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GAS-LIQUID CHROMATOGRAPHIC ANALYSES

XLIV*. BENZOYL AND PENTAFLUOROBENZOYL ESTERS OF LOWER SATURATED BRANCHED-CHAIN AND UNSATURATED ALCOHOLS ON SE-30 AND OV-351 CAPILLARY COLUMNS

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SUMMARY

Low-polarity (SE-30) and polar (OV-351) capillary columns were used to investigate the gas chromatographic separation of the mixtures of benzoyl and pentafluorobenzoyl esters of some lower saturated branched-chain and unsaturated alcohols. Relative retention data and Kováts retention indices for the compounds were determined. The reductions in the retention due to the perfluoro substitution were in the ranges -118 to -138 (SE-30) and -299 to -369 (OV-351) retention index units. The results are compared with the behaviour of the corresponding aliphatic and aromatic esters reported earlier.

INTRODUCTION

Previously, the gas chromatographic (GC) retention behaviour of some lower saturated branched-chain¹⁻⁵ and unsaturated^{3,4,6-8} esters of acetic and haloacetic acids^{1,6}, propanoic and monochloropropanoic acids^{2,3,7}, butanoic and monochlorobutanoic acids^{2,4,7} and benzoic and monochlorobenzoic acids^{5,8} was investigated. Low-polarity (SE-30) and polar (OV-351) quartz capillary columns with temperature programming^{1,2,5-8} or isothermal operation^{3-5,8} were used to show the effect of branching and unsaturation in the alkyl chain and halogenation in the acyl chain.

This work extends the earlier studies with branched-chain and unsaturated esters¹⁻⁸ and with esters of benzoic and halobenzoic acids^{5,8-11} by showing the GC separation of the mixtures of benzoyl and pentafluorobenzoyl esters of some lower saturated branched-chain and unsaturated alcohols on SE-30 and OV-351 capillary columns. Relative retention data, Kováts retention indices and increments in the retention indices due to the perfluoro substitution on the acyl chain were determined and the results compared with those of the corresponding monochlorinated aromatic esters^{5,8}.

* For Part XLIII, see I. O. O. Korhonen, *J. Chromatogr.*, 329 (1985) 43.

EXPERIMENTAL

Materials

The branched-chain and unsaturated esters of benzoic (1–14) and pentafluorobenzoic (F/1–F/14) acids were synthesized from the corresponding alcohols (Fluka, Buchs, Switzerland or Merck-Schuchardt, Darmstadt, F.R.G.) and benzoyl (Merck-Schuchardt) and pentafluorobenzoyl (Fluka) chlorides as described earlier¹². The purity of the esters was checked by GLC.

Commercial mixtures of *n*-alkanes used as reference compounds were obtained from different sources.

Methods

GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the following operating conditions: injection and flame-ionization detection (FID) temperatures, 250°C; nitrogen carrier gas flow-rates for methane at 160°C, 14.2 (SE-30) and 15.8 cm sec⁻¹ (OV-351); splitting ratio, *ca.* 1:20; and chart speed, 10 mm min⁻¹. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.33 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

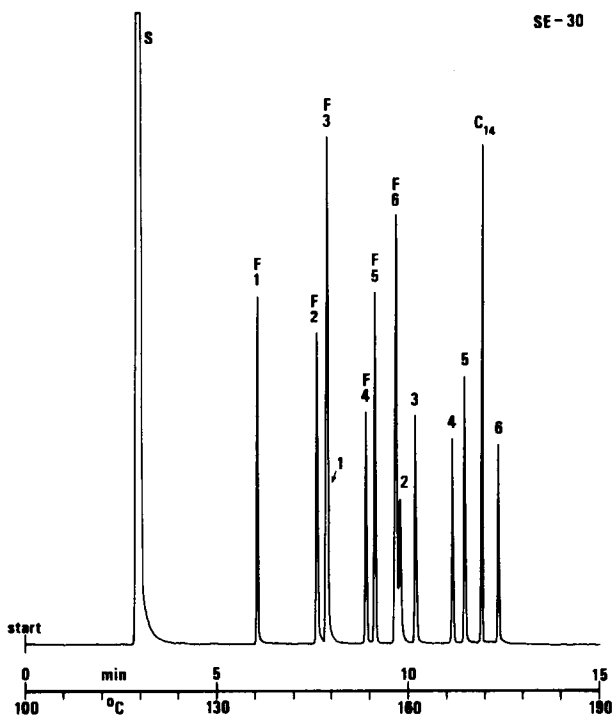


Fig. 1. Chromatogram of a mixture of saturated branched-chain esters of benzoic (1–6) and pentafluorobenzoic (F/1–F/6) acids, separated on an SE-30 quartz capillary column with temperature programming from 100°C at 6°C min⁻¹ until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane; peaks are listed in Table I.

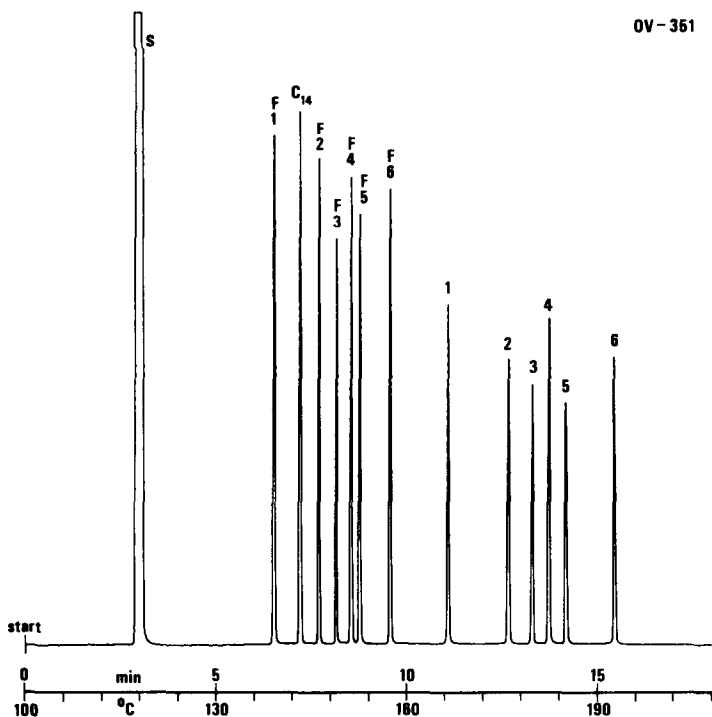


Fig. 2. Chromatogram of the same mixture as in Fig. 1, obtained on an OV-351 quartz capillary column with temperature programming from 100°C at $6^{\circ}\text{C min}^{-1}$ until elution of peaks had ceased. S = Solvent; C_{14} = *n*-tetradecane; peaks are listed in Table I.

by Orion Analytica (Espoo, Finland). The column temperature was programmed from 100°C at $6^{\circ}\text{C min}^{-1}$ until elution of peaks had ceased; the isothermal data were determined at 140, 160 and 180°C .

The chromatographic data were recorded with a Hewlett-Packard Model 3390A reporting integrator using standard programs. The retention times were measured from the time of sample injection and the Kováts retention indices were calculated off-line by using two appropriate adjacent *n*-alkanes as described earlier¹³; the dead volumes were determined by the injection of methane.

The mixture of (i) branched-chain and (ii) unsaturated esters contained suitable amounts of the individual GC-pure compounds for the sensitivity of the flame-ionization detector; the order of elution of the compounds was confirmed by using a standard additions method. A mixture of *n*-alkanes was chromatographed between mixtures (i) and (ii).

RESULTS AND DISCUSSION

Chromatograms of a mixture of the saturated branched-chain esters of benzoic (1–6) and pentafluorobenzoic (F/1–F/6) acids, obtained on SE-30 and OV-351 with temperature programming, are presented in Figs. 1 and 2. The corresponding separations of a mixture of the unsaturated esters (7–14 and F/7–F/14) are shown in Figs.

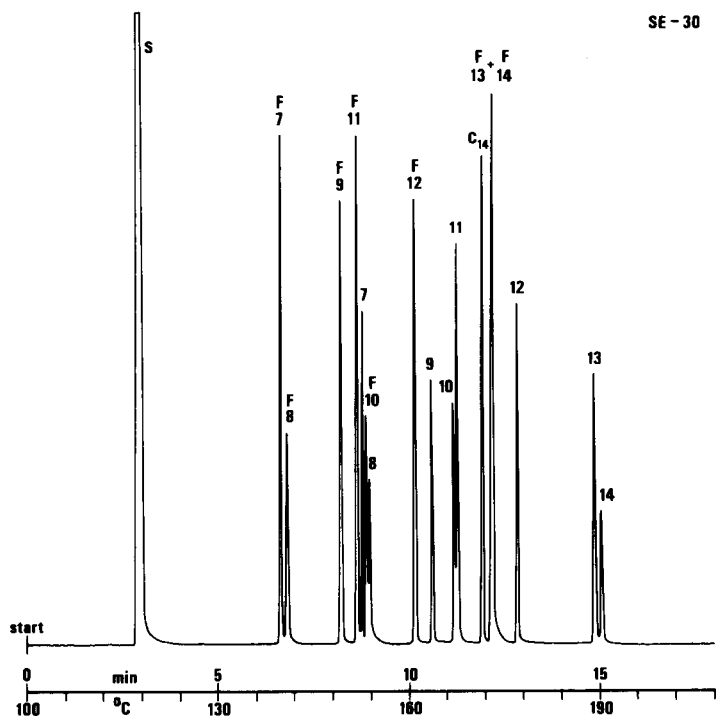


Fig. 3. Chromatogram of a mixture of unsaturated esters of benzoic (7–14) and pentafluorobenzoic (F/7–F/14) acids, separated on SE-30 with temperature programming from 100°C at 6°C min⁻¹ until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane; peaks are listed in Table I.

3 (SE-30) and 4 (OV-351). The absolute and relative retention data for all these esters are given in Table I, and the Kováts retention indices together with the retention index increments for the pentafluoro isomers are shown in Table II and Figs. 5 and 6. Table III gives the retention indices for the pentafluoro isomers on both columns at three isothermal temperatures, the corresponding retention indices for the esters of the benzoic and monochlorobenzoic acids having been reported earlier^{5,8}.

The branched-chain esters of benzoic and pentafluorobenzoic acids are eluted in the same order on both the low-polarity (Fig. 1) and highly polar (Fig. 2) stationary phases, the fluorinated isomers being eluted first¹¹. On SE-30 the peaks of 2-methylpropyl pentafluorobenzoate (F/3) and methylethyl benzoate (1) overlap, as do partially also those of 3-methylbutyl pentafluorobenzoate (F/6) and 1-methylpropyl benzoate (2) (Fig. 1). The retentions of the perfluoro isomers are 0.76–0.80 (Table I) as great as those of the parent isomers, *i.e.*, the reductions in their retentions are in the range from –118 to –136 retention index units (i.u.) (Table II).

On OV-351 the retention due to the fluoro substitution is markedly reduced, so that all of the isomers are eluted earlier than the first-eluted parent isomer (Fig. 2). The ratio between the retentions of the esters is in the range 0.59–0.62 (Table I), the reductions in the retention of the fluoro isomers being in the range from –299 to –348 i.u. (Table II).

Unlike the branched-chain esters, fluoro substitution with the unsaturated es-

ters causes on both columns a reversed retention sequence of the following esters: (*E*)-2-butenyl (F/11) and 1-methyl-3-butenyl (F/10) esters on SE-30 (Fig. 3) and 4-pentenyl (F/12) and 2-propynyl (F/8) esters on OV-351 (Fig. 4). These trends are more pronounced, as observed previously, with the corresponding ester pairs of *o*-chlorobenzoic acid⁸, where on SE-30 the 1-methyl-3-butenyl and (*E*)-2-butenyl esters were coincident and the 4-pentenyl and 2-propynyl esters on OV-351 were eluted close together and in the reverse order to the benzoyl and *m*- and *p*-chlorobenzoyl esters⁸.

The closely related isomeric (*E*)- and (*Z*)-3-hexenyl pentafluorobenzoates (F/13 and F/14) were poorly separated on both columns, unlike the corresponding parent isomers (13 and 14), as is evident in Figs. 3 and 4. The esters were prepared from a mixture of (*E*)- and (*Z*)-3-hexen-1-ols (isomer ratio 60:40) and, owing to a lack of the pure isomers, accurate retention times of F/13 and F/14 could not be measured on SE-30 because of complete overlapping of the peaks. It seems evident, however, that the retention sequence of the isomers remains unchanged, the (*E*)-isomer (F/13) being eluted first, as occurred on OV-351, where F/14 is eluted as an unresolved shoulder with F/13 (Fig. 4). Earlier results⁸ with the corresponding (*E*)- and (*Z*)-monochlorobenzoates again indicated the similarity of the *o*-chloro and pentafluoro isomers, *viz.*, the *o*-isomers on both columns are eluted closer together than the parent and *m*- and *p*-isomers, but overlapping of the peaks did not occur.

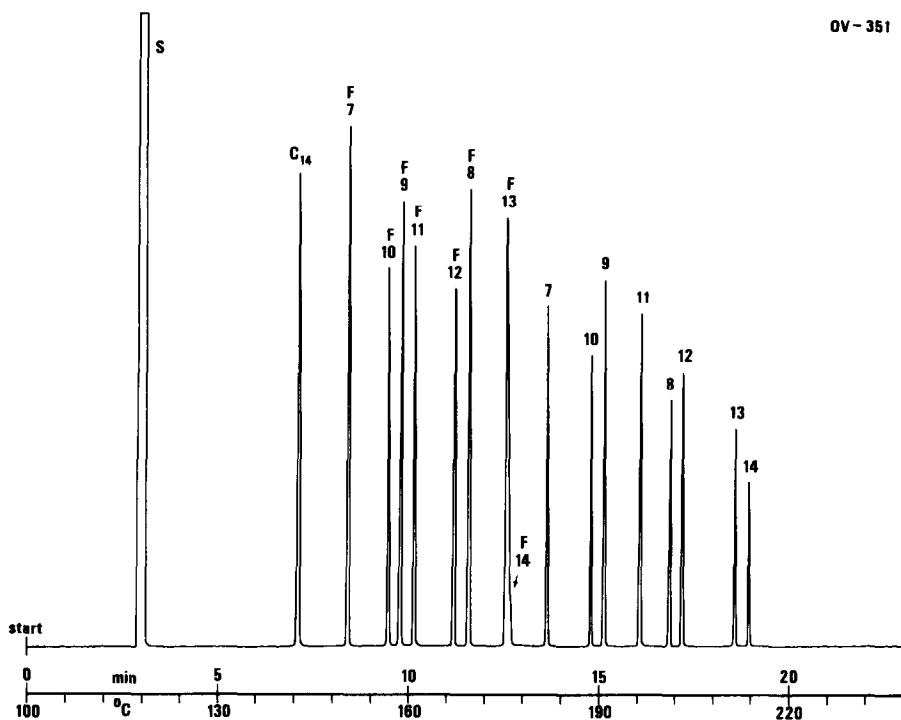


Fig. 4. Chromatogram of the same mixture as in Fig. 3, obtained on OV-351 with temperature programming from 100°C at 6°C min⁻¹ until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane; peaks are listed in Table I.

TABLE I

RETENTION DATA FOR SOME LOWER SATURATED BRANCHED-CHAIN AND UNSATURATED ESTERS OF BENZOIC AND PENTAFLUOROBENZOIC ACIDS, DETERMINED ON SE-30 AND OV-351 CAPILLARY COLUMNS WITH TEMPERATURE PROGRAMMING

Conditions as in Figs. 1-4.

Peak No.	Compound	Column						
		SE-30			OV-351			
		ART*	RRT**	RRT***	ART*	RRT**	RRT***	RRT§
1	Methylethyl benzoate	7.91	0.66	1.00	11.08	1.54	1.00	1.40
2	1-Methylpropyl benzoate	9.78	0.82	1.00	12.67	1.76	1.00	1.30
3	2-Methylpropyl benzoate	10.17	0.85	1.00	13.30	1.84	1.00	1.31
4	1,2-Dimethylpropyl benzoate	11.15	0.94	1.00	13.76	1.91	1.00	1.23
5	1-Methylbutyl benzoate	11.46	0.96	1.00	14.19	1.97	1.00	1.24
6	3-Methylbutyl benzoate	12.35	1.04	1.00	15.42	2.14	1.00	1.25
F/1	Methylethyl pentafluorobenzoate	6.02	0.51	0.76	6.51	0.90	0.59	1.08
F/2	1-Methylpropyl pentafluorobenzoate	7.61	0.64	0.78	7.71	1.07	0.61	1.01
F/3	2-Methylpropyl pentafluorobenzoate	7.84	0.66	0.77	8.19	1.14	0.62	1.04
F/4	1,2-Dimethylpropyl pentafluorobenzoate	8.89	0.75	0.80	8.53	1.18	0.62	0.96
F/5	1-Methylbutyl pentafluorobenzoate	9.11	0.76	0.79	8.78	1.22	0.62	0.96
F/6	3-Methylbutyl pentafluorobenzoate	9.66	0.81	0.78	9.56	1.33	0.62	0.99

7	2-Propenyl benzoate	8.78	0.74	1.00	13.62	1.89	1.00	1.55
8	2-Propynyl benzoate	8.91	0.75	1.00	16.88	2.34	1.00	1.89
9	3-Butenyl benzoate	10.59	0.89	1.00	15.16	2.10	1.00	1.43
10	1-Methyl-3-butenyl benzoate	11.17	0.94	1.00	14.81	2.05	1.00	1.33
11	(E)-2-Butenyl benzoate	11.21	0.94	1.00	16.15	2.24	1.00	1.44
12	4-Pentenyl benzoate	12.80	1.07	1.00	17.19	2.38	1.00	1.34
13	(E)-3-Hexenyl benzoate	14.81	1.24	1.00	18.59	2.58	1.00	1.26
14	(Z)-3-Hexenyl benzoate	15.03	1.26	1.00	18.95	2.63	1.00	1.26
F/7	2-Propenyl pentafluorobenzoate	6.60	0.55	0.75	8.43	1.17	0.62	1.28
F/8	2-Propynyl pentafluorobenzoate	6.79	0.57	0.76	11.59	1.61	0.69	1.71
F/9	3-Butenyl pentafluorobenzoate	8.19	0.69	0.77	9.85	1.37	0.65	1.20
F/10	1-Methyl-3-butenyl pentafluorobenzoate	8.85	0.74	0.79	9.48	1.31	0.64	1.07
F/11	(E)-2-Butenyl pentafluorobenzoate	8.61	0.72	0.77	10.17	1.41	0.63	1.18
F/12	4-Pentenyl pentafluorobenzoate	10.11	0.85	0.79	11.23	1.56	0.65	1.11
F/13	(E)-3-Hexenyl pentafluorobenzoate	12.18 ^{**}	1.02	0.82	12.60	1.75	0.68	1.03
F/14	(Z)-3-Hexenyl pentafluorobenzoate	12.18 ^{**}	1.02	0.81	12.69	1.76	0.67	1.04
C ₁₄	<i>n</i> -Tetradecane	11.92	1.00	—	7.21	1.00	—	0.60

* Absolute retention times (min) were measured from sample injection (Figs. 1-4).

** Relative retention time for *n*-tetradecane (C₁₄) taken as 1.00.

*** Relative retention time for the corresponding ester of benzoic acid (1-14) taken as 1.00.

§ Relative retention time for the corresponding compound on SE-30 taken as 1.00.

§§ Approximate values due to a mixture of the (*E*)- and (*Z*)-isomers used and overlapping of the peaks.

TABLE II

RETENTION INDICES FOR SATURATED BRANCHED-CHAIN AND UNSATURATED ESTERS OF BENZOIC AND PENTAFLUOROBENZOIC ACIDS AND INCREMENTAL EFFECTS FOR FLUORINE SUBSTITUTION, DETERMINED ON SE-30 AND OV-351 WITH TEMPERATURE PROGRAMMING

Conditions as in Figs. 1-4.

Compound*	SE-30		OV-351		OV-351/SE-30		OV-351 - SE-30	
	I^{**}	$\Delta I_{F_5}^{***}$	I^{**}	$\Delta I_{F_5}^{***}$	I^{**}	$\Delta I_{F_5}^{***}$	I^{**}	$\Delta I_{F_5}^{***}$
1	1189	—	1657	—	1.39	—	468	—
2	1292	—	1752	—	1.36	—	460	—
3	1312	—	1789	—	1.36	—	477	—
4	1361	—	1816	—	1.33	—	455	—
5	1377	—	1842	—	1.34	—	465	—
6	1421	—	1914	—	1.35	—	493	—
F/1	1070	-119	1358	-299	1.27	2.51	288	-180
F/2	1171	-121	1444	-308	1.23	2.55	273	-187
F/3	1185	-127	1478	-311	1.25	2.45	293	-184
F/4	1243	-118	1502	-314	1.21	2.66	259	-196
F/5	1255	-122	1518	-324	1.21	2.66	263	-202
F/6	1285	-136	1566	-348	1.22	2.56	281	-212
Average	—	-124	—	-317	—	2.56	—	-194
7	1238	—	1808	—	1.46	—	570	—
8	1245	—	1998	—	1.60	—	753	—
9	1333	—	1899	—	1.42	—	566	—
10	1362	—	1878	—	1.38	—	516	—
11	1364	—	1956	—	1.43	—	592	—
12	1443	—	2016	—	1.40	—	573	—
13	1540	—	2101	—	1.36	—	561	—
14	1551	—	2122	—	1.37	—	571	—
F/7	1111	-127	1496	-312	1.35	2.46	385	-185
F/8	1123	-122	1688	-310	1.50	2.54	565	-188
F/9	1205	-128	1583	-316	1.31	2.47	378	-188
F/10	1241	-121	1561	-317	1.26	2.62	320	-196
F/11	1228	-136	1603	-353	1.31	2.60	375	-217
F/12	1309	-134	1666	-350	1.27	2.61	357	-216
F/13	1413 [§]	-127 [§]	1748	-353	1.24 [§]	2.78 [§]	335 [§]	-226 [§]
F/14	1413 [§]	-138 [§]	1753	-369	1.24 [§]	2.67 [§]	340 [§]	-231 [§]
Average	—	-129	—	-335	—	2.60	—	-206

* Compounds are listed in Table I.

** Determined with temperature programming from 100°C at 6°C min⁻¹ until elution of peaks had ceased.

*** $\Delta I_{F_5} = I_{\text{pentafluorobenzoic acid ester}} - I_{\text{benzoic acid ester}}$.

§ Approximate values due to a mixture of the (*E*)- and (*Z*)-isomers used and overlapping of the peaks.

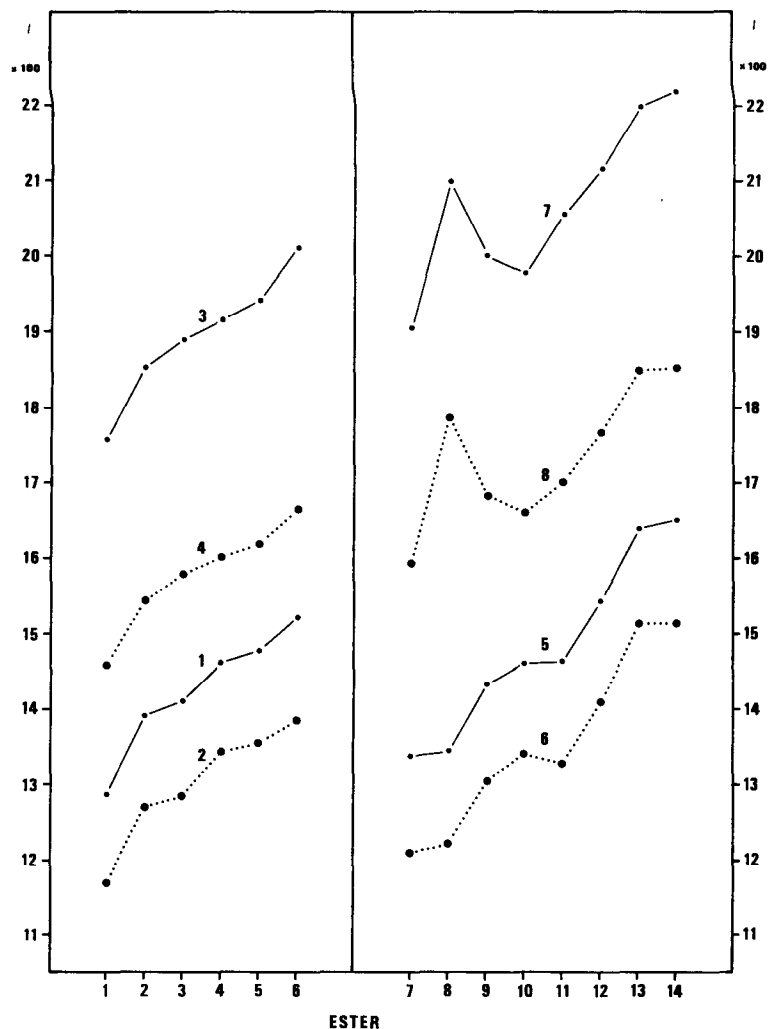


Fig. 5. Retention indices (I) of saturated branched-chain and unsaturated esters of benzoic and pentafluorobenzoic acids, obtained on SE-30 and OV-351 capillary columns with temperature programming (Figs. 1–4). Benzoates on SE-30 (curves 1 and 5) and on OV-351 (curves 3 and 7); pentafluorobenzoates on SE-30 (curves 2 and 6) and on OV-351 (curves 4 and 8). For identification of the esters (1–14), see Table I.

The relative retentions for the unsaturated fluoro isomers presented in Table I are generally in the same ranges as those for the branched-chain esters, *viz.*, 0.75–0.82 on SE-30 and 0.62–0.69 on OV-351. The incremental effects shown in Table II and Fig. 6 are in the range from –121 to –138 i.u. on SE-30 and from –310 to –369 i.u. on OV-351, these values generally being lower than those for the branched-chain esters.

The results given in this paper are in accordance with those reported earlier for the corresponding aliphatic^{1–4,6,7} and aromatic esters^{5,8} and *n*-alkyl pentafluorobenzoates¹¹. It seems evident, however, that the effect of perfluoro substitution on

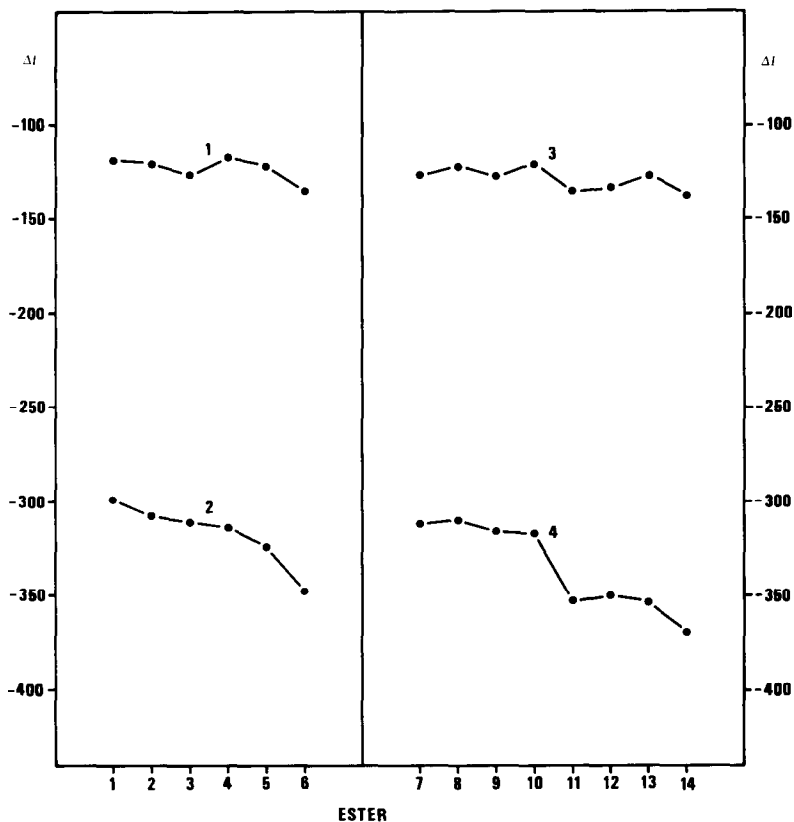


Fig. 6. Increments of the retention indices for pentafluorobenzoyl esters of saturated branched-chain and unsaturated alcohols. $\Delta I = I_{\text{pentafluorobenzoyl ester}} - I_{\text{benzoyl ester}}$ (Table II). Retention increments on SE-30 (curves 1 and 3) and on OV-351 (curves 2 and 4). For identification of the esters (1-14), see Table I.

the aromatic acyl chain might be more pronounced than monochloro substitution (*o*-chloro substitution), as shown by the reversed retention order of some isomers.

In practice, conversion of trace amounts of alcohols into their pentafluorobenzoyl esters before their GC analysis with electron-capture detection is recommended. This might be especially useful with volatile alcohols, those retention times can be increased by esterification and the compounds can be separated, *e.g.*, from the solvent peak. Earlier results with branched-chain and unsaturated alcohols show that, *e.g.*, at 140°C the retention enhancements on SE-30 are *ca.* 550 i.u. and on OV-351 *ca.* 250 i.u., as is evident from the data in Table III and ref. 3.

TABLE III

RETENTION INDICES FOR SATURATED BRANCHED-CHAIN AND UNSATURATED ESTERS OF PENTAFLUOROBENZOIC ACID, DETERMINED ON SE-30 AND OV-351 CAPILLARY COLUMNS AT ISOTHERMAL TEMPERATURES

Compound*	Column						$\frac{I_{OV-351}}{I_{SE-30}}$ (160°C)	$I_{OV-351} - I_{SE-30}$ (160°C)
	SE-30			OV-351				
	140°C	160°C	180°C	140°C	160°C	180°C		
F/1	1068	1085	1063	1330	1326	1288	1.22	241
F/2	1170	1177	1165	1424	1421	1408	1.21	244
F/3	1186	1192	1178	1460	1457	1440	1.22	265
F/4	1241	1246	1237	1490	1485	1475	1.19	239
F/5	1253	1257	1247	1506	1498	1483	1.19	241
F/6	1283	1286	1285	1559	1558	1541	1.21	272
F/7	1113	1121	1104	1470	1474	1463	1.31	353
F/8	1122	1127	1107	1682	1676	1664	1.49	549
F/9	1207	1211	1198	1562	1561	1548	1.29	350
F/10	1242	1246	1233	1540	1541	1536	1.24	295
F/11	1228	1233	1216	1586	1586	1574	1.29	353
F/12	1308	1312	1300	1663	1663	1658	1.27	351
F/13	1408**	1414**	1404**	1745	1746	1743	1.23	332
F/14	1408**	1414**	1404**	1746	1747	1743	1.24	333

* Compounds are listed in Table I.

** Approximate values due to a mixture of the (*E*)- and (*Z*)-isomers used and overlapping of the peaks.

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