Journal of Chromatography, 288 (1984) 329–346
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 16,565

GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XXVI*. SEPARATION OF UNSATURATED ALCOHOLS AND THEIR ACETYL AND HALOACETYL DERIVATIVES ON CAPILLARY COLUMNS COATED WITH SE-30 AND OV-351

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(Received January 6th, 1984)

SUMMARY

The gas chromatographic retention behaviour of seven unsaturated alcohols and the corresponding esters of acetic, mono-, di- and trichloroacetic and mono-, di- and tribromoacetic acids on a low-polarity (SE-30) and a highly polar (OV-351) capillary column with temperature programming is reported. The relative retention data and the retention indices, with the retention index increments due to the methylene unit and the various halogen substituents, were determined. The retention order of the individual components in the mixtures is discussed, together with the influence of unsaturation and boiling point. The results are compared with those of earlier studies.

INTRODUCTION

The gas chromatography (GC) of unsaturated esters, particularly with unsaturation in the acyl chain, has been extensively studied with a wide range of non-polar and polar stationary phases[1,2], the effect of the position of unsaturation, chain branching and boiling point having been considered. However, few papers have appeared on the systematic GC of halogenated unsaturated esters, *i.e.*, methyl esters of chlorinated propenoic[3,4] and 2-butenoic[5] acids and C_3–C_6 unsaturated esters of monochlorinated propanoic and butanoic acids[6].

This paper extends the earlier studies[6,7] by showing the retention behaviour of seven C_3–C_6 unsaturated alcohols and their acetyl and haloacetyl derivatives, containing one to three chlorine or bromine atoms. Analyses were carried out on SE-30 and OV-351 quartz capillary columns with temperature programming. The retentions relative to the alcohols, non-halogenated esters, *n*-tetradecane and the compounds on SE-30 are given and the elution order of the 56 individual components is discussed. The Kováts retention indices and the retention index increments were

* For Part XXV, see ref. 7.

0021-9673/84/$03.00

determined and the effect of unsaturation and boiling point for the alcohols and the acetate esters is discussed. The results are compared with those of earlier observations[1,6].

EXPERIMENTAL

Materials and methods

The unsaturated alcohols (1–7) listed in Table I were commercial products[6]. The corresponding esters of acetic acid (8–14 = A1–A7), monochloroacetic acid (15–21 = MCl1–MCl7), dichloroacetic acid (22–28 = DCl1–DCl7), trichloroacetic acid (29–35 = TCl1–TCl7), monobromoacetic acid (36–42 = MBr1–MBr7), dibromoacetic acid (43–49 = DBr1–DBr7) and tribromoacetic acid (50–56 = TBr1–TBr7) were prepared from the corresponding alcohols and acid chlorides[7] as described earlier[8].

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

GC was carried out on a Perkin-Elmer Sigma 3 instrument on SE-30 and OV-351 quartz capillary columns under the operating conditions reported previously[7,9], the retention data and the Kováts retention indices being determined as described earlier[7].

RESULTS AND DISCUSSION

Figs. 1–4 show the chromatograms of two mixtures, one containing unsaturated alcohols and their acetyl and chloroacetyl derivatives and the other alcohols with their acetyl and bromoacetyl derivatives, separated on SE-30 and OV-351. The relative retention data of the compounds are presented in Table I, and the plots of the retention are shown in Figs. 5 and 6.

As is evident in Figs. 1 and 3, only one complete overlapping occurred on a non-polar column, *viz.*, *trans*-3-hexenyl acetate (13 = A6) with 3-butenyl monochloroacetate (17 = MCl3), together with some partially resolved peaks.

The highly polar OV-351 column gave very poor resolution for the components in the mixture of the chlorinated esters (Fig. 2), giving four complete overlappings, *viz.*, 17 = MCl3 with 22 = DCl1, 31 = TCl3 with 25 = DCl4, 20 = MCl6 with 30 = TCl2 and 23 = DCl2 with 34 = TCl6. All fourteen brominated esters (36–49 = MBr1–MBr7 and DBr1–DBr7) analysed are, however, also resolvable on a polar column (Fig. 4).

It has been shown previously[12] that the retention behaviour of saturated esters on a non-polar stationary phase is closely related to the boiling points of the compounds and that with unsaturation a reduction in retention occurs, the reduction being accentuated in the presence of conjugation[13,14]. On a polar column, however, increased retention with an unsaturated ester of similar boiling point relative to the saturated ester is observed[14]. These trends are evident in Table II, where the effects of unsaturation and boiling point for alcohols and acetate esters on both columns are shown.

As shown previously[6], the alcohols are generally eluted on SE-30 in order of their boiling points, the only exceptions being 2-propyn-1-ol (2) and 4-penten-1-ol

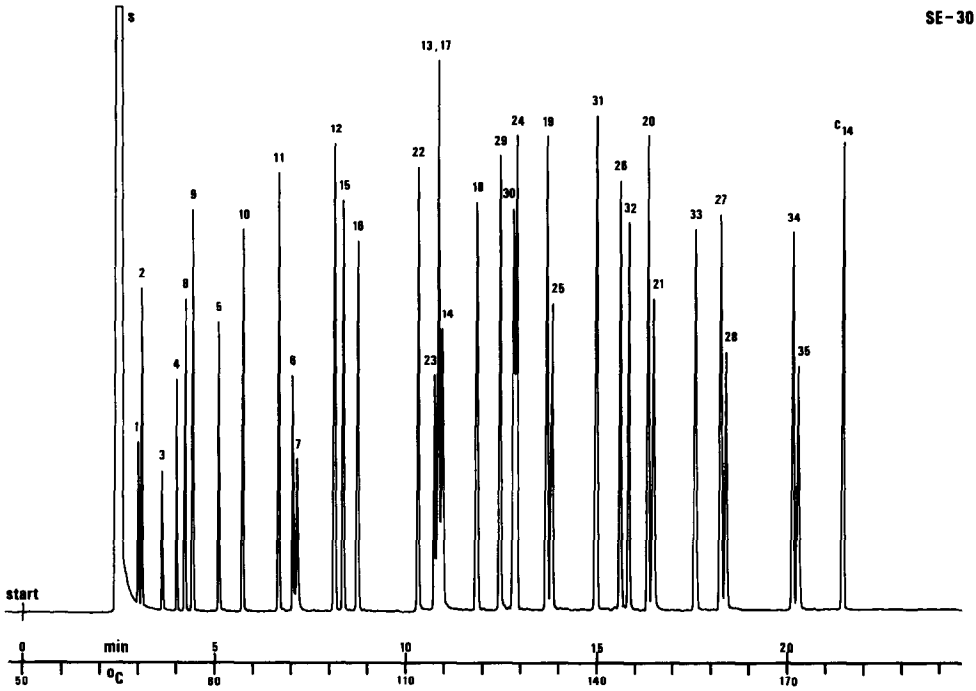

Fig. 1. Chromatogram of a mixture of unsaturated alcohols (1–7) and the corresponding esters of acetic acid (8–14 = A1–A7) and chlorinated acetic acids (15–35, *i.e.*, MCl1–MCl7, DCl1–DCl7 and TCl1–TCl7), operated on an SE-30 quartz capillary column from 50°C at 6°C min^{-1}. S = Solvent; C_{14} = *n*-tetradecane. Peaks identified in Table I.

(5). The reduction in the retention index due to the presence of the double bond is in the range 29–43 index units (i.u.). 2-Propen-1-ol (1) shows a decrease of 29 i.u., in spite of its similar boiling point to 1-propanol. The greatest reduction, 43 i.u., for 4-penten-2-ol (4) is due to the greatest deviation of the boiling points (−5.4°C). With 2, which has a boiling point over 16°C higher than that of 1-propanol, an increased retention might be expected. However, a decrease of 15 i.u. is found, and an increase of only 14 i.u. with respect to 2-propen-1-ol (1).

A completely different retention order for the alcohols on OV-351 is observed[6], the increased retention due to the double bond being in the range 11–80 i.u. The lowest increase was detected for the branched-chain alcohol 4, whereas 1 showed the greatest increase. On the polar column the elution order is greatly influenced by the structures of the compounds given in Table III. This is clearly evident with 2-propyn-1-ol (2), showing an enhancement of 303 i.u. with respect to 1-propanol and 223 i.u. with respect to 2-propen-1-ol (1). The difference between the retention indices of 2 and 3-buten-1-ol (3) is 171 i.u., in spite of their similar boiling points (Table II).

The elution order of the acetate esters on SE-30 follows that of the corresponding alcohols, the reduction due to unsaturation being in the range 21–42 i.u. In contrast to the alcohols, the boiling points of the unsaturated acetate esters are higher than those of their saturated homologues (Table II), which might be expected to show a smaller reduction in retention than the unsaturated alcohols. With the esters

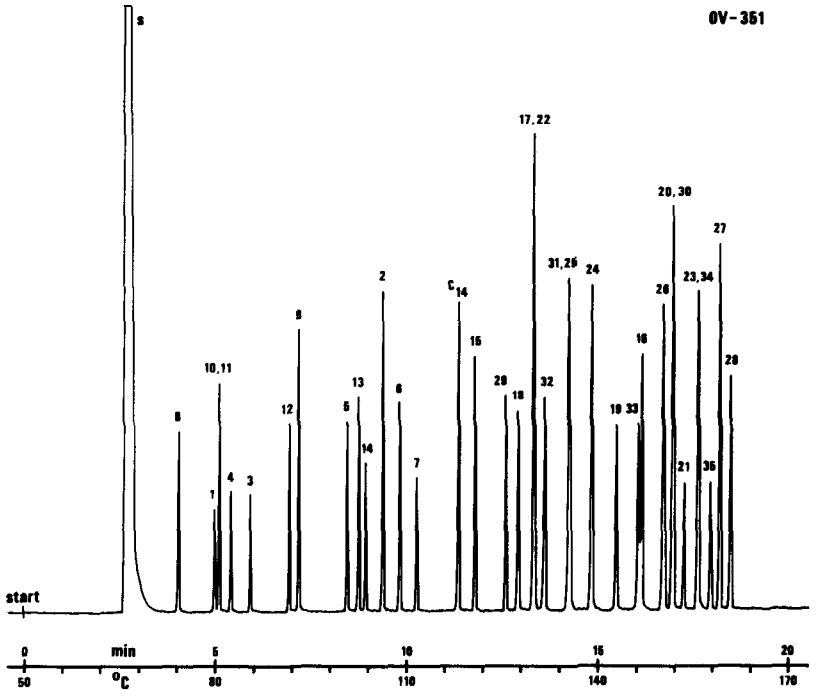

Fig. 2. Chromatogram of the same mixture as in Fig. 1, separated on an OV-351 quartz capillary column.

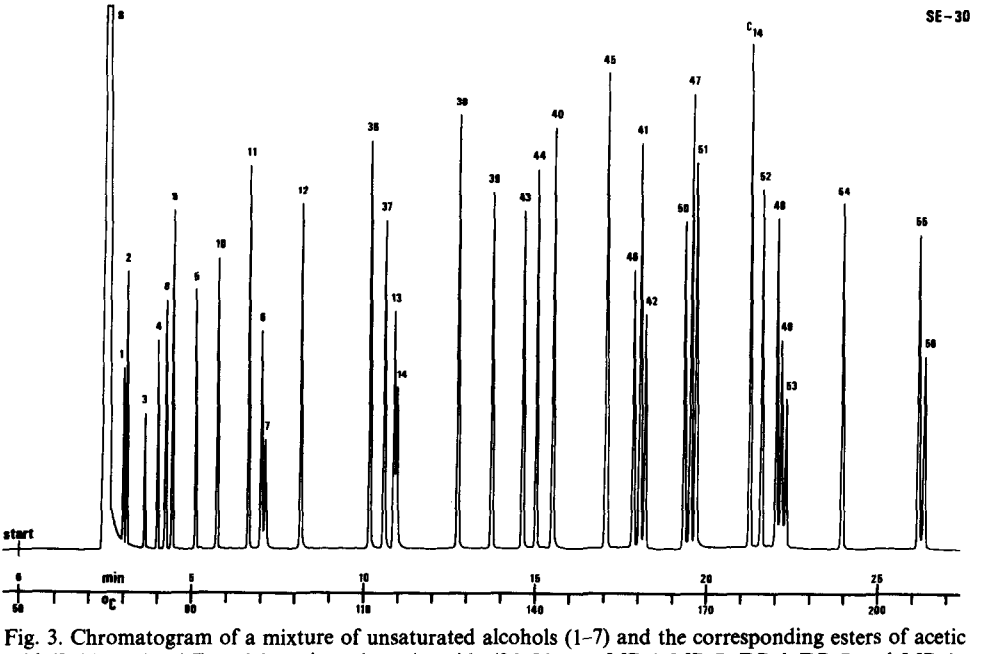

Fig. 3. Chromatogram of a mixture of unsaturated alcohols (1–7) and the corresponding esters of acetic acid (8–14 = A1–A7) and brominated acetic acids (36–56, *i.e.*, MBr1–MBr7, DBr1–DBr7 and MBr1–MBr7), operated on SE-30 from 50°C at 6°C min^{-1}. S = Solvent; C_{14} = *n*-tetradecane. Peaks identified in Table I.

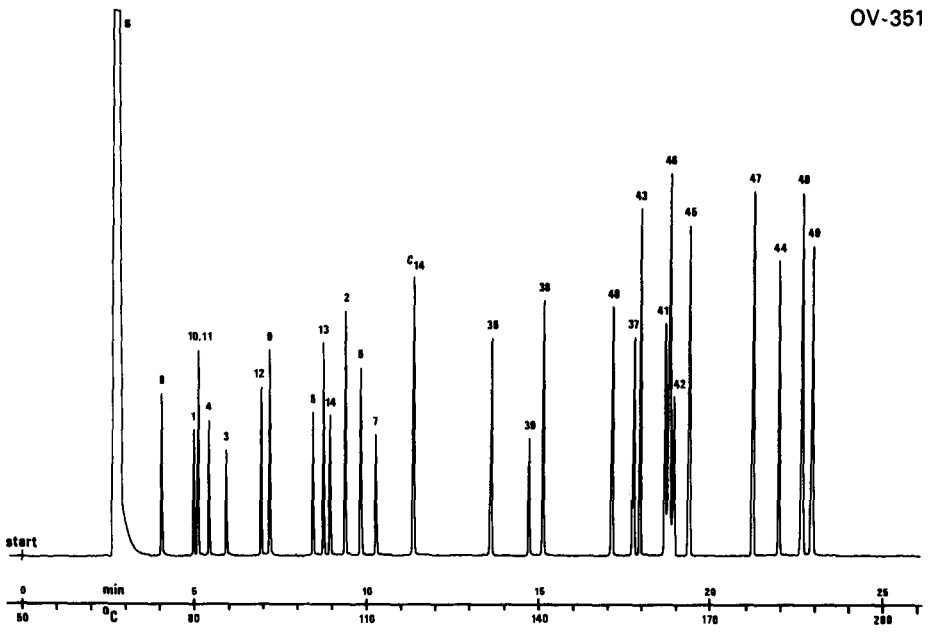

Fig. 4. Chromatogram of the same mixture as in Fig. 3, except for the tribromo isomers (50–56 = TBr1–TBr7), separated on OV-351.

8–10 and 12 (A1–A3 and A5), however, a larger reduction is detected.

n-Butyl and 1-methylbutyl acetates and 2-propynyl (9 = A2) and *n*-hexyl acetates are eluted on OV-351 in the opposite order to the corresponding alcohols. 3-Butenyl (10 = A3) and 1-methyl-3-butenyl (11 = A4) esters overlap, the alcohols (4 and 3) being separated (Figs. 2 and 4). As reported previously[6], the corresponding higher, *i.e.*, propanoate and butanoate, esters are separated, 1-methyl-3-butenyl esters being eluted first. The enhancement due to unsaturation is in the range 35–258 i.u., being lower for the esters 8 = A1, 9 = A2 and 12 = A5 than for the corresponding alcohols 1, 2 and 5.

The previous work of Allen and Haken[14] shows that with vinyl and ethyl esters a reduced retention is experienced with unsaturated esters on both non-polar and polar stationary phases (SE-30, OV-17, OV-25 and XE-60). An expected enhanced retention, with increasing polarity of the phase, was not observed and the reduction was little affected by the four stationary phases used. With the allyl (2-propenyl) esters, however, reduced retentions (−30 i.u.) on SE-30 and increased retentions (3–25 i.u.) on the more polar phases occurred[14], the results being in good agreement with those of 2-propenyl acetate (8 = A1) given in Table II.

Previously, the retention behaviour of, *e.g.*, *trans*- and *cis*-3-hexenyl esters of lower (C_1–C_6) *n*-alkanoic acids on packed columns with several stationary phases was studied isothermally by Ashes and Haken[1], the effects of unsaturation and isomerism being considered. The retention indices reported for the *trans*- and *cis*-acetate esters[1] (13 and 14, *i.e.*, A6 and A7) and for *n*-hexyl acetate[15] on SE-30 are 975, 978 and 988 i.u., respectively, giving deviations of −13 and −10 i.u. The corresponding retention indices on OV-225 are 1235, 1247 and 1229 (6 and 18) i.u., and on Silar

TABLE I

RETENTION DATA FOR UNSATURATED ALCOHOLS AND THE CORRESPONDING ALKYL ESTERS OF ACETIC ACID AND HALOGENATED ACETIC ACIDS, ANALYSED ON SE-30 AND OV-351

Conditions as in Figs. 1–4.

Peak No.	*Compound*		*Column*								
			SE-30				*OV-351*				
			*ART***	*RRT****	*RRT*****	*RRT*\$*	*ART***	*RRT****	*RRT*****	*RRT*\$*	*RRT*\$\$*
1	1	2-Propen-1-ol	2.94	0.14	1.00	0.69	5.01	0.44	1.00	1.24	1.70
2	2	2-Propyn-1-ol	3.06	0.14	1.00	0.69	9.41	0.83	1.00	1.31	3.08
3	3	3-Buten-1-ol	3.62	0.17	1.00	0.63	5.95	0.52	1.00	1.16	1.64
4	4	4-Penten-2-ol	4.00	0.19	1.00	0.60	5.42	0.48	1.00	1.06	1.36
5	5	4-Penten-1-ol	5.10	0.24	1.00	0.63	8.48	0.74	1.00	1.21	1.66
6	6	*trans*-3-Hexen-1-ol	7.04	0.33	1.00	0.65	9.85	0.86	1.00	1.12	1.40
7	7	*cis*-3-Hexen-1-ol	7.13	0.33	1.00	0.65	10.29	0.90	1.00	1.15	1.44
8	A1	2-Propenyl acetate	4.24	0.20	1.44	1.00	4.05	0.36	0.81	1.00	0.96
9	A2	2-Propynyl acetate	4.42	0.21	1.44	1.00	7.21	0.63	0.77	1.00	1.63
10	A3	3-Butenyl acetate	5.76	0.27	1.59	1.00	5.11	0.45	0.86	1.00	0.89
11	A4	1-Methyl-3-butenyl acetate	6.68	0.31	1.67	1.00	5.11	0.45	0.94	1.00	0.76
12	A5	4-Pentenyl acetate	8.16	0.38	1.60	1.00	6.98	0.61	0.82	1.00	0.86
13	A6	*trans*-3-Hexenyl acetate	10.89	0.51	1.55	1.00	8.79	0.77	0.89	1.00	0.81
14	A7	*cis*-3-Hexenyl acetate	10.95	0.51	1.54	1.00	8.95	0.79	0.87	1.00	0.82
15	MCl1	2-Propenyl monochloroacetate	8.38	0.39	2.85	1.98	11.80	1.04	2.36	2.91	1.41
16	MCl2	2-Propynyl monochloroacetate	8.74	0.41	2.86	1.98	16.19	1.42	1.72	2.25	1.85
17	MCl3	3-Butenyl monochloroacetate	10.94	0.51	3.02	1.90	13.39	1.18	2.25	2.62	1.22
18	MCl4	1-Methyl-3-butenyl monochloroacetate	11.88	0.55	2.97	1.78	12.93	1.14	2.39	2.53	1.09
19	MCl5	4-Pentenyl monochloroacetate	13.70	0.64	2.69	1.68	15.51	1.36	1.83	2.22	1.13
20	MCl6	*trans*-3-Hexenyl monochloroacetate	16.36	0.76	2.32	1.50	17.02	1.49	1.73	1.94	1.04
21	MCl7	*cis*-3-Hexenyl monochloroacetate	16.50	0.77	2.31	1.51	17.30	1.52	1.68	1.93	1.05
22	DCl1	2-Propenyl dichloroacetate	10.32	0.48	3.51	2.43	13.39	1.18	2.67	3.31	1.30
23	DCl2	2-Propynyl dichloroacetate	10.75	0.50	3.51	2.43	17.68	1.55	1.88	2.45	1.64
24	DCl3	3-Butenyl dichloroacetate	12.90	0.60	3.56	2.24	14.89	1.31	2.50	2.91	1.15
25	DCl4	1-Methyl-3-butenyl dichloroacetate	13.83	0.64	3.46	2.07	14.29	1.25	2.64	2.80	1.03
26	DCl5	4-Pentenyl dichloroacetate	15.62	0.72	3.06	1.91	16.75	1.47	1.98	2.40	1.07

27	DCl6	*trans*-3-Hexenyl dichloroacetate	18.28	0.85	2.60	1.68	18.26	1.60	1.85	2.08	1.00
28	DCl7	*cis*-3-Hexenyl dichloroacetate	18.40	0.85	2.58	1.68	18.51	1.63	1.80	2.07	1.01
29	TCl1	2-Propenyl trichloroacetate	12.49	0.58	4.25	2.95	12.61	1.11	2.52	3.11	1.01
30	TCl2	2-Propynyl trichloroacetate	12.82	0.59	4.19	2.90	17.02	1.49	1.81	2.36	1.33
31	TCl3	3-Butenyl trichloroacetate	15.01	0.70	4.15	2.61	14.26	1.25	2.40	2.79	0.95
32	TCl4	1-Methyl-3-butenyl trichloroacetate	15.86	0.74	3.97	2.37	13.63	1.20	2.51	2.67	0.86
33	TCl5	4-Pentenyl trichloroacetate	17.61	0.82	3.45	2.16	16.09	1.41	1.90	2.31	0.91
34	TCl6	*trans*-3-Hexenyl trichloroacetate	20.17	0.94	2.87	1.85	17.70	1.55	1.80	2.01	0.88
35	TCl7	*cis*-3-Hexenyl trichloroacetate	20.29	0.94	2.85	1.85	17.99	1.58	1.75	2.01	0.89
36	MBr1	2-Propenyl monobromoacetate	10.26	0.48	3.49	2.42	13.70	1.20	2.73	3.38	1.34
37	MBr2	2-Propynyl monobromoacetate	10.66	0.49	3.48	2.41	17.89	1.57	1.90	2.48	1.68
38	MBr3	3-Butenyl monobromoacetate	12.84	0.60	3.55	2.23	15.29	1.34	2.57	2.99	1.19
39	MBr4	1-Methyl-3-butenyl monobromoacetate	13.81	0.64	3.45	2.07	14.85	1.30	2.74	2.91	1.08
40	MBr5	4-Pentenyl monobromoacetate	15.60	0.72	3.06	1.91	17.29	1.52	2.04	2.48	1.11
41	MBr6	*trans*-3-Hexenyl monobromoacetate	18.15	0.84	2.58	1.67	18.80	1.65	1.91	2.14	1.04
42	MBr7	*cis*-3-Hexenyl monobromoacetate	18.26	0.85	2.56	1.67	19.07	1.67	1.85	2.13	1.04
43	DBr1	2-Propenyl dibromoacetate	14.80	0.69	5.03	3.49	18.09	1.59	3.61	4.47	1.22
44	DBr2	2-Propynyl dibromoacetate	15.19	0.70	4.96	3.44	22.09	1.94	2.35	3.06	1.45
45	DBr3	3-Butenyl dibromoacetate	17.18	0.80	4.75	2.98	19.50	1.71	3.28	3.82	1.14
46	DBr4	1-Methyl-3-butenyl dibromoacetate	17.92	0.83	4.48	2.68	18.90	1.66	3.49	3.70	1.05
47	DBr5	4-Pentenyl dibromoacetate	19.74	0.92	3.87	2.42	21.38	1.88	2.52	3.06	1.08
48	DBr6	*trans*-3-Hexenyl dibromoacetate	22.20	1.03	3.15	2.04	22.79	2.00	2.31	2.59	1.03
49	DBr7	*cis*-3-Hexenyl dibromoacetate	22.32	1.04	3.13	2.04	23.09	2.03	2.24	2.58	1.03
50	TBr1	2-Propenyl tribromoacetate	19.51	0.90	6.64	4.60					
51	TBr2	2-Propynyl tribromoacetate	19.82	0.92	6.48	4.48					
52	TBr3	3-Butenyl tribromoacetate	21.70	1.01	5.99	3.77					
53	TBr4	1-Methyl-3-butenyl tribromoacetate	22.38	1.04	5.60	3.35					
54	TBr5	4-Pentenyl tribromoacetate	24.06	1.12	4.72	2.95					
55	TBr6	*trans*-3-Hexenyl tribromoacetate	26.30	1.22	3.74	2.42					
56	TBr7	*cis*-3-Hexenyl tribromoacetate	26.43	1.23	3.71	2.41					
C_{14}		*n*-Tetradecane	21.56	1.00	–	–	11.39	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 (1–7) taken as 1.00.
§ Relative retention time for the corresponding compound on SE-30 taken as 1.00.
§§ Relative retention time for the corresponding acetate ester (8–14 = A1–A7) taken as 1.00.

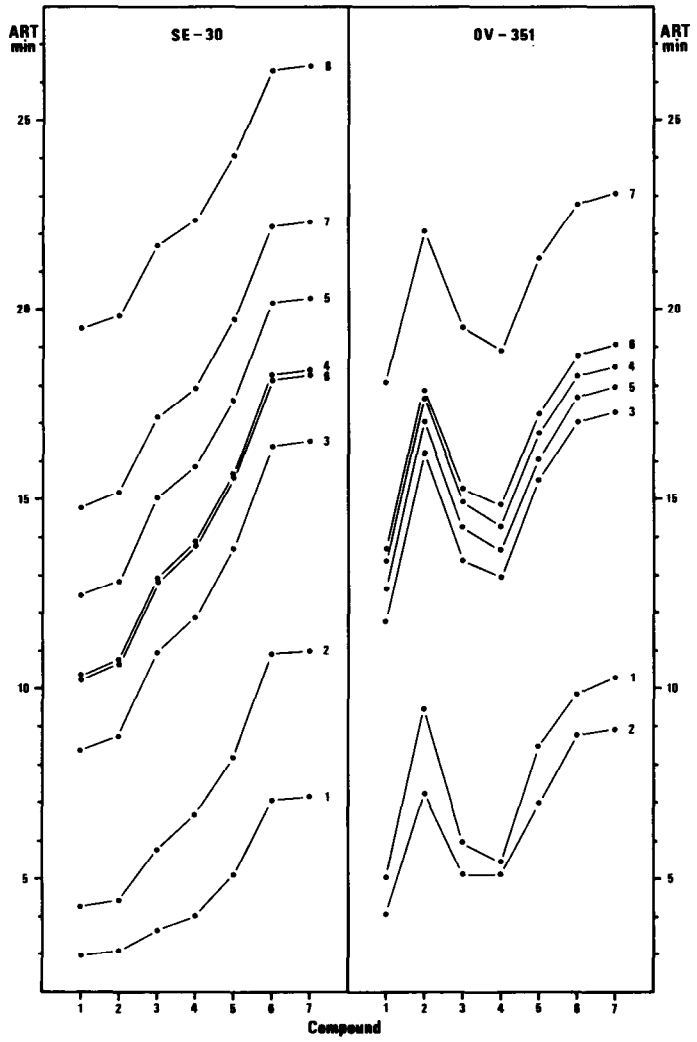

Fig. 5. Plots showing the retentions of unsaturated alcohols (1–7, curve 1) and the corresponding esters of acetic acid (8–14 = A1–A7, curve 2), monochloroacetic acid (15–21 = MCl1–MCl7, curve 3), dichloroacetic acid (22–28 = DCl1–DCl7, curve 4), trichloroacetic acid (29–35 = TCl1–TCl7, curve 5), monobromoacetic acid (36–42 = MBr1–MBr7, curve 6), dibromoacetic acid (43–49 = DBr1–DBr7, curve 7) and tribromoacetic acid (50–56 = TBr1–TBr7, curve 8), analysed on SE-30 and OV-351. ART = Absolute retention time (min), measured from sample injection (Figs. 1–4 and Table I).

5CP, now available as APOLAR 5CP[1] 1313, 1330 and 1303 (10 and 27) i.u., the deviations being given in parentheses. Table II shows that the values obtained on an SE-30 capillary column with temperature programming are in accord with the earlier results[1,15]. The retention indices on OV-351 are between those on OV-225 and APOLAR 5CP. The disparities found are obviously due to the intermediate polarity of OV-351 with respect to the other phases, the retention index generally increasing with increasing column polarity. The deviations are greater on capillary columns (Table

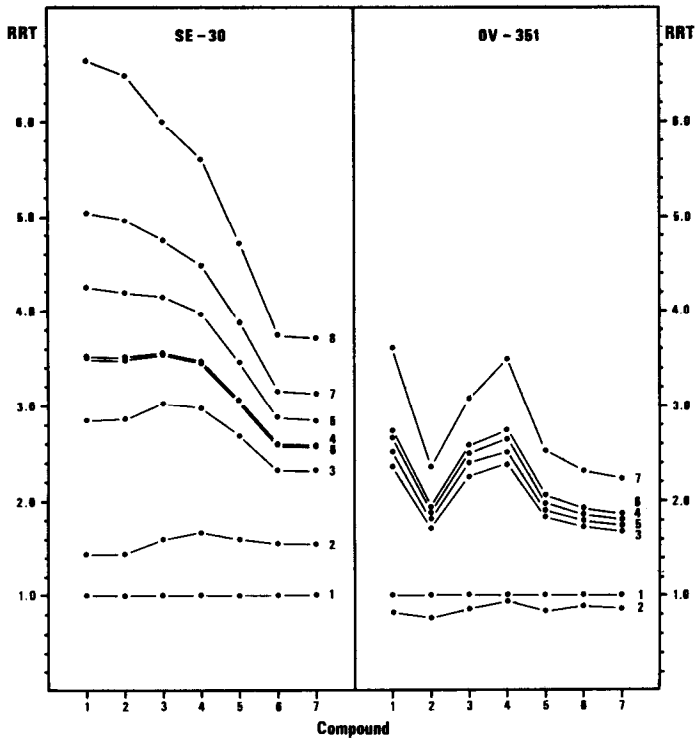

Fig. 6. Plots showing retentions of the eight series as in Fig. 5 (curves 1–8). Relative retention time (RRT) for the unsaturated alcohols (1–7) taken as 1.00 (Table I).

II), but as previously shown[1], the magnitude of the deviations is not greatest for the most polar phase, as would be expected, but for the phase containing donor phenyl substituent groups, *i.e.*, for 100% phenyl.

Figs. 1 and 3 show that on SE-30 four alcohols (1–4) are eluted earlier than the first eluted acetate ester, *i.e.*, 2-propenyl acetate (8 = A1), although alcohol 4 has a boiling point about 13°C higher than that of 8. The increased retention of the esters on a non-polar column is evident in Figs. 5 and 6 and in Table II, the enhancements being in the range 126–160 i.u. A polar column (Figs. 2 and 4–6), however, shows a reduction from 17 to 105 i.u. in the retention of the esters (Table II), the effect being smallest with the branched-chain ester (11 = A4).

The retention indices of the eight homologous series studied, with the increments of the retention indices due to methylene units and halogen substituents, are presented in Tables IV and V, determined on SE-30 and OV-351, respectively.

The retention order of the halogenated esters on a non-polar column follows that of the non-halogenated acetate esters (Table IV). The isomers are eluted in the order monochloro < monobromo < dichloro < trichloro < dibromo < tribromo (Figs. 5 and 6), as expected, based on earlier work[7]. The unsaturated monobromo and dichloro isomers are, however, eluted closer together than the branched-chain esters[7].

The 1-methyl-3-butenyl (series 4) and 3-butenyl (series 3) esters of the halo-

TABLE II

EFFECT OF UNSATURATION AND BOILING POINT OF ALCOHOLS AND ACETATE ESTERS ON SE-30 AND OV-351

Peak No.	*Compound*	*Boiling point (°C/mmHg)**	*Column*					
			SE-30			*OV-351*		
			*I***	*ΔI****	*ΔI*§	*I***	*ΔI****	*ΔI*§
1	1 2-Propen-1-ol	97.16	532	−29		1097	80	
2	2 2-Propyn-1-ol	113.6	546	−15		1320	303	
	1-Propanol	97.15	561			1017		
3	3 3-Buten-1-ol	113.5	609	−37		1149	30	
	1-Butanol	117.25	646			1119		
4	4 4-Penten-2-ol	114.5	639	−43		1120	11	
	2-Pentanol	119.85	682			1109		
5	5 4-Penten-1-ol	139	717	−29		1276	60	
	1-Pentanol	137.9	746			1216		
6	6 *trans*-3-Hexen-1-ol	152–153.5	814	−34		1340	22	
7	7 *cis*-3-Hexen-1-ol	154–155	818	−30		1359	41	
	1-Hexanol	157.85	848			1318		
8	A1 2-Propenyl acetate	102–103	658	−37	126	1014	57	−83
9	A2 2-Propynyl acetate	122.4–123.6	672	−23	126	1215	258	−105
	n-Propyl acetate	101.6	695		134	957		−60
10	A3 3-Butenyl acetate	125–128	751	−42	142	1103	46	−46
	n-Butyl acetate	126.5	793		147	1057		−62
11	A4 1-Methyl-3-butenyl acetate	138	799	−29	160	1103	35	−17
	1-Methylbutyl acetate	133.5	828		146	1068		−41
12	A5 4-Pentenyl acetate	46–47/12	861	−31	144	1204	52	−72
	n-Pentyl acetate	149.3	892		146	1152		−64
13	A6 *trans*-3-Hexenyl acetate	61/12	967	−23	153	1291	43	−49
14	A7 *cis*-3-Hexenyl acetate	66/16	969	−21	151	1299	51	−60
	n-Hexyl acetate	171.5	990		142	1248		−70

* From refs. 10 and 11. Pressure 760 mmHg unless indicated otherwise.

** Values for *n*-alcohols and *n*-alkyl acetates are determined based on the data given in ref. 9, whereas values for 2-pentanol and 1-methylbutyl acetate are taken from ref. 7.

*** Deviation due to the unsaturation, *i.e.*, $I_{\text{Unsaturated compound}} - I_{\text{Saturated compound}}$.

§ $\Delta I = I_{\text{Ester}} - I_{\text{Alcohol}}$.

genated acetic acids are resolvable on OV-351, their elution order corresponding to that obtained for the alcohols. The acetate esters 10 = A3 and 11 = A4 are coincident, however. The retention order obtained is monochloro < trichloro < dichloro < monobromo < dibromo (Figs. 5 and 6), the tribromo isomers showing no peaks on a polar column[7,9].

Series 1, 3 and 5 (Table III) permit consideration of the retention index increase for the methylene unit. As shown, on SE-30 (Table IV) the increments for the alcohols 3 and 5 are 77 and 108 i.u., respectively, and for 3-butenyl (series 3) and 4-pentenyl

TABLE III

STRUCTURES OF THE COMPOUNDS STUDIED

A: $R_1 = R_2 = R_3 = H$. MCl: $R_1 = R_2 = H$, $R_3 = Cl$. DCl: $R_1 = H$, $R_2 = R_3 = Cl$. TCl: $R_1 = R_2 = R_3 = Cl$. MBr: $R_1 = R_2 = H$, $R_3 = Br$. DBr: $R_1 = H$, $R_2 = R_3 = Br$. TBr: $R_1 = R_2 = R_3 = Br$.

Alcohol (R = H)	*Structure*	*Ester ($R = CR_1R_2R_3CO$)*	*Series*
2-Propen-1-ol (1)	$R-O-CH_2-CH=CH_2$	2-Propenyl	1
2-Propyn-1-ol (2)	$R-O-CH_2-C\equiv CH$	2-Propynyl	2
3-Buten-1-ol (3)	$R-O-CH_2-CH_2-CH=CH_2$	3-Butenyl	3
4-Penten-2-ol (4)	$R-O-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH=CH_2$	1-Methyl-3-butenyl	4
4-Penten-1-ol (5)	$R-O-CH_2-CH_2-CH_2-CH=CH_2$	4-Pentenyl	5
trans-3-Hexen-1-ol (6)	$R-O-CH_2-CH_2$, H, CH_2-CH_3, H	*trans*-3-Hexenyl	6
cis-3-Hexen-1-ol (7)	$R-O-CH_2-CH_2$, H, H, CH_2-CH_3	*cis*-3-Hexenyl	7

(series 5) esters in the ranges 93–99 and 103–110 i.u., respectively. On OV-351 (Table V) the corresponding increases are 52 for 3, 127 for 5, 72–89 for 3-butenyl esters and 91–110 i.u. for 4-pentenyl esters, the increments being considerably lower for the halogenated 3-butenyl esters than on SE-30.

By replacing the α-hydrogen atom in the 3 series with a methyl group, an enhancement of 31–36 i.u. on SE-30 and a reduction of 21–34 i.u. on OV-351 in the retention of the halogenated esters in the 4 series are observed. On SE-30 enhancements of 30 and 36 i.u. are observed for 4-penten-2-ol (4) and for the corresponding saturated alcohol, *i.e.*, 2-pentanol, respectively, the latter being determined based on the data given in Table II with respect to 1-butanol. On OV-351 the corresponding values are −29 and −10 i.u. (Tables V and II). SE-30 shows enhanced retentions of 48 i.u. for 1-methyl-3-butenyl acetate (11 = A4) and 35 i.u. for the corresponding saturated ester, the values on OV-351 being 0 and 11 i.u., respectively.

TABLE IV

RETENTION INDICES OF UNSATURATED ALCOHOLS AND CORRESPONDING ESTERS OF ACETIC ACID AND HALOGENATED ACETIC ACIDS AND INCREMENTS OF RETENTION INDICES FOR METHYLENE UNITS AND HALOGEN SUBSTITUENTS ON SE-30

Conditions as in Figs. 1 and 3.

Peak No.	*Compound*	*I*	ΔI_{CH_2}*	$\Delta I_{\alpha\text{-}CH_2}$**	$\Sigma\Delta I_X$***	ΔI_{1X}§	ΔI_{2X}§	ΔI_{3X}§
1	1	532	–					
2	2	546						
3	3	609	77	–				
4	4	639		30				
5	5	717	108					
6	6	814						
7	7	818						
8	A1	658	–					
9	A2	672						
10	A3	751	93	–				
11	A4	799		48				
12	A5	861	110					
13	A6	967						
14	A7	969						
15	MCl1	870	–		212	212		
16	MCl2	885			213	213		
17	MCl3	969	99	–	218	218		
18	MCl4	1004		35	205	205		
19	MCl5	1072	103		211	211		
20	MCl6	1177			210	210		
21	MCl7	1182			213	213		
22	DCl1	946	–		288	212	76	
23	DCl2	962			290	213	77	
24	DCl3	1042	96	–	291	218	73	
25	DCl4	1077		35	278	205	73	
26	DCl5	1147	105		286	211	75	
27	DCl6	1256			289	210	79	
28	DCl7	1261			292	213	79	
29	TCl1	1027	–		369	212	76	81
30	TCl2	1039			367	213	77	77
31	TCl3	1122	95	–	371	218	73	80
32	TCl4	1157		35	358	205	73	80
33	TCl5	1228	106		367	211	75	81
34	TCl6	1337			370	210	79	81
35	TCl7	1342			373	213	79	81
36	MBr1	943	–		285	285		
37	MBr2	958			286	286		
38	MBr3	1040	97	–	289	289		
39	MBr4	1076		36	277	277		
40	MBr5	1146	106		285	285		
41	MBr6	1251			284	284		
42	MBr7	1255			286	286		

TABLE IV (*continued*)

Peak No.	*Compound*	*I*	ΔI_{CH_2}*	$\Delta I_{\alpha\text{-}CH_2}$**	$\Sigma\Delta I_X$***	ΔI_{1X}§	ΔI_{2X}§	ΔI_{3X}§
43	DBr1	1114	–		456	285	171	
44	DBr2	1130			458	286	172	
45	DBr3	1210	96	–	459	289	170	
46	DBr4	1241		31	442	277	165	
47	DBr5	1318	108		457	285	172	
48	DBr6	1427			460	284	176	
49	DBr7	1433			464	286	178	
50	TBr1	1308	–		650	285	171	194
51	TBr2	1322			650	286	172	192
52	TBr3	1405	97	–	654	289	170	195
53	TBr4	1436		31	637	277	165	195
54	TBr5	1513	108		652	285	172	195
55	TBr6	1623			656	284	176	196
56	TBr7	1629			660	286	178	196

* Series 1 → 3 → 5.

** Effect of replacement of the α-hydrogen atom in series 3 by a methyl group (3 → 4).

*** $\Sigma\Delta I_X = I(M_x) - I(A_x); I(D_x) - I(A_x); I(T_x) - I(A_x)$.

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

The enhancements of the retention indices on SE-30, with the values on OV-351 given in parentheses, for the halogen atoms are in the following ranges (Table VI): for the first, second and third chlorine atoms 205–218 (379–427), 73–79 (63–78) and 77–81 (−27 to −37) i.u., respectively, and for the first, second and third bromine atoms 277–289 (472–516), 165–178 (209–234) and 192–196 (−) i.u., respectively. The trends observed between the increments on the non-polar and polar columns are the same as previously reported for branched-chain esters of halogenated acetic acids[7]. Based on the one ester series pair, *i.e.*, 1-methyl-3-butenyl series (4) and 1-methylbutyl series[7], it seems evident that increments due to halogen substitution would be greater with the unsaturated esters, the deviations, however, being small, *i.e.*, from 2 to 11 i.u. on both columns.

Table V shows that the OV-351/SE-30 retention index ratio is maximal with 2-propyn-1-ol (2) and all its derivatives (series 2) and minimal with *trans*-3-hexen-1-ol (6) and its esters (series 6). The ratio of the absolute retention times, given in Table I, generally shows the same trends, the retention, however, being minimal with 4-penten-2-ol (4) and its esters (11 and 32, *i.e.*, A4 and TC14).

The difference between the retention indices, $I_{OV\text{-}351} - I_{SE\text{-}30}$, illustrated in Fig. 7 (Table V), decreases with the seven ester series in the order 2 > 1 > 3 > 5 > 7 > 6 > 4, the sequence with the alcohols being 2 > 1 > 5 > 7 > 3 > 6 > 4 (not included in Fig. 7). The values for series 2 are considerably higher owing to the terminal triple bond and the branched-chain compounds (series 4) show the lowest difference, as expected, owing to the α-methyl substituent, which has a greater effect on the retention on the polar than the non-polar column[7]. As shown, the disparity increases in the order acetate < trichloroacetate < dichloroacetate < monochlo-

TABLE V

RETENTION INDICES OF UNSATURATED ALCOHOLS AND CORRESPONDING ESTERS OF ACETIC ACID AND HALOGENATED ACETIC ACIDS AND INCREMENTS OF RETENTION INDICES FOR METHYLENE UNITS AND HALOGEN SUBSTITUENTS ON OV-351

Conditions as in Figs. 2 and 4.

Peak No.	*Compound*	*I*	ΔI_{CH_2}*	$\Delta I_{\alpha\text{-}CH_2}$**	$\Sigma\Delta I_X$***	ΔI_{1X}§	ΔI_{2X}§	ΔI_{3X}§	$\frac{I_{OV\text{-}351}}{I_{SE\text{-}30}}$§§	$I_{OV\text{-}351} - I_{SE\text{-}30}$§§
1	1	1097	–						2.06	565
2	2	1320							2.42	774
3	3	1149	52	–					1.89	540
4	4	1120		−29					1.75	481
5	5	1276	127						1.78	559
6	6	1340							1.65	526
7	7	1359							1.66	541
8	A1	1014	–						1.54	356
9	A2	1215							1.81	543
10	A3	1103	89	–					1.47	352
11	A4	1103		0					1.38	304
12	A5	1204	101						1.40	343
13	A6	1291							1.34	324
14	A7	1299							1.34	330
15	MCl1	1429	–		415	415			1.64	559
16	MCl2	1642			427	427			1.86	757
17	MCl3	1504	75	–	401	401			1.55	535
18	MCl4	1482		−22	379	379			1.48	478
19	MCl5	1607	103		403	403			1.50	535
20	MCl6	1686			395	395			1.43	509
21	MCl7	1701			402	402			1.44	519

22	DCl1	1504	–		490	415	75		1.59	558
23	DCl2	1720			505	427	78		1.79	758
24	DCl3	1576	72	–	473	401	72		1.51	534
25	DCl4	1548		−28	445	379	66		1.44	471
26	DCl5	1672	96		468	403	65		1.46	525
27	DCl6	1751			460	395	65		1.39	495
28	DCl7	1764			465	402	63		1.40	503
29	TCl1	1467	–		453	415	75	−37	1.43	440
30	TCl2	1686			471	427	78	−34	1.62	647
31	TCl3	1546	79	–	443	401	72	−30	1.38	424
32	TCl4	1516		−30	413	379	66	−32	1.31	359
33	TCl5	1637	91		433	403	65	−35	1.33	409
34	TCl6	1721			430	395	65	−30	1.29	384
35	TCl7	1737			438	402	63	−27	1.29	395
36	MBr1	1519	–		505	505			1.61	576
37	MBr2	1731			516	516			1.81	773
38	MBr3	1596	77	–	493	493			1.53	556
39	MBr4	1575		−21	472	472			1.46	499
40	MBr5	1700	104		496	496			1.48	554
41	MBr6	1779			488	488			1.42	528
42	MBr7	1793			494	494			1.43	538
43	DBr1	1742	–		728	505	223		1.56	628
44	DBr2	1965			750	516	234		1.74	835
45	DBr3	1818	76	–	715	493	222		1.50	608
46	DBr4	1784		−34	681	472	209		1.44	543
47	DBr5	1928	110		724	496	228		1.46	610
48	DBr6	2003			712	488	224		1.40	576
49	DBr7	2022			723	494	229		1.41	589

*,**,***,§ As in Table IV.

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

TABLE VI

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

Conditions as in Figs. 1–4.

*Increment**	*Column*	
	SE-30	*OV-351*
ΔI_{CH_2}	93–110	72–110
$\Delta I_{\alpha\text{-}CH_2}$	31–48	0 to −34
ΔI_{1Cl}	205–218	379–427
ΔI_{2Cl}	73–79	63–78
ΔI_{3Cl}	77–81	−27 to −37
ΔI_{1Br}	277–289	472–516
ΔI_{2Br}	165–178	209–234
ΔI_{3Br}	192–196	–

* As in Table IV.

roacetate < dibromoacetate, the deviations for the alcohols generally being between the monochloro and monobromo isomers (Table V).

The GC retention behaviour of the geometric isomers of chlorinated esters[3–6] and particularly of fatty esters[16,17] has been extensively studied. Chlorine substitution adjacent to the double bond has a negligible effect on retention on a non-polar column, the *trans*-isomer being eluted first, owing to the lower boiling point. With a polar column the elution order is greatly influenced by molecular structure, owing to the interaction between a chlorine atom and an alkoxy group or between two chlorine atoms[3–5]. For this reason, better separations of pairs of isomers are obtained on polar columns.

Isomeric hexenyl esters with a non-halogenated double bond are eluted close together on both polar and non-polar columns, the *trans*-isomer being eluted first and the elution order remains unaltered[1,6], as in this present work. The disparity between *trans*- and *cis*-3-hexenyl acetates (13 and 14, *i.e.*, A6 and A7) on non-polar and donor stationary phases varied in the range 0–13 i.u. and on acceptor phases between 7 and 25 i.u.[1]. Tables IV and V show the disparities for the series on SE-30 to be 2–6 i.u. and on OV-351 8–19 i.u., the values varying little with the halogen substitution.

CONCLUSIONS

Better separations were obtained on a low-polarity SE-30 than on a highly polar OV-351 capillary column, the latter being in addition unsuitable for tribrominated esters. SE-30 separated all the chlorinated and brominated esters, but the analysis of a complex mixture of all these halogenated esters would lead to several overlapping peaks. Only one compound pair, *viz.*, 13 = A6 and 17 = MCl3, is unresolvable on SE-30. The esters are separated from each other on OV-351, where 17 overlaps with 22 = DCl1, this being the only unresolvable compound in the mixtures analysed.

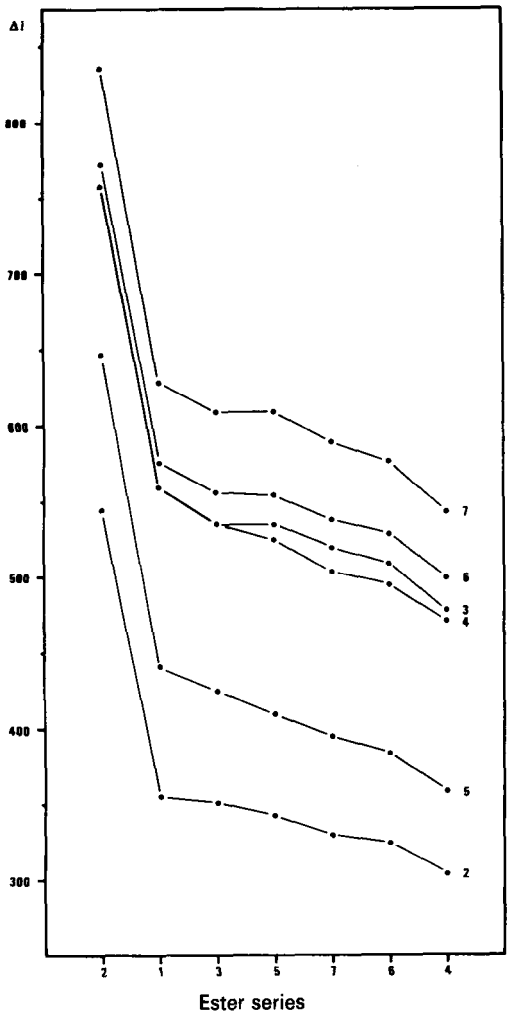

Fig. 7. Plot showing enhanced retention of the esters on OV-351. $\Delta I = I_{OV\text{-}351} - I_{SE\text{-}30}$ (Table V). Curves 2–7 as in Fig. 5.

ACKNOWLEDGEMENTS

This work was supported financially by the Foundation for Research on Natural Resources in Finland, the Kalle and Dagmar Välimaa Foundation (Cultural Foundation of Finland) and the Academy of Finland. This aid is gratefully acknowledged.

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