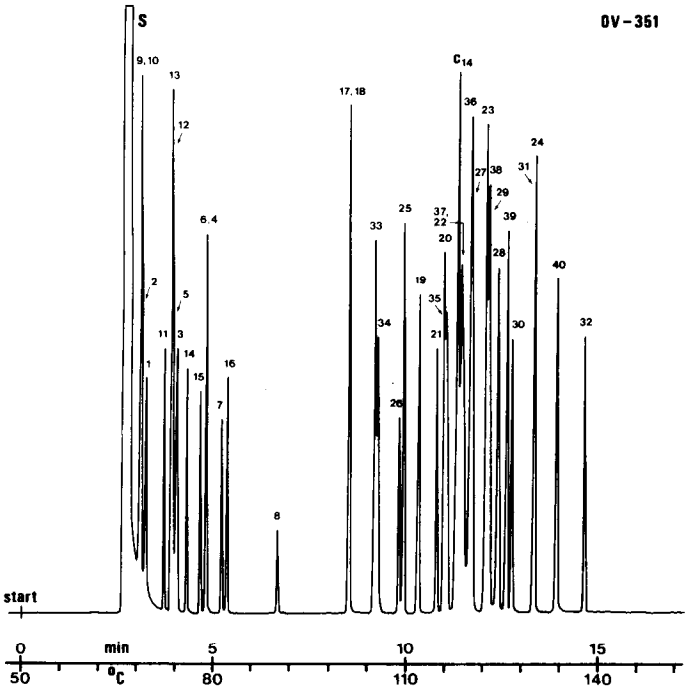


Fig. 2. Chromatogram of the same mixture as in Fig. 1, analysed on OV-351.

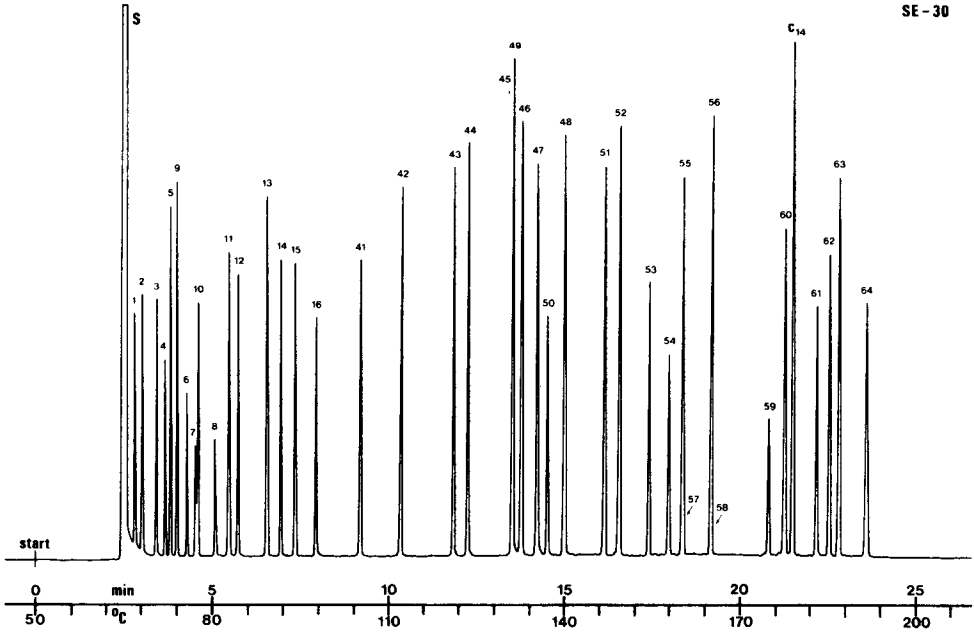


Fig. 3. Chromatogram of a mixture of branched-chain alcohols (1–8) and the corresponding alkyl esters of acetic acid (9–16) and brominated acetic acids (41–64), analysed on SE-30. S = Solvent; C_{14} = *n*-tetradecane; peaks are identified in Table I.

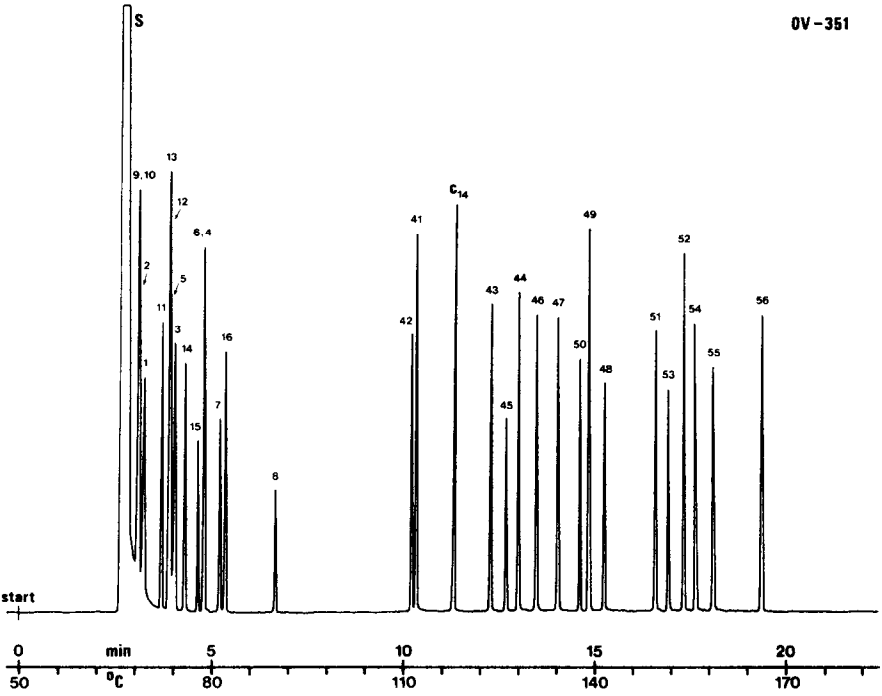


Fig. 4. Chromatogram of the same mixture as in Fig. 3, without the tribromo isomers (57–64), analysed on OV-351.

TABLE I

RETENTION DATA FOR BRANCHED-CHAIN ALCOHOLS AND THE CORRESPONDING ALKYL ESTERS OF ACETIC ACID AND CHLORINATED AND BROMINATED ACETIC ACIDS ON SE-30 AND OV-351

Conditions as in Figs. 1–4.

Peak	*Compound*	*Column*								
		SE-30				*OV-351*				
		*ART***	*RRT****	*RRT*****	*RRT*§*	*ART***	*RRT****	*RRT*****	*RRT*§*	*RRT*§§*
1	2-Propanol	2.80	0.13	1.00	0.70	3.26	0.29	1.00	1.05	1.16
2	2-Methyl-2-propanol	3.03	0.14	1.00	0.66	3.12	0.28	1.00	1.00	1.03
3	2-Butanol	3.45	0.16	1.00	0.63	4.06	0.36	1.00	1.09	1.18
4	2-Methyl-1-propanol	3.68	0.17	1.00	0.64	4.81	0.42	1.00	1.21	1.31
5	2-Methyl-2-butanol	3.82	0.18	1.00	0.58	3.92	0.35	1.00	1.00	1.03
6	3-Methyl-2-butanol	4.31	0.20	1.00	0.62	4.81	0.42	1.00	1.12	1.12
7	2-Pentanol	4.55	0.21	1.00	0.62	5.21	0.46	1.00	1.11	1.15
8	3-Methyl-1-butanol	5.09	0.24	1.00	0.64	6.79	0.60	1.00	1.27	1.33
9	Methylethyl acetate	4.00	0.19	1.43	1.00	3.11	0.27	0.95	1.00	0.78
10	Dimethylethyl acetate	4.61	0.21	1.52	1.00	3.11	0.27	1.00	1.00	0.67
11	1-Methylpropyl acetate	5.49	0.25	1.59	1.00	3.71	0.33	0.91	1.00	0.68
12	2-Methylpropyl acetate	5.73	0.27	1.56	1.00	3.99	0.35	0.83	1.00	0.70
13	1,1-Dimethylpropyl acetate	6.57	0.30	1.72	1.00	3.93	0.35	1.00	1.00	0.60
14	1,2-Dimethylpropyl acetate	6.96	0.32	1.61	1.00	4.31	0.38	0.90	1.00	0.62
15	1-Methylbutyl acetate	7.37	0.34	1.62	1.00	4.68	0.41	0.90	1.00	0.64
16	3-Methylbutyl acetate	7.98	0.37	1.57	1.00	5.36	0.47	0.79	1.00	0.67
17	Methylethyl monochloroacetate	7.79	0.36	2.78	1.95	8.56	0.76	2.63	2.75	1.10
18	Dimethylethyl monochloroacetate	8.88	0.41	2.93	1.93	8.56	0.76	2.74	2.75	0.96
19	1-Methylpropyl monochloroacetate	10.20	0.47	2.96	1.86	10.35	0.91	2.55	2.79	1.01
20	2-Methylpropyl monochloroacetate	10.59	0.49	2.88	1.85	11.02	0.97	2.29	2.76	1.04
21	1,1-Dimethylpropyl monochloroacetate	11.64	0.54	3.05	1.77	10.80	0.95	2.76	2.75	0.93
22	1,2-Dimethylpropyl monochloroacetate	12.10	0.56	2.81	1.74	11.49	1.01	2.39	2.67	0.95
23	1-Methylbutyl monochloroacetate	12.60	0.58	2.77	1.71	12.10	1.07	2.32	2.59	0.96
24	3-Methylbutyl monochloroacetate	13.41	0.62	2.63	1.68	13.39	1.18	1.97	2.50	1.00

(*Continued on p. 56*)

TABLE I (*continued*)

Peak	*Compound*	*Column*								
		SE-30				*OV-351*				
		*ART**	*RRT***	*RRT****	*RRT*§	*ART**	*RRT***	*RRT****	*RRT*§	*RRT*§§
25	Methylethyl dichloroacetate	9.58	0.44	3.42	2.40	9.97	0.88	3.06	3.21	1.04
26	Dimethylethyl dichloroacetate	10.69	0.50	3.53	2.32	9.84	0.87	3.15	3.16	0.92
27	1-Methylpropyl dichloroacetate	12.16	0.56	3.52	2.21	11.76	1.04	2.90	3.17	0.97
28	2-Methylpropyl dichloroacetate	12.57	0.58	3.42	2.19	12.42	1.10	2.58	3.11	0.99
29	1,1-Dimethylpropyl dichloroacetate	13.58	0.63	3.55	2.07	12.16	1.07	3.10	3.09	0.90
30	1,2-Dimethylpropyl dichloroacetate	14.03	0.65	3.26	2.02	12.79	1.13	2.66	2.97	0.91
31	1-Methylbutyl dichloroacetate	14.50	0.67	3.19	1.97	13.38	1.18	2.57	2.86	0.92
32	3-Methylbutyl dichloroacetate	15.27	0.71	3.00	1.91	14.70	1.30	2.16	2.74	0.96
33	Methylethyl trichloroacetate	11.64	0.54	4.16	2.91	9.23	0.81	2.83	2.97	0.79
34	Dimethylethyl trichloroacetate	12.72	0.59	4.20	2.76	9.30	0.82	2.98	2.99	0.73
35	1-Methylpropyl trichloroacetate	14.21	0.66	4.12	2.59	11.07	0.98	2.73	2.98	0.78
36	2-Methylpropyl trichloroacetate	14.61	0.68	3.97	2.55	11.72	1.03	2.44	2.94	0.80
37	1,1-Dimethylpropyl trichloroacetate	15.61	0.72	4.09	2.38	11.55	1.02	2.95	2.94	0.74
38	1,2-Dimethylpropyl trichloroacetate	16.01	0.74	3.71	2.30	12.16	1.07	2.53	2.82	0.76
39	1-Methylbutyl trichloroacetate	16.40	0.76	3.60	2.23	12.65	1.12	2.43	2.70	0.77
40	3-Methylbutyl trichloroacetate	17.14	0.79	3.37	2.15	13.97	1.23	2.06	2.61	0.82
41	Methylethyl monobromoacetate	9.26	0.43	3.31	2.32	10.41	0.92	3.19	3.35	1.12
42	Dimethylethyl monobromoacetate	10.40	0.48	3.43	2.26	10.29	0.91	3.30	3.31	0.99
43	1-Methylpropyl monobromoacetate	11.92	0.55	3.46	2.17	12.32	1.09	3.03	3.32	1.03
44	2-Methylpropyl monobromoacetate	12.32	0.57	3.35	2.15	13.04	1.15	2.71	3.27	1.06
45	1,1-Dimethylpropyl monobromoacetate	13.52	0.63	3.54	2.06	12.70	1.12	3.24	3.23	0.94
46	1,2-Dimethylpropyl monobromoacetate	13.83	0.64	3.21	1.99	13.51	1.19	2.81	3.13	0.98
47	1-Methylbutyl monobromoacetate	14.29	0.66	3.14	1.94	14.08	1.24	2.70	3.01	0.99
48	3-Methylbutyl monobromoacetate	15.08	0.70	2.96	1.89	15.28	1.35	2.25	2.85	1.01

49	Methylethyl dibromoacetate	13.60	0.63	4.86	3.40	14.84	1.31	4.55	4.77	1.09
50	Dimethylethyl dibromoacetate	14.52	0.67	4.79	3.15	14.64	1.29	4.69	4.71	1.01
51	1-Methylpropyl dibromoacetate	16.18	0.75	4.69	2.95	16.58	1.46	4.08	4.47	1.02
52	2-Methylpropyl dibromoacetate	16.62	0.77	4.52	2.90	17.30	1.53	3.60	4.34	1.04
53	1,1-Dimethylpropyl dibromoacetate	17.45	0.81	4.57	2.66	16.90	1.49	4.31	4.30	0.97
54	1,2-Dimethylpropyl dibromoacetate	18.00	0.83	4.18	2.59	17.62	1.56	3.66	4.09	0.98
55	1-Methylbutyl dibromoacetate	18.41	0.85	4.05	2.50	18.09	1.60	3.47	3.87	0.98
56	3-Methylbutyl dibromoacetate	19.24	0.89	3.78	2.41	19.32	1.71	2.85	3.60	1.00
57	Methylethyl tribromoacetate	18.35	0.85	6.55	4.59					
58	Dimethylethyl tribromoacetate	19.26	0.89	6.36	4.18					
59	1-Methylpropyl tribromoacetate	20.83	0.97	6.04	3.79					
60	2-Methylpropyl tribromoacetate	21.31	0.99	5.79	3.72					
61	1,1-Dimethylpropyl tribromoacetate	22.22	1.03	5.82	3.38					
62	1,2-Dimethylpropyl tribromoacetate	22.60	1.05	5.24	3.25					
63	1-Methylbutyl tribromoacetate	22.88	1.06	5.03	3.10					
64	3-Methylbutyl tribromoacetate	23.62	1.10	4.64	2.96					
C_{14}	*n*-Tetradecane	21.57	1.00	–	–	11.33	1.00	–	–	0.53

* Absolute retention times (min) were measured from sample injection (Figs. 1–4).
** Relative retention time for *n*-tetradecane (C_{14}) taken as 1.00.
*** Relative retention time for the corresponding alcohol (1–8) taken as 1.00.
§ Relative retention time for the corresponding alkyl acetate (9–16) taken as 1.00.
§§ Relative retention time for the corresponding compound on SE-30 taken as 1.00.

As expected, the retention order is unaltered with the halogenated esters (Fig. 5), the individual components being eluted in the order monochloro < monobromo < dichloro < trichloro < dibromo < tribromo isomers. Bearing in mind the retention behaviour of the monochlorinated branched-chain esters of propanoic and butanoic acids[1], the monochloro isomer eluted earlier than 2-chloropropanoate, the monobromo and dichloro isomers between 2- and 3-chloropropanoates, the trichloro isomer between 3- and 4-chlorobutanoates and the di- and tribromo isomers after 4-chlorobutanoate.

Figs. 1 and 3 show the fairly good separations of the mixtures on SE-30, only the compound pairs 21 and 33, 45 and 49, 55 and 57, and 56 and 58 showing complete overlapping. In addition, some partially resolved peaks are observed (Fig. 1). The

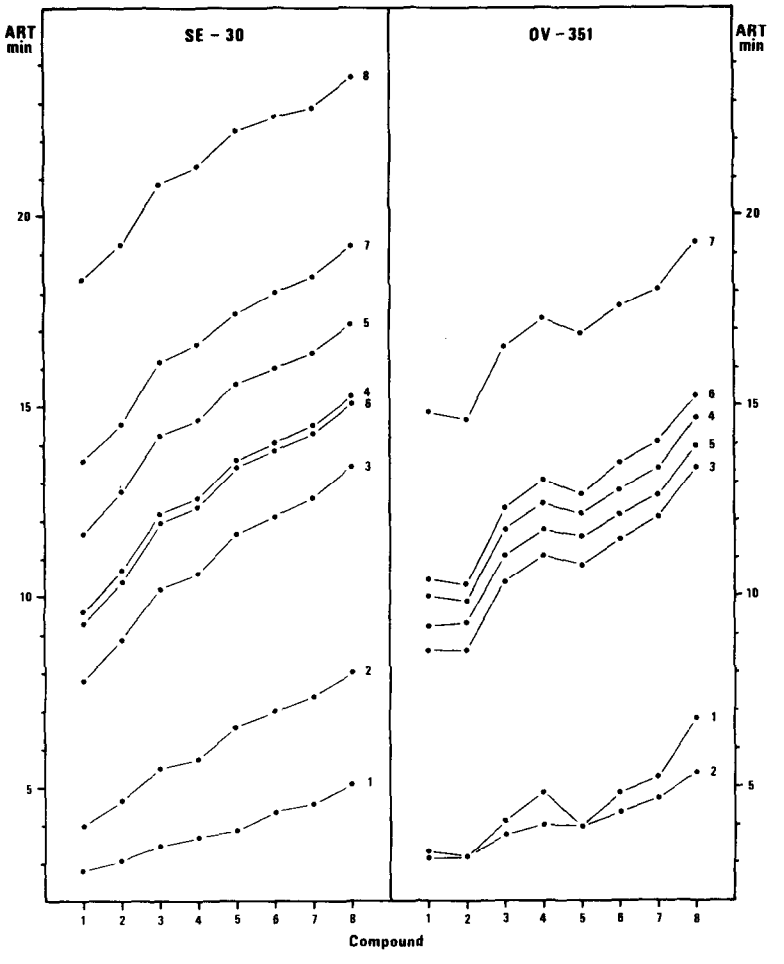


Fig. 5. Plot showing retention of branched-chain alcohols (1–8, curve 1), alkyl acetates (A1–A8, curve 2), monochloroacetates (MCl1–MCl8, curve 3), dichloroacetates (DCl1–DCl8, curve 4), trichloroacetates (TCl1–TCl8, curve 5), monobromoacetates (MBr1–MBr8, curve 6), dibromoacetates (DBr1–DBr8, curve 7) and tribromoacetates (TBr1–TBr8, curve 8), analysed on SE-30 and OV-351. ART = Absolute retention time, measured from sample injection (Table I).

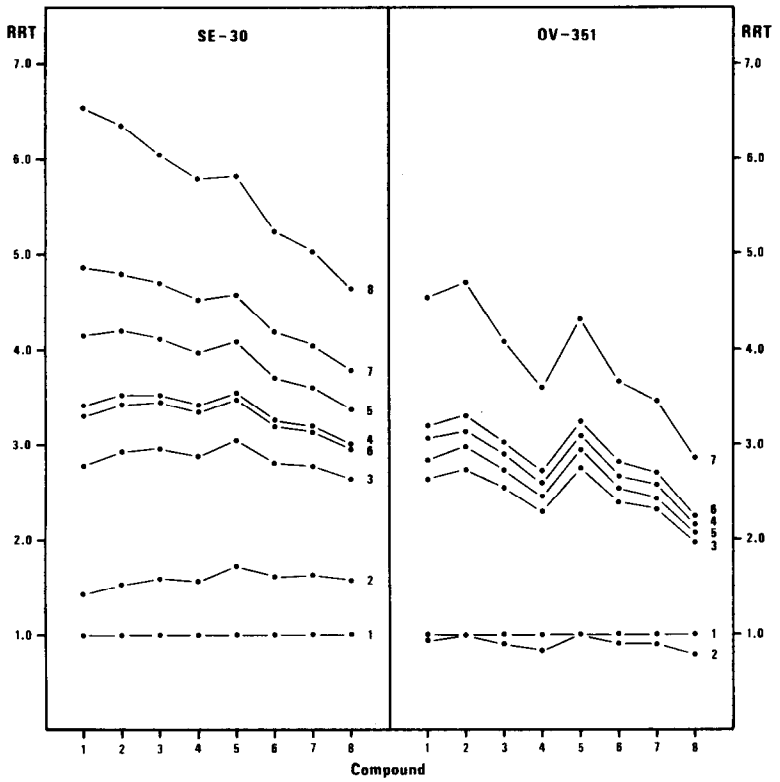


Fig. 6. Plot showing retention of the eight series as in Fig. 5 (curves 1–8). Relative retention time (RRT) for the branched-chain alcohols (1–8) taken as 1.00 (Table I).

isomeric chloro esters are eluted closer together, two monochloro isomers (17 and 18) appearing earlier than the first eluted dichloro isomer (25) and, correspondingly, two dichloro isomers (25 and 26) having lower retentions than the first eluted trichloro isomer (33). Owing to the increased size of the halogen substituents, enhanced retention between the bromo esters is observed, five monobromo isomers (41–45) being eluted earlier than methylethyl dibromoacetate (49) and six dibromo isomers (49–54) earlier than the first eluted tribromo isomer (57).

With the polar column the elution sequence is greatly influenced by the compound structures given in Table III. The alcohol pairs 2 and 1, and 5 and 3, are eluted in the reverse order to that on SE-30 and the alcohols 4 and 6 have the same retention[6]. With the alkyl acetates, the methylethyl (9) and dimethylethyl (10) isomers are coincident, the elution order being reversed with 2-methylpropyl (12) and 1,1-dimethylpropyl (13) esters and with *n*-butyl and 1,2-dimethylpropyl (14) esters (Table II).

Generally the halogenated esters follow the pattern of the alkyl acetates, the elution order of the methylethyl and dimethylethyl isomers being variable, *i.e.*, the monochloro isomers (17 and 18) are coincident and the dimethylethyl dichloro (26), monobromo (42) and dibromo (50) isomers have lower retentions than the corresponding methylethyl isomers (25, 41 and 49), whereas the trichloro isomers (33 and

TABLE II

CORRELATION BETWEEN THE BOILING POINTS AND THE RETENTION TIMES (RRT) OF THE LOWER ALKYL ACETATES ON SE-30 AND OV-351

No.	*Ester*	*B.p. (°C)**	*RRT***	
			SE-30	*OV-351*
	Methyl acetate	57	0.13	0.24
	Ethyl acetate	77.1	0.16	0.27
9	Methylethyl acetate	93	0.19	0.27
10	Dimethylethyl acetate	95	0.21	0.27
	n-Propyl acetate	101.6	0.22	0.32
11	1-Methylpropyl acetate	112.2	0.25	0.33
12	2-Methylpropyl acetate	117.2	0.27	0.35
13	1,1-Dimethylpropyl acetate	124.5	0.30	0.35
	n-Butyl acetate	126.5	0.30	0.40
14	1,2-Dimethylpropyl acetate	129	0.32	0.38
15	1-Methylbutyl acetate	133.5	0.34	0.41
16	3-Methylbutyl acetate	142	0.37	0.47
	n-Pentyl acetate	149.3	0.41	0.53

* From ref. 9, except for compound 14 (ref. 10).

** Relative retention time for *n*-tetradecane taken as 1.00; values for *n*-alkyl acetates taken from ref. 6.

34) are eluted in the reverse order (Figs. 2, 4 and 5). The alkyl acetates in general have lower retentions than the corresponding alcohols, the halogenated isomers being eluted in the order monochloro < trichloro < dichloro < monobromo < dibromo isomers. The tribromo isomers showed no peaks on the highly polar column used, as reported earlier with the *n*-alkyl tribromo isomers[6]. By comparing the retention behaviour of the acetate esters with that of the monochlorinated propanoate and butanoate esters[6], it is evident that the monochloro isomer eluted between 2-chloropropanoate and 2-chlorobutanoate, the trichloro, dichloro and monobromo isomers between 2- and 3-chlorobutanoates and the dibromo isomer after 4-chlorobutanoate.

Figs. 2 and 4 show the much poorer resolutions of the mixtures on OV-351 as on SE-30. Several overlappings occurred with the alcohols and alkyl acetates, owing to the reduced retention of the latter. Additional overlappings are found with the chlorinated derivatives (Fig. 2), but Fig. 4 shows that all the bromo isomers are resolved. It seems, however, that in the presence of the tribromo isomers some overlapping would have occurred.

The relative retentions, relative to the alcohols, are shown in Fig. 6. It can be seen that on SE-30 the retention is maximized with 1,1-dimethylpropyl isomers (13, 21, 29 and 45), dimethylethyl trichloroacetate (34) and methylethyl esters (49 and 57) and minimized with methylethyl acetate (9) and halogenated 3-methylbutyl isomers (24, 32, 40, 48, 56 and 64). OV-351 showed the maximum retention for the 1,1-dimethylpropyl isomers (13 and 21) and dimethylethyl isomers (26, 34, 42 and 50), the minimum retention occurring with all 3-methylbutyl isomers (16, 24, 32, 40, 48 and 56).

Table IV shows the correlation between the retention indices determined with temperature programming in this work and with isothermal operation as reported

TABLE III

STRUCTURES OF THE ESTERS STUDIED

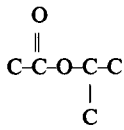
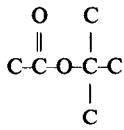
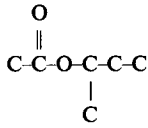
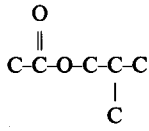
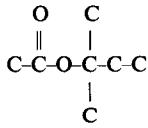
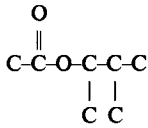
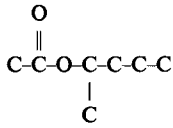
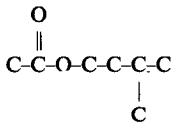
Ester series	*Structure*
Methylethyl (1)	
Dimethylethyl (2)	
1-Methylpropyl (3)	
2-Methylpropyl (4)	
1,1-Dimethylpropyl (5)	
1,2-Dimethylpropyl (6)	
1-Methylbutyl (7)	
3-Methylbutyl (8)	

TABLE IV

CORRELATION BETWEEN THE RETENTION INDICES (*I*) OF ISOALKYL ESTERS, DETERMINED UNDER ISOTHERMAL AND TEMPERATURE-PROGRAMMED CONDITIONS

Ester	*Column*				
	*SE-30**	*OV-101***	*SE-30****	*OV-351**	*OV-225****
A1	639	646.8	643	878	840
A4	749	757.2	750	1009	977
A8	853	859.7	859	1117	1087
MCl1	845	850.7		1280	
MCl4	956	959.6		1392	
MCl8	1061	1062.5		1504	
DCl1	918	920.8		1345	
DCl4	1030	1028.8		1458	
DCl8	1133	1129.6		1567	
TCl1	995	995.9		1312	
TCl4	1106	1103.8		1425	
TCl8	1208	1203.3		1532	
MBr1	906	916.2		1365	
MBr4	1021	1025.8		1488	
MBr8	1125	1127.9		1595	

* Present work with temperature programming.
** From ref. 2 at 80°C.
*** From ref. 11 at 150°C.

earlier[2,11]. The agreement between the values is exceptional in spite of the different columns and operating conditions used. The comparison is defective owing to the absence of the isothermal data for the halogenated esters on polar columns, as only the data for A1, A4 and A8, *i.e.*, for isoalkyl acetates, have been published. According to the results of Ashes and Haken[11], the values for isoalkyl acetates on acceptor stationary phases varied with the polarity of the phase in the following ranges: A1 (735–949), A4 (859–1086) and A8 (965–1186), the highest values occurring on the most polar stationary phase, XF-1150. The values on OV-225 given in Table IV are lower than those on OV-351, but this is due to the higher polarity of the latter phase.

Retention indices of the eight series and increments of retention indices for methylene units and halogen substituents determined on SE-30 and OV-351 are given in Tables V and VI, a summary of the retention increments being presented in Table VII.

The methylene increments in the three series of the esters, *i.e.*, 1 → 3 → 7, 1 → 4 → 8 and 2 → 5, are in the ranges 87–107, 102–128 and 104–131 on SE-30 and lower on OV-351, *viz.*, 74–96, 106–131 and 102–125 retention index units (i.u.), respectively. The increments determined for the isoalkyl esters (A4, A8, MC14, MC18, DC14, DC18, TC14, TC18, MBr4 and MBr8) on SE-30 given in Table V are in good agreement with the values of Komárek *et al.*[2].

The effect due to replacement of an α-hydrogen atom in the 1, 3 and 4 series,

TABLE V

RETENTION INDICES OF THE COMPOUNDS STUDIED AND INCREMENTS OF RETENTION INDICES FOR METHYLENE UNITS AND HALOGEN SUBSTITUENTS ON SE-30

Conditions as shown in Figs. 1 and 3.

*Compound**	*I*	ΔI_{CH_2}**	$\Delta I_{\alpha\text{-}CH_2}$***	$\Delta I_{\beta\text{-}CH_2}$***	$\Delta I_{\gamma\text{-}CH_2}$***	$\Sigma\Delta I_x$§	ΔI_{1x}§§	ΔI_{2x}§§	ΔI_{3x}§§
1	515	–	–	–					
2	543	–	28	–					
3	594	79	–	79	–				
4	614	99	–						
5	625	82	31	82					
6	663		49	69					
7	682	88			88				
8	716	102							
A1	639	–	–	–					
A2	687	–	48	–					
A3	737	98	–	98	–				
A4	749	110	–						
A5	793	106	56	106					
A6	811		62	74					
A7	828	91			91				
A8	853	104							
MCl1	845	–	–	–		206	206		
MCl2	891	–	46	–		204	204		
MCl3	941	96	–	96	–	204	204		
MCl4	956	111	–			207	207		
MCl5	995	104	54	104		202	202		
MCl6	1012		56	71		201	201		
MCl7	1031	90			90	203	203		
MCl8	1061	105				208	208		

(*Continued on p. 64*)

TABLE V (*continued*)

*Compound**	*I*	ΔI_{CH_2}**	$\Delta I_{\alpha\text{-}CH_2}$***	$\Delta I_{\beta\text{-}CH_2}$***	$\Delta I_{\gamma\text{-}CH_2}$***	$\Sigma\Delta I_x$§	ΔI_{1x}§§	ΔI_{2x}§§	ΔI_{3x}§§
DCl1	918	–	–	–		279	206	73	
DCl2	960	–	42	–		273	204	69	
DCl3	1015	97	–	97	–	278	204	74	
DCl4	1030	112	–			281	207	74	
DCl5	1068	108	53	108		275	202	73	
DCl6	1084		54	69		273	201	72	
DCl7	1102	87			87	274	203	71	
DCl8	1133	103				280	208	72	
TCl1	995	–	–	–		356	206	73	77
TCl2	1035	–	40	–		348	204	69	75
TCl3	1091	96	–	96	–	354	204	74	76
TCl4	1106	111	–			357	207	74	76
TCl5	1147	112	56	112		354	202	73	79
TCl6	1163		57	72		352	201	72	79
TCl7	1178	87			87	350	203	71	76
TCl8	1208	102				355	208	72	75
MBr1	906	–	–	–		267	267		
MBr2	949	–	43	–		262	262		
MBr3	1006	100	–	100	–	269	269		
MBr4	1021	115	–			272	272		
MBr5	1065	116	59	116		272	272		
MBr6	1077		56	71		266	266		
MBr7	1094	88			88	266	266		
MBr8	1125	104				272	272		

DBr1	1068	–	–	–		429	267	162	
DBr2	1103	–	35	–		416	262	154	
DBr3	1169	101	–	101	–	432	269	163	
DBr4	1187	119	–			438	272	166	
DBr5	1221	118	52	118		428	272	156	
DBr6	1244		57	75		433	266	167	
DBr7	1262	93			93	434	266	168	
DBr8	1296	109				443	272	171	
TBr1	1259	–	–	–		620	267	162	191
TBr2	1297	–	38	–		610	262	154	194
TBr3	1366	107	–	107	–	629	269	163	197
TBr4	1387	128	–			638	272	166	200
TBr5	1428	131	62	131		635	272	156	207
TBr6	1446		59	80		635	266	167	202
TBr7	1458	92			92	630	266	168	196
TBr8	1492	105				639	272	171	196

* Branched-chain alcohols (1–8), the corresponding alkyl esters of acetic acid (A1–A8), monochloroacetic acid (MCl1–MCl8), dichloroacetic acid (DCl1–DCl8), trichloroacetic acid (TCl1–TCl8), monobromoacetic acid (MBr1–MBr8), dibromoacetic acid (DBr1–DBr8) and tribromoacetic acid (TBr1–TBr8). Compounds listed in Table I.

** Obtained from the series 1→ 3 → 7, 1 → 4 → 8 and 2 → 5.

*** Obtained by replacement of α-hydrogen atom (1 → 2, 3 → 5 and 4 → 6), β-hydrogen atom (1 → 3, 2 → 5 and 3 → 6) and γ-hydrogen atom (3 → 7) by a methyl group in eight homologous series.

§ $\Sigma\Delta I_x = I(M_x) - I(A_x); I(D_x) - I(A_x); I(T_x) - I(A_x)$.

§§ $\Delta I_{1x} = I(M_x) - I(A_x); \Delta I_{2x} = I(D_x) - I(M_x); \Delta I_{3x} = I(T_x) - I(D_x)$.

TABLE VI

RETENTION INDICES OF THE COMPOUNDS STUDIED AND INCREMENTS OF RETENTION INDICES FOR METHYLENE UNITS AND HALOGEN SUBSTITUENTS ON OV-351

Conditions as shown in Figs. 2 and 4.

*Compound**	I	ΔI_{CH_2}**	$\Delta I_{\alpha\text{-}CH_2}$***	$\Delta I_{\beta\text{-}CH_2}$***	$\Delta I_{\gamma\text{-}CH_2}$***	$\Sigma\Delta I_x$§	ΔI_{1x}§§	ΔI_{2x}§§	ΔI_{3x}§§	$\frac{I_{OV\text{-}351}}{I_{SE\text{-}30}}$§§§	$I_{OV\text{-}351} - I_{SE\text{-}30}$§§§
1	909	–	–	–						1.77	394
2	880	–	−29	–						1.62	337
3	1015	106	–	106	–					1.71	421
4	1079	170	–							1.76	465
5	1003	123	−12	123						1.60	378
6	1079		0	64						1.63	416
7	1109	94			94					1.63	427
8	1194	115								1.67	478
A1	878	–	–	–						1.37	239
A2	878	–	0	–						1.28	191
A3	974	96	–	96	–					1.32	237
A4	1009	131	–							1.35	260
A5	1003	125	29	125						1.26	210
A6	1036		27	62						1.28	225
A7	1068	94			94					1.29	240
A8	1117	108								1.31	264
MCl1	1280	–	–	–		402	402			1.51	435
MCl2	1280	–	0	–		402	402			1.44	389
MCl3	1362	82	–	82	–	388	388			1.45	421
MCl4	1392	112	–			383	383			1.46	436
MCl5	1382	102	20	102		379	379			1.39	387
MCl6	1414		22	52		378	378			1.40	402
MCl7	1443	81			81	375	375			1.40	412
MCl8	1504	112				387	387			1.42	443

DCl1	1345	–	–	–		467	402	65		1.47	427
DCl2	1339	–	−6	–		461	402	59		1.39	379
DCl3	1427	82	–	82	–	453	388	65		1.41	412
DCl4	1458	113	–			449	383	66		1.42	428
DCl5	1446	107	19	107		443	379	64		1.35	378
DCl6	1476		18	49		440	378	62		1.36	392
DCl7	1504	77			77	436	375	61		1.36	402
DCl8	1567	109				450	387	63		1.38	434
TCl1	1312	–	–	–		434	402	65	−33	1.32	317
TCl2	1315	–	3	–		437	402	59	−24	1.27	280
TCl3	1395	83	–	83	–	421	388	65	−32	1.28	304
TCl4	1425	113	–			416	383	66	−33	1.29	319
TCl5	1417	102	22	102		414	379	64	−29	1.24	270
TCl6	1446		21	51		410	378	62	−30	1.24	283
TCl7	1469	74			74	401	375	61	−35	1.25	291
TCl8	1532	107				415	387	63	−35	1.27	324
MBr1	1365	–	–	–		487	487			1.51	459
MBr2	1359	–	−6	–		481	481			1.43	410
MBr3	1454	89	–	89	–	480	480			1.45	448
MBr4	1488	123	–			479	479			1.46	467
MBr5	1472	113	18	113		469	469			1.38	407
MBr6	1510		22	56		474	474			1.40	433
MBr7	1538	84			84	470	470			1.41	444
MBr8	1595	107				478	478			1.42	470
DBr1	1574	–	–	–		696	487	209		1.47	506
DBr2	1564	–	−10	–		686	481	205		1.42	461
DBr3	1663	89	–	89	–	689	480	209		1.42	494
DBr4	1701	127	–			692	479	213		1.43	514
DBr5	1680	116	17	116		677	469	208		1.38	459
DBr6	1717		16	54		681	474	207		1.38	473
DBr7	1742	79			79	674	470	204		1.38	480
DBr8	1807	106				690	478	212		1.39	511

*,**,***,§,§§ As in Table V.

§§§ For retention indices on SE-30, see Table V.

TABLE VII

SUMMARY OF RETENTION INCREMENTS OF METHYLENE UNITS AND HALOGEN SUBSTITUENTS WITH THE ESTERS ON SE-30 AND OV-351

Conditions as shown in Figs. 1–4.

*Increment**	*Column*	
	SE-30	*OV-351*
ΔI_{CH_2}	87–131	74–131
$\Delta I_{\alpha\text{-}CH_2}$	35–62	−29 to 29
$\Delta I_{\beta\text{-}CH_2}$	69–131	49–125
$\Delta I_{\gamma\text{-}CH_2}$	87–93	74–94
$\Delta I_{\text{mono Cl}}$	201–208	375–402
$\Delta I_{\text{di Cl}}$	69–74	59–66
$\Delta I_{\text{tri Cl}}$	75–79	−24 to −35
$\Delta I_{\text{mono Br}}$	262–272	469–487
$\Delta I_{\text{di Br}}$	154–171	204–213
$\Delta I_{\text{tri Br}}$	191–207	–

* As in Tables V and VI.

a β-hydrogen atom in the 1, 2 and 3 series and a γ-hydrogen atom in the 3 series with a methyl group is shown in Tables V–VII. Owing to the increase in molecular weight, an enhanced retention is always observed on SE-30, as expected, the increments for the α-, β- and γ-substitution being in the ranges 35–62, 69–131 and 87–93 i.u., respectively. On OV-351, however, the additional methyl group in the α-position generally causes a reduction in the retention of the dimethylethyl series (Table VI), the increments varying between 3 and −10 i.u. The α-substitution in the 3 series (3 → 5) might be expected, based on earlier observations, to produce a smaller increase than α-substitution in the 4 series (4 → 6), but Table VI shows that nearly the same increases are observed, the values being in the ranges 17–29 and 16–27 i.u., respectively. Higher increments for the β- and γ-substitution were obtained, those in the 1,1-dimethylpropyl series (2 → 5) being the highest, 102–125 i.u.

The increases in the retention indices on SE-30 for the first, second and third chlorine atoms are 201–208, 69–74 and 75–79 i.u., respectively, the corresponding increases with the mono-, di- and tribromo isomers, owing to the increased size of the halogen substituent(s), being considerable higher, *i.e.*, 262–272, 154–171 and 191–207 i.u. (Table VII). The increased retention of the monochloro esters is greater on OV-351 than on SE-30, *i.e.*, 375–402 i.u., owing to the increased polarity of the stationary phase. The second chlorine atom causes a negligible reduction in retention compared with that on SE-30, whereas a significant reduction occurred with the third chlorine substituent (−24 to −35 i.u.), leading to a reversed order of elution of the di- and trichloro isomers. With the brominated esters, the increases on a polar column for the first and second halogen atoms are 469–487 and 204–213 i.u., both greater than those on SE-30 (Table VII).

The retention index ratios on the two columns are given in Table VI. The highest values are observed for the methylethyl esters, although the variation is small. The enhanced retention of the various isomers, due to polar interactions, *i.e.*, $I_{\text{OV-351}} - I_{\text{SE-30}}$ (Table VI), is highest with the 3-methylbutyl and 2-methylpropyl series and

decreases, as expected, with increasing α-methyl substitution, being lowest with the dimethylethyl and 1,1-dimethylpropyl series.

The effects of chain branching[1,12,13] and the various halogen substituents[2,14] in the homologous series of esters on both polar and non-polar stationary phases have previously been extensively studied, and it is evident that similar results and trends are also apparent with the halogenated branched-chain esters investigated in this work.

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