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GAS-LIQUID CHROMATOGRAPHIC ANALYSES

XXXVII*. CAPILLARY COLUMN STUDIES OF BENZOYL AND MONOCHLOROBENZOYL ESTERS OF LOWER SATURATED BRANCHED-CHAIN ALCOHOLS

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SUMMARY

The gas chromatographic retention behaviour of methylethyl, 1-methylpropyl, 2-methylpropyl, 1,2-dimethylpropyl, 1-methylbutyl and 3-methylbutyl esters of benzoic and *o*-, *m*- and *p*-chlorobenzoic acids on low-polarity (SE-30) and polar (OV-351) capillary columns under several temperature-programmed and isothermal conditions is reported. The retention data and the Kováts retention indices for all 24 components are given and the separation of a complex mixture is discussed. The retention index increments have been used to examine the effects of chain branching and chlorine substitution. The results are compared with those for *n*-alkyl benzoates and monochlorobenzoates.

INTRODUCTION

In contrast to aromatic esters, the gas chromatographic (GC) retention behaviour of aliphatic esters has previously been extensively studied¹. The GC of branched-chain esters has received little attention, however, and most frequently methylethyl, 2-methylpropyl and 3-methylbutyl alkanoates have been investigated^{2,3}.

Previously, eight lower (C₃–C₅) branched-chain alkanols and their propanoyl, monochloropropanoyl, butanoyl and monochlorobutanoyl derivatives have been separated by GC on SE-30 and OV-351 capillary columns with temperature programming⁴, and more recently the isothermal capillary GC of these series of esters has been reported^{5,6}. In addition, the retention behaviour of the same series of alkanols and their acetyl, chloroacetyl and bromoacetyl derivatives on the same columns has been investigated and the effects of chain branching and various halogen substituents based on retention index increments were examined⁷.

This paper describes the isothermal and temperature-programmed capillary GC of methylethyl, 1-methylpropyl, 2-methylpropyl, 1,2-dimethylpropyl, 1-methyl-

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butyl and 3-methylbutyl esters of benzoic acid and *o*-, *m*- and *p*-chlorobenzoic acids on SE-30 and OV-351 capillary columns. The relative retentions and Kováts retention indices for all 24 individual components in the four homologous series were determined and examined, together with the effects of chain branching and chlorine substitution, shown by retention index increments. The results are compared with those for the corresponding *n*-alkyl esters¹ and aliphatic branched-chain esters⁴⁻⁷.

EXPERIMENTAL

Materials

Branched-chain esters of benzoic (1-6), *o*-chlorobenzoic (*o*/1-*o*/6), *m*-chlorobenzoic (*m*/1-*m*/6) and *p*-chlorobenzoic (*p*/1-*p*/6) acids were obtained from commercial branched-chain alkanols (Fluka, Buchs, Switzerland) and acid chlorides¹ as described earlier⁸. The esters studied are listed in Table I.

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

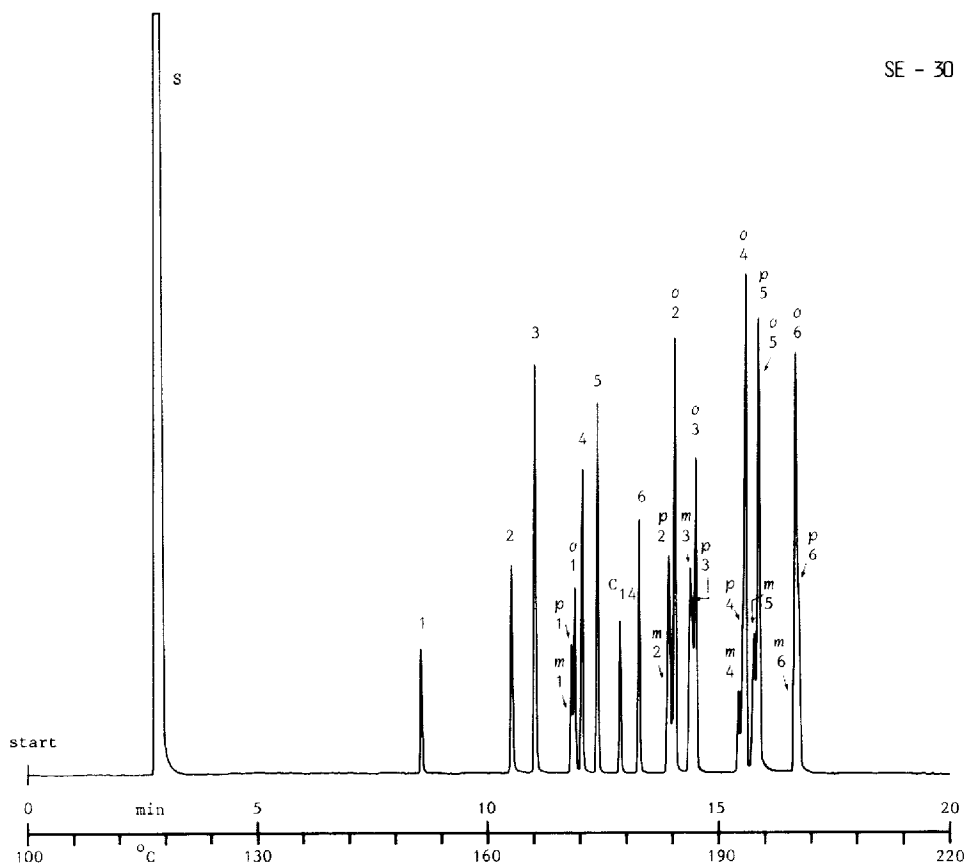


Fig. 1. Chromatogram of a mixture of the branched-chain esters of benzoic (1-6), *o*-chlorobenzoic (*o*/1-*o*/6), *m*-chlorobenzoic (*m*/1-*m*/6) and *p*-chlorobenzoic (*p*/1-*p*/6) acids, separated on an SE-30 quartz capillary column with temperature programming from 100°C at 6°C min⁻¹ until elution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

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, 275°C; nitrogen carrier gas velocities for methane at 160°C, 13.9 (SE-30) and 14.6 cm sec⁻¹ (OV-351); splitting ratio, 1:25; 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 by Orion Analytica (Espoo, Finland). The column temperature was programmed from 100 to 300°C (SE-30) and from 100 to 230°C (OV-351) at 2, 6 and 10°C min⁻¹ and, if necessary, held on OV-351 at 230°C 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 *n*-alkanes⁹, the dead volume first being determined by the injection of methane. Owing to the incomplete resolution of a

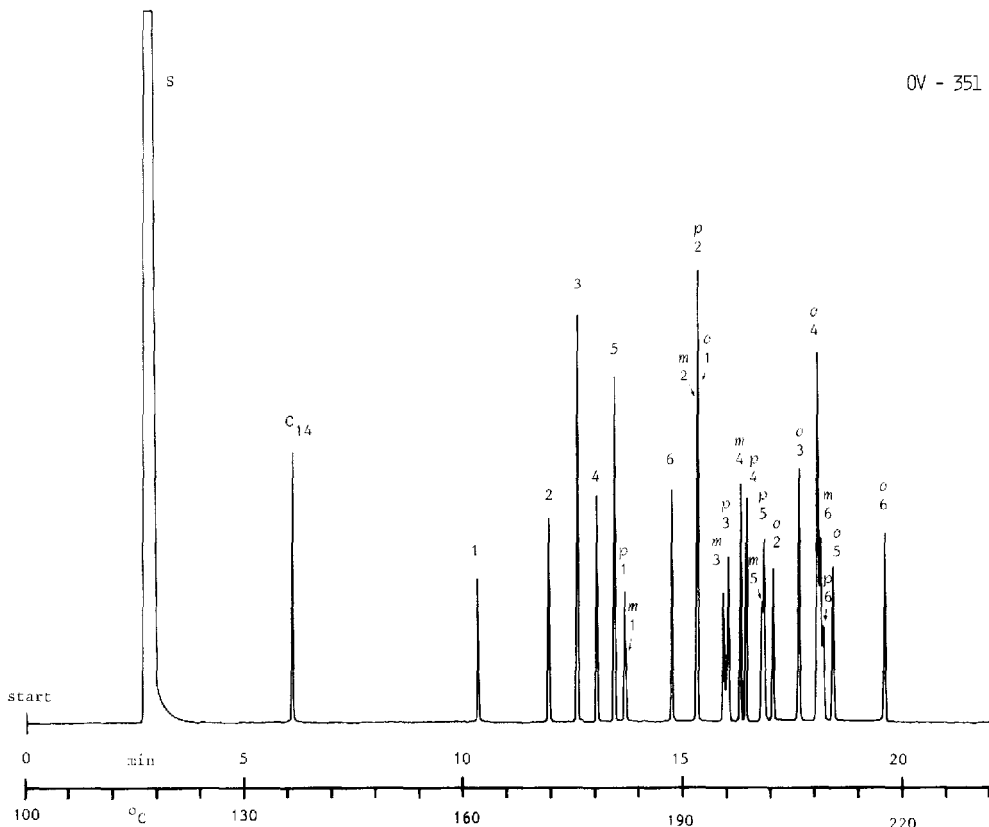


Fig. 2. Chromatogram of the same mixture as in Fig. 1, obtained on an OV-351 quartz capillary column with temperature programming from 100°C at 6°C min⁻¹ until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane; peaks are listed in Table I.

complex mixture of all components, four mixtures containing (i) benzoates, (ii) *o*-chloro-, (iii) *m*-chloro- and (iv) *p*-chlorobenzoates were analysed separately, together with appropriate *n*-alkanes. The elution order of the individual components presented in Figs. 1 and 2 was confirmed by using the standard addition method.

RESULTS AND DISCUSSION

Separation of a mixture of six saturated branched-chain esters of benzoic (1–6), *o*-chlorobenzoic (*o*/1–*o*/6), *m*-chlorobenzoic (*m*/1–*m*/6) and *p*-chlorobenzoic (*p*/1–*p*/6) acids obtained on low-polarity SE-30 and polar OV-351 capillary columns

TABLE I

RETENTION DATA FOR BRANCHED-CHAIN ALKYL ESTERS OF BENZOIC, *o*-CHLOROBENZOIC, *m*-CHLOROBENZOIC AND *p*-CHLOROBENZOIC ACIDS, OBTAINED ON SE-30 AND OV-351 CAPILLARY COLUMNS WITH TEMPERATURE PROGRAMMING

Conditions as in Figs. 1 and 2.

Peak No.	Compound	Column						
		SE-30			OV-351			
		ART*	RRT**	RRT***	ART*	RRT**	RRT***	RRT§
1	Methylethyl benzoate	8.52	0.66	1.00	10.33	1.69	1.00	1.21
2	1-Methylpropyl benzoate	10.49	0.82	1.00	11.95	1.95	1.00	1.14
3	2-Methylpropyl benzoate	10.99	0.85	1.00	12.61	2.06	1.00	1.15
4	1,2-Dimethylpropyl benzoate	12.03	0.93	1.00	13.05	2.13	1.00	1.08
5	1-Methylbutyl benzoate	12.36	0.96	1.00	13.46	2.20	1.00	1.09
6	3-Methylbutyl benzoate	13.27	1.03	1.00	14.78	2.42	1.00	1.11
<i>o</i> /1	Methylethyl <i>o</i> -chlorobenzoate	11.87	0.92	1.39	15.33	2.50	1.48	1.29
<i>o</i> /2	1-Methylpropyl <i>o</i> -chlorobenzoate	14.02	1.09	1.34	17.04	2.78	1.43	1.22
<i>o</i> /3	2-Methylpropyl <i>o</i> -chlorobenzoate	14.49	1.13	1.32	17.64	2.88	1.40	1.22
<i>o</i> /4	1,2-Dimethylpropyl <i>o</i> -chlorobenzoate	15.59	1.21	1.30	18.08	2.95	1.39	1.16
<i>o</i> /5	1-Methylbutyl <i>o</i> -chlorobenzoate	15.87	1.23	1.28	18.42	3.01	1.37	1.16
<i>o</i> /6	3-Methylbutyl <i>o</i> -chlorobenzoate	16.66	1.29	1.26	19.60	3.20	1.33	1.18
<i>m</i> /1	Methylethyl <i>m</i> -chlorobenzoate	11.79	0.92	1.38	13.70	2.24	1.33	1.16
<i>m</i> /2	1-Methylpropyl <i>m</i> -chlorobenzoate	13.91	1.08	1.33	15.32	2.50	1.28	1.10
<i>m</i> /3	2-Methylpropyl <i>m</i> -chlorobenzoate	14.37	1.12	1.31	15.92	2.60	1.26	1.11
<i>m</i> /4	1,2-Dimethylpropyl <i>m</i> -chlorobenzoate	15.41	1.20	1.28	16.29	2.66	1.25	1.06
<i>m</i> /5	1-Methylbutyl <i>m</i> -chlorobenzoate	15.77	1.23	1.28	16.79	2.74	1.25	1.06
<i>m</i> /6	3-Methylbutyl <i>m</i> -chlorobenzoate	16.61	1.29	1.25	18.12	2.96	1.23	1.09
<i>p</i> /1	Methylethyl <i>p</i> -chlorobenzoate	11.81	0.92	1.39	13.65	2.23	1.32	1.16
<i>p</i> /2	1-Methylpropyl <i>p</i> -chlorobenzoate	13.94	1.08	1.33	15.32	2.50	1.28	1.10
<i>p</i> /3	2-Methylpropyl <i>p</i> -chlorobenzoate	14.40	1.12	1.31	16.02	2.62	1.27	1.11
<i>p</i> /4	1,2-Dimethylpropyl <i>p</i> -chlorobenzoate	15.51	1.21	1.29	16.41	2.68	1.26	1.06
<i>p</i> /5	1-Methylbutyl <i>p</i> -chlorobenzoate	15.85	1.23	1.28	16.82	2.75	1.25	1.06
<i>p</i> /6	3-Methylbutyl <i>p</i> -chlorobenzoate	16.73	1.30	1.26	18.20	2.97	1.23	1.09
C ₁₄	<i>n</i> -Tetradecane	12.87	1.00	—	6.12	1.00	—	0.48

* Absolute retention times (min) were measured from sample injection (Figs. 1 and 2).

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

*** Relative retention time for the corresponding branched-chain ester of benzoic acid (1–6) taken as 1.00.

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

with temperature programming is shown in Figs. 1 and 2, respectively. The corresponding retention data, with relative retentions for *n*-tetradecane, benzoic acid esters and the compounds on SE-30 taken as 1.00, are presented in Table I.

As would be expected based on observations of the normal-chain esters¹, the monochlorinated isomers are eluted on SE-30 close together, the elution order being *m*- ≤ *p*- ≤ *o*-isomer (Fig. 1). The peaks of the *m*- and *p*-isomers most frequently overlap, whereas the parent esters are resolved from the chlorinated isomers.

On a polar OV-351 column the retention is increased (Table I) and it is evident that the elution order between the isomers in the four homologous series remains unchanged, whereas that of the individual components in a mixture is markedly changed (Fig. 2). These changes are due to the relatively lower retention times of the parent esters and to the increased retentions of the *o*-isomers with respect to the *m*- and *p*-isomers¹.

The retention indices of the esters studied, determined on SE-30 and OV-351,

TABLE II

RETENTION INDICES FOR BRANCHED-CHAIN ALKYL ESTERS OF BENZOIC, *o*-CHLORO-BENZOIC, *m*-CHLOROBENZOIC AND *p*-CHLOROBENZOIC ACIDS, DETERMINED ON SE-30 AT VARIOUS COLUMN TEMPERATURES

Compound*	Column (SE-30) temperature					
	Programmed from 100°C at			Isothermal at		
	2°C min ⁻¹	6°C min ⁻¹	10°C min ⁻¹	140°C	160°C	180°C
1	1183	1186	1191	1192	1194	1205
2	1280	1286	1291	1288	1293	1301
3	1305	1310	1315	1312	1318	1327
4	1353	1360	1365	1361	1367	1376
5	1370	1376	1379	1376	1381	1390
6	1412	1419	1424	1417	1425	1434
<i>o</i> /1	1345	1352	1358	1354	1361	1378
<i>o</i> /2	1446	1455	1461	1450	1460	1470
<i>o</i> /3	1467	1477	1483	1471	1480	1490
<i>o</i> /4	1519	1529	1538	1521	1530	1540
<i>o</i> /5	1534	1543	1550	1534	1542	1551
<i>o</i> /6	1570	1581	1589	1571	1580	1590
<i>m</i> /1	1341	1348	1354	1350	1356	1369
<i>m</i> /2	1440	1449	1455	1446	1456	1465
<i>m</i> /3	1462	1471	1477	1466	1475	1488
<i>m</i> /4	1512	1521	1527	1514	1523	1531
<i>m</i> /5	1529	1538	1543	1531	1538	1547
<i>m</i> /6	1569	1579	1586	1570	1579	1589
<i>p</i> /1	1342	1349	1354	1351	1356	1370
<i>p</i> /2	1441	1451	1460	1446	1456	1465
<i>p</i> /3	1463	1473	1480	1467	1477	1489
<i>p</i> /4	1515	1526	1534	1518	1527	1535
<i>p</i> /5	1532	1542	1550	1533	1540	1551
<i>p</i> /6	1573	1585	1590	1574	1583	1593

* Compounds listed in Table I.

TABLE III

RETENTION INDICES FOR BRANCHED-CHAIN ALKYL ESTERS OF BENZOIC, *o*-CHLORO-BENZOIC, *m*-CHLOROBENZOIC AND *p*-CHLOROBENZOIC ACIDS, DETERMINED ON OV-351 AT VARIOUS COLUMN TEMPERATURES

Com- pound*	Column (OV-351) temperature						$I_{OV-351} - I_{SE-30}^{**}$ (160°C)
	Programmed from 100°C at			Isothermal at			
	2°C min ⁻¹	6°C min ⁻¹	10°C min ⁻¹	140°C	160°C	180°C	
1	1660	1669	1685	1676	1683	1704	489
2	1749	1762	1780	1766	1774	1792	481
3	1785	1800	1817	1801	1811	1830	493
4	1810	1825	1840	1824	1833	1851	466
5	1824	1849	1863	1846	1854	1873	473
6	1904	1924	1938	1913	1925	1944	500
<i>o</i> /1	1936	1955	1976	1940	1954	1975	593
<i>o</i> /2	2031	2054	2065	2030	2041	2067	581
<i>o</i> /3	2066	2089	2099	2062	2075	2099	595
<i>o</i> /4	2089	2115	2124	2084	2098	2122	568
<i>o</i> /5	2112	2135	2145	2106	2119	2140	577
<i>o</i> /6	2178	2204	2215	2166	2180	2204	600
<i>m</i> /1	1833	1863	1878	1852	1869	1883	513
<i>m</i> /2	1935	1957	1969	1936	1956	1969	500
<i>m</i> /3	1969	1989	2004	1969	1988	2003	513
<i>m</i> /4	1989	2010	2023	1988	2007	2023	484
<i>m</i> /5	2017	2039	2049	2015	2033	2050	495
<i>m</i> /6	2092	2117	2125	2084	2102	2123	523
<i>p</i> /1	1833	1860	1878	1852	1870	1885	514
<i>p</i> /2	1935	1957	1969	1939	1958	1975	502
<i>p</i> /3	1973	1994	2009	1975	1994	2012	517
<i>p</i> /4	1995	2017	2030	1996	2014	2032	487
<i>p</i> /5	2020	2041	2054	2019	2036	2054	496
<i>p</i> /6	2096	2122	2129	2089	2107	2127	524

* Compounds listed in Table I.

** For the retention indices on SE-30, see Table II.

are shown in Tables II and III, respectively. Fig. 3 illustrates the retentions of the four series of esters obtained on both stationary phases at 160°C, whereas the retention enhancements that occurred on a polar column, *i.e.*, $I_{OV-351} - I_{SE-30}$, are shown in Fig. 4.

As usual, the retention increased on both columns with increasing temperature and the elution order of the isomers remained unchanged. Owing to the branched-chain alkyl groups, as expected, the retention enhancements that occurred on a polar column are lower [from 46 to 79 retention index units (*i.u.*)] than with the corresponding normal-chain esters¹, *viz.*, at 160°C 466–500 *i.u.* for benzoates (1–6), 568–600 *i.u.* for *o*-chlorobenzoates (*o*/1–*o*/6), 484–523 *i.u.* for *m*-chlorobenzoates (*m*/1–*m*/6) and 487–524 *i.u.* for *p*-chlorobenzoates (*p*/1–*p*/6), as shown in Table III. The 1,2-dimethylpropyl series (4) with α -methyl substitution show the smallest and the 3-methylbutyl series (6) with γ -methyl substitution the largest disparities between the columns used (Fig. 4).

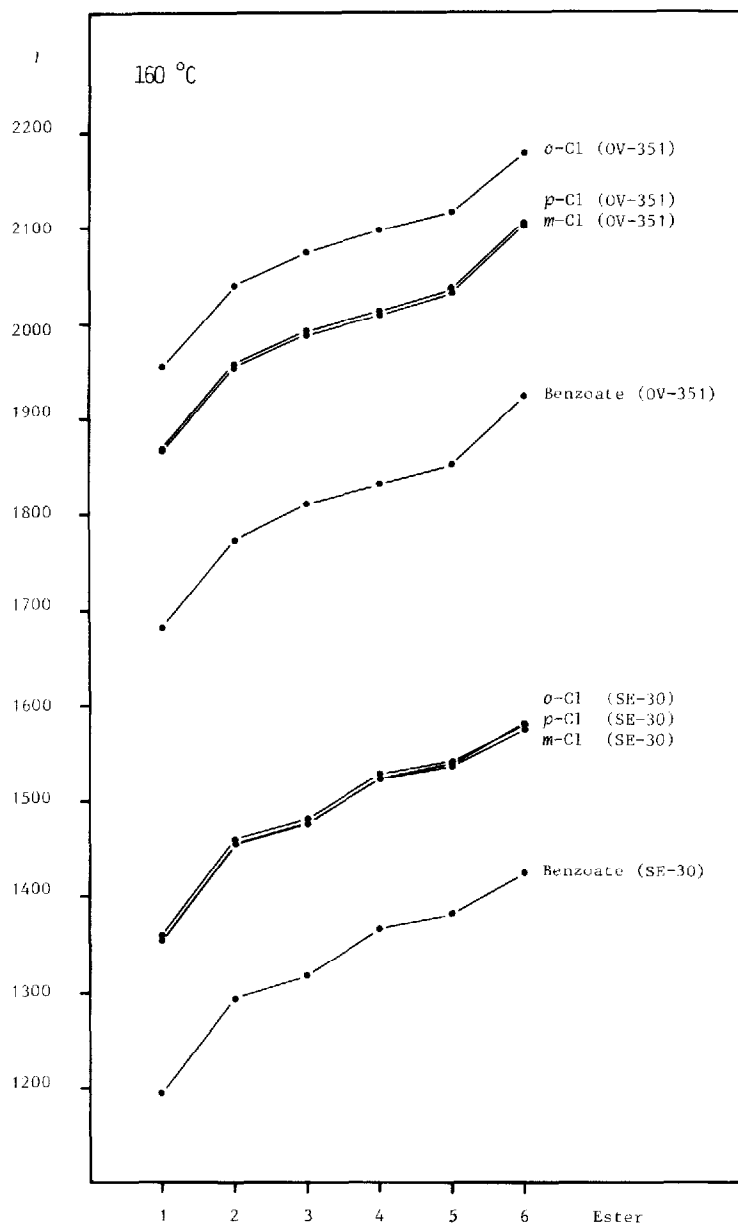


Fig. 3. Retention indices (I) of the six branched-chain esters of benzoic acid and its monochlorinated derivatives, obtained on SE-30 and OV-351 at 160°C. For identification of esters 1-6, see Table I.

As with the normal-chain esters¹, the retention indices of the branched-chain esters (1-3, 5 and 6) are very similar on the packed¹⁰ and capillary columns coated with the low-polarity SE-30 stationary phase. For the retention indices on OV-351, a comparison could not be made owing to the lack of the retention data for the esters studied on the polar columns.

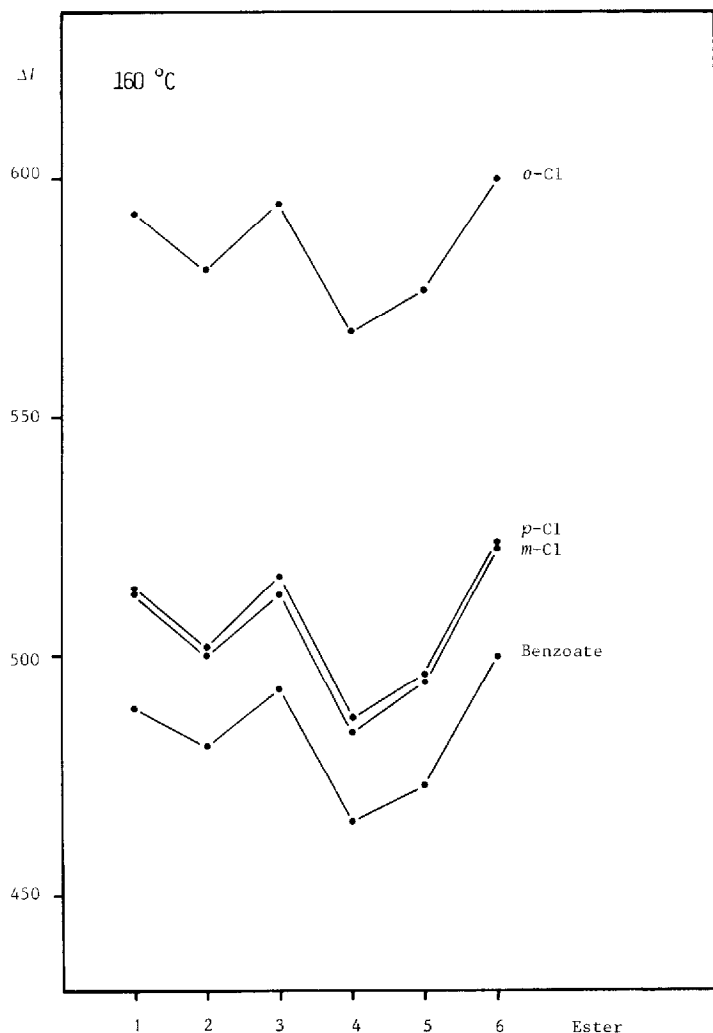


Fig. 4. Retention enhancements of the four series of esters on a polar column at 160°C. $\Delta I = I_{OV-351} - I_{SE-30}$ (Table III). For identification of esters 1-6, see Table I.

The retention increments for chlorine substitution are shown in Tables IV (SE-30) and V (OV-351), and Table VI indicates the separation of the monochloro isomers on both columns. The values observed are comparable to those for the normal-chain esters¹, *i.e.*, approximately 160 i.u. for all isomers on SE-30 and 270 i.u. for the *o*-isomers and 180 i.u. for the *m*- and *p*-isomers on OV-351. The higher values for the *o*-isomers are due to the maximization of the polar effects¹. The retention increment ratios on the two columns presented in Table VI are lower than those with the normal-chain esters¹, indicating that the steric effects are most apparent with the branched-chain esters, as expected⁵.

TABLE IV
RETENTION INCREMENTS FOR CHLORINE SUBSTITUTION ON SE-30 AT VARIOUS COLUMN TEMPERATURES

Compound*	Column (SE-30) temperature					
	Programmed from 100°C at			Isothermal at		
	2°C min ⁻¹	6°C min ⁻¹	10°C min ⁻¹	140°C	160°C	180°C
<i>o</i> /1	162	166	167	162	167	173
<i>o</i> /2	166	169	170	162	167	169
<i>o</i> /3	162	167	168	159	162	163
<i>o</i> /4	166	169	173	160	163	164
<i>o</i> /5	164	167	171	158	161	161
<i>o</i> /6	158	162	165	154	155	156
Average	163	167	169	159	163	164
<i>m</i> /1	158	162	163	158	162	164
<i>m</i> /2	160	163	164	158	163	164
<i>m</i> /3	157	161	162	154	157	161
<i>m</i> /4	159	161	162	153	156	155
<i>m</i> /5	159	162	164	155	157	157
<i>m</i> /6	157	160	162	153	154	155
Average	158	162	163	155	158	159
<i>p</i> /1	159	163	163	159	162	165
<i>p</i> /2	161	165	169	158	163	164
<i>p</i> /3	158	163	165	155	159	162
<i>p</i> /4	162	166	169	157	160	159
<i>p</i> /5	162	166	171	157	159	161
<i>p</i> /6	161	166	166	157	158	159
Average	161	165	167	157	160	162

* Compounds listed in Table I.

Owing to the small amounts of the esters studied the presentation of the retention index increments for the methylene units may not be realistic, but values at 160°C are shown in Table VII. Two series of esters, *viz.*, 1 → 2 → 5 and 1 → 3 → 6, show increments of 82–100 and 100–124 i.u. on SE-30 and 77–91 and 105–128 i.u. on OV-351, respectively. From Table VII it is also evident that the effect due to the replacement of an α -, β - or γ -hydrogen atom with a methyl group in the branched-chain esters is greater than that due to the corresponding replacement in the normal-chain esters. As expected, a retention enhancement always occurred on SE-30 owing to an increase in the molecular weight. On OV-351, however, the additional methyl group introduced into the α -positions of the normal-chain esters causes a reduction in the retention (from -2 to -29 i.u.), whereas such reductions were not observed with the series 3 → 4 (Table VII).

The effects of chain branching with the aliphatic esters⁴⁻⁷ and the chlorine substitution with the normal-chain aromatic esters¹ have been studied and discussed previously, and it is evident that the same trends are also apparent with the branched-chain aromatic esters investigated in this work.

TABLE V

RETENTION INCREMENTS FOR CHLORINE SUBSTITUTION ON OV-351 AT VARIOUS COLUMN TEMPERATURES

Compound*	Column (OV-351) temperature						$\frac{\Delta I_{OV-351}}{\Delta I_{SE-30}^{**}}$ (160°C)
	Programmed from 100°C at			Isothermal at			
	2°C min ⁻¹	6°C min ⁻¹	10°C min ⁻¹	140°C	160°C	180°C	
<i>o</i> /1	276	286	291	264	271	271	1.62
<i>o</i> /2	282	292	285	264	267	275	1.60
<i>o</i> /3	281	289	282	261	264	269	1.63
<i>o</i> /4	279	290	284	260	265	271	1.63
<i>o</i> /5	288	286	282	260	265	267	1.65
<i>o</i> /6	274	280	277	253	255	260	1.65
Average	280	287	284	260	265	269	1.63
<i>m</i> /1	173	194	193	176	186	179	1.15
<i>m</i> /2	186	195	189	170	182	177	1.12
<i>m</i> /3	184	189	187	168	177	173	1.13
<i>m</i> /4	179	185	183	164	174	172	1.12
<i>m</i> /5	193	190	186	169	179	177	1.14
<i>m</i> /6	188	193	187	171	177	179	1.15
Average	184	191	188	170	179	176	1.13
<i>p</i> /1	173	191	193	176	187	181	1.15
<i>p</i> /2	186	195	189	173	184	183	1.13
<i>p</i> /3	188	194	192	174	183	182	1.15
<i>p</i> /4	185	192	190	172	181	181	1.13
<i>p</i> /5	196	192	191	173	182	181	1.14
<i>p</i> /6	192	198	191	176	182	183	1.15
Average	187	194	191	174	183	182	1.14

* Compounds listed in Table I.

** For the retention increments on SE-30, see Table IV.

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TABLE VI
SEPARATION BETWEEN MONOCHLOROBENZOATES ON SE-30 AND OV-351 CAPILLARY COLUMNS AT VARIOUS TEMPERATURES AND THE RETENTION INCREMENT RATIOS BETWEEN THE COLUMNS

Temperature	Column		OV-351						$\frac{\Delta I_{OV-351}}{\Delta I_{SE-30}}$					
	SE-30		ΔI_{b-cl}	ΔI_{m-cl}	ΔI_{p-cl}	$\Delta I_{b-cl} - \Delta I_{m-cl}$	$\Delta I_{p-cl} - \Delta I_{m-cl}$	$\Delta I_{b-cl} - \Delta I_{p-cl}$	$\Delta I_{p-cl} - \Delta I_{m-cl}$	$\frac{\Delta I_{OV-351}}{\Delta I_{SE-30}}$	$\frac{\Delta I_{OV-351}}{\Delta I_{SE-30}}$			
Programmed from 100°C at:														
	2°C min ⁻¹	163	158	161	2	3	280	184	187	93	3	1.72	1.16	1.16
	6°C min ⁻¹	167	162	165	2	3	287	191	194	93	3	1.72	1.18	1.18
10°C min ⁻¹	169	163	167	2	4	284	188	191	93	3	1.68	1.15	1.14	
Isothermal at:														
	140°C	159	155	157	2	2	260	170	174	86	4	1.64	1.10	1.11
	160°C	163	158	160	3	2	265	179	183	82	4	1.63	1.13	1.14
180°C	164	159	162	2	3	269	176	182	87	6	1.64	1.11	1.12	

TABLE VII
RETENTION INCREMENTS FOR METHYLENE UNITS ON SE-30 AND OV-351 AT 160°C

Compound*	Stationary phase							
	SE-30		OV-351					
	ΔI_{CH_2} **	$\Delta I_{\alpha-CH_2}$ ***	$\Delta I_{\beta-CH_2}$ ***	$\Delta I_{\gamma-CH_2}$ ***				
1	—	30	—	—	—	-2	—	—
2	99	29	99	—	91	-3	91	—
3	124	—	54	—	128	—	34	—
4	—	49	74	—	—	22	59	—
5	88	21	—	88	80	-25	—	80
6	107	—	—	65	114	—	—	46
<i>o</i> /1	—	34	—	—	—	-17	—	—
<i>o</i> /2	99	38	99	—	87	-14	87	—
<i>o</i> /3	119	—	58	—	121	—	20	—
<i>o</i> /4	—	50	70	—	—	23	57	—
<i>o</i> /5	82	22	—	82	78	-25	—	78
<i>o</i> /6	100	—	—	60	105	—	—	36
<i>m</i> /1	—	33	—	—	—	-18	—	—
<i>m</i> /2	100	38	100	—	87	-9	87	—
<i>m</i> /3	119	—	57	—	119	—	23	—
<i>m</i> /4	—	48	67	—	—	19	51	—
<i>m</i> /5	82	21	—	82	77	-24	—	77
<i>m</i> /6	104	—	—	62	114	—	—	45
<i>p</i> /1	—	32	—	—	—	-15	—	—
<i>p</i> /2	100	37	100	—	88	-12	88	—
<i>p</i> /3	121	—	58	—	124	—	24	—
<i>p</i> /4	—	50	71	—	—	20	56	—
<i>p</i> /5	84	22	—	84	78	-29	—	78
<i>p</i> /6	106	—	—	65	113	—	—	42

* Compounds listed in Table I.

** Obtained from series 1 → 2 → 5 and 1 → 3 → 6.

*** Obtained by replacement of α -hydrogen atom (ethyl ester¹ → 1, *n*-propyl ester¹ → 2, *n*-butyl ester¹ → 5, 3 → 4), β -hydrogen atom (*n*-propyl ester¹ → 3, 1 → 2, 2 → 4) and γ -hydrogen atom (*n*-butyl ester¹ → 6, 2 → 5) by a methyl group in four homologous series.

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