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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XXXVIII*. CAPILLARY COLUMN STUDIES OF UNSATURATED ESTERS OF BENZOIC AND MONOCHLOROBENZOIC ACIDS

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SUMMARY

Eight lower (C_3–C_6) unsaturated esters of benzoic acid and *ortho-*, *meta-* and *para*-chlorobenzoic acids were separated on low-polarity (SE-30) and polar (OV-351) capillary columns under various operating conditions. The retention data and the Kováts retention indices for all 32 individual components are given and the retention index increments were used to examine the effect of unsaturation and chlorine substitution. The results are compared with those reported previously for the corresponding normal- and branched-chain esters.

INTRODUCTION

Previously, the gas chromatographic (GC) retention behaviour of some lower unsaturated esters of aliphatic carboxylic acids have been reported[1,2], while more recently the GC of lower (C_3–C_6) unsaturated esters of acetic and haloacetic acids[3], propanoic and monochloropropanoic acids[4,5] and butanoic and monochlorobutanoic acids[4,6] and methyl esters of chlorinated propenoic[7–9] and 2-butenoic acids[9] has been studied on capillary columns coated with low-polarity (SE-30, OV-101) and polar (OV-351) stationary phases.

Studies on the GC retention behaviour of aromatic esters are few[10–12], earlier parts of this series showing the behaviour of the C_1–C_{12} normal-chain[11] and C_3–C_5 branched-chain[12] alkyl esters of benzoic acid and monochlorobenzoic acids. Piás and Gascó have reported[13] the retention indices of a wide number of alcohols and their benzoyl derivatives on several low-polarity (SE-30, OV-3, OV-7, OV-11, OV-17 and OV-25) packed columns, the retention behaviour of some unsaturated components also being shown.

This paper describes the isothermal and temperature-programmed capillary GC of eight lower (C_3–C_6) unsaturated esters of benzoic and monochlorobenzoic acids. (*E*)-2-Butenyl esters have not been previously studied in this laboratory, unlike seven other series of esters[3–6]. Low-polarity SE-30 and polar OV-351 quartz capillary

* For Part XXXVII, see ref. 12.

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TABLE I

RETENTION DATA FOR UNSATURATED ESTERS OF BENZOIC, *o*-CHLOROBENZOIC, *m*-CHLOROBENZOIC AND *p*-CHLOROBENZOIC ACIDS, OBTAINED ON SE-30 AND OV-351 CAPILLARY COLUMNS

Conditions as in Figs. 1 and 2.

Peak No.	*Compound*	*Column*						
		SE-30			*OV-351*			
		*ART**	*RRT***	*RRT****	*ART**	*RRT***	*RRT****	*RRT§*
1	2-Propenyl benzoate	9.34	0.74	1.00	12.98	1.99	1.00	1.39
2	2-Propynyl benzoate	9.52	0.75	1.00	16.39	2.52	1.00	1.72
3	3-Butenyl benzoate	11.34	0.89	1.00	14.56	2.24	1.00	1.28
4	1-Methyl-3-butenyl benzoate	11.98	0.94	1.00	14.19	2.18	1.00	1.18
5	(*E*)-2-Butenyl benzoate	12.06	0.95	1.00	15.56	2.39	1.00	1.29
6	4-Pentenyl benzoate	13.65	1.07	1.00	16.59	2.55	1.00	1.22
7	(*E*)-3-Hexenyl benzoate	15.71	1.24	1.00	17.92	2.75	1.00	1.14
8	(*Z*)-3-Hexenyl benzoate	15.90	1.25	1.00	18.30	2.81	1.00	1.15
o/1	2-Propenyl *o*-chlorobenzoate	12.76	1.00	1.37	18.12	2.78	1.40	1.42
o/2	2-Propynyl *o*-chlorobenzoate	12.99	1.02	1.36	21.48	3.30	1.31	1.65
o/3	3-Butenyl *o*-chlorobenzoate	14.78	1.16	1.30	19.64	3.02	1.35	1.33
o/4	1-Methyl-3-butenyl *o*-chlorobenzoate	15.40	1.21	1.29	19.21	2.95	1.35	1.25
o/5	(*E*)-2-Butenyl *o*-chlorobenzoate	15.40	1.21	1.28	20.41	3.14	1.31	1.33
o/6	4-Pentenyl *o*-chlorobenzoate	17.00	1.34	1.25	21.46	3.30	1.29	1.26
o/7	(*E*)-3-Hexenyl *o*-chlorobenzoate	19.10	1.50	1.22	22.91	3.52	1.28	1.20
o/8	(*Z*)-3-Hexenyl *o*-chlorobenzoate	19.20	1.51	1.21	23.17	3.56	1.27	1.21

m/1	2-Propenyl *m*-chlorobenzoate	12.69	1.00	1.36	16.53	2.54	1.27	1.30
m/2	2-Propynyl *m*-chlorobenzoate	12.87	1.01	1.35	19.94	3.06	1.22	1.55
m/3	3-Butenyl *m*-chlorobenzoate	14.70	1.16	1.30	18.08	2.78	1.24	1.23
m/4	1-Methyl-3-butenyl *m*-chlorobenzoate	15.29	1.20	1.28	17.55	2.70	1.24	1.15
m/5	(*E*)-2-Butenyl *m*-chlorobenzoate	15.37	1.21	1.27	18.99	2.92	1.22	1.24
m/6	4-Pentenyl *m*-chlorobenzoate	16.94	1.33	1.24	20.01	3.07	1.21	1.18
m/7	(*E*)-3-Hexenyl *m*-chlorobenzoate	18.86	1.49	1.20	21.19	3.25	1.18	1.12
m/8	(*Z*)-3-Hexenyl *m*-chlorobenzoate	19.11	1.50	1.20	21.60	3.32	1.18	1.13
p/1	2-Propenyl *p*-chlorobenzoate	12.65	1.00	1.35	16.42	2.52	1.27	1.30
p/2	2-Propynyl *p*-chlorobenzoate	12.80	1.01	1.34	19.82	3.04	1.21	1.55
p/3	3-Butenyl *p*-chlorobenzoate	14.72	1.16	1.30	18.00	2.76	1.24	1.22
p/4	1-Methyl-3-butenyl *p*-chlorobenzoate	15.41	1.21	1.29	17.51	2.69	1.23	1.14
p/5	(*E*)-2-Butenyl *p*-chlorobenzoate	15.44	1.22	1.28	18.89	2.90	1.21	1.22
p/6	4-Pentenyl *p*-chlorobenzoate	17.03	1.34	1.25	20.04	3.08	1.21	1.18
p/7	(*E*)-3-Hexenyl *p*-chlorobenzoate	18.95	1.49	1.21	21.20	3.26	1.18	1.12
p/8	(*Z*)-3-Hexenyl *p*-chlorobenzoate	19.19	1.51	1.21	21.61	3.32	1.18	1.13
C_{14}	*n*-Tetradecane	12.70	1.00	–	6.51	1.00	–	0.51

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

** Relative retention time for *n*-tetradecane (C_{14}) taken as 1.00.

*** Relative retention time for the corresponding unsaturated ester of benzoic acid (1–8) taken as 1.00.

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

columns were used. The retention data and the Kováts retention indices for all 32 compounds were determined, together with the retention index increments for the methylene unit, unsaturation and the position of chlorine substitution. The results are compared with those reported previously for aliphatic esters[3–6] and the corresponding normal-[11] and branched-chain[12] aromatic esters.

EXPERIMENTAL

Materials

The unsaturated esters of benzoic (1–8), *ortho*-chlorobenzoic (*o*/1–*o*/8), *meta*-chlorobenzoic (*m*/1–*m*/8) and *para*-chlorobenzoic (*p*/1–*p*/8) acids were prepared from commercial unsaturated alcohols (Fluka, Buchs, Switzerland or Merck–Schuchardt, Darmstadt, F.R.G.) and benzoyl (Merck–Schuchardt) and monochlorobenzoyl chlorides[11] as described earlier[14]. The esters investigated are listed in Table I.

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

Methods

GC analyses were performed 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, 14.0 (SE-30) and 14.9 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 280°C (SE-30) and from 100 to 230°C (OV-351) at 2, 6 and 10°C min^{-1}, and held on OV-351 at 230°C until elution of peaks had ceased. The isothermal data were obtained at 140, 160 and 180°C.

The retention times were measured from the time of sample injection; a Hewlett-Packard Model 3390A reporting integrator was used. The Kováts retention indices were calculated off-line by using two appropriate *n*-alkanes[15]; the dead volumes were determined by the injection of methane.

Each of the four mixtures of the esters were analysed separately, together with appropriate *n*-alkanes, and if overlapping occurred the components were injected separately in turn.

RESULTS AND DISCUSSION

Table I shows the absolute and relative retention times for the unsaturated aromatic esters studied, determined on SE-30 (Fig. 1) and OV-351 (Fig. 2) with temperature programming.

The retention order between the esters on SE-30 is the same as previously reported for the corresponding aliphatic esters[3–6]. The (*E*)-2-butenyl esters, not having been analysed previously, are eluted later than the 1-methyl-3-butenyl esters. The retention order between the isomeric 3-hexenyl esters, *i.e.*, the *E*- (*trans*-) isomer is eluted earlier than the *Z*- (*cis*-) isomer, is reversed as reported previously for these

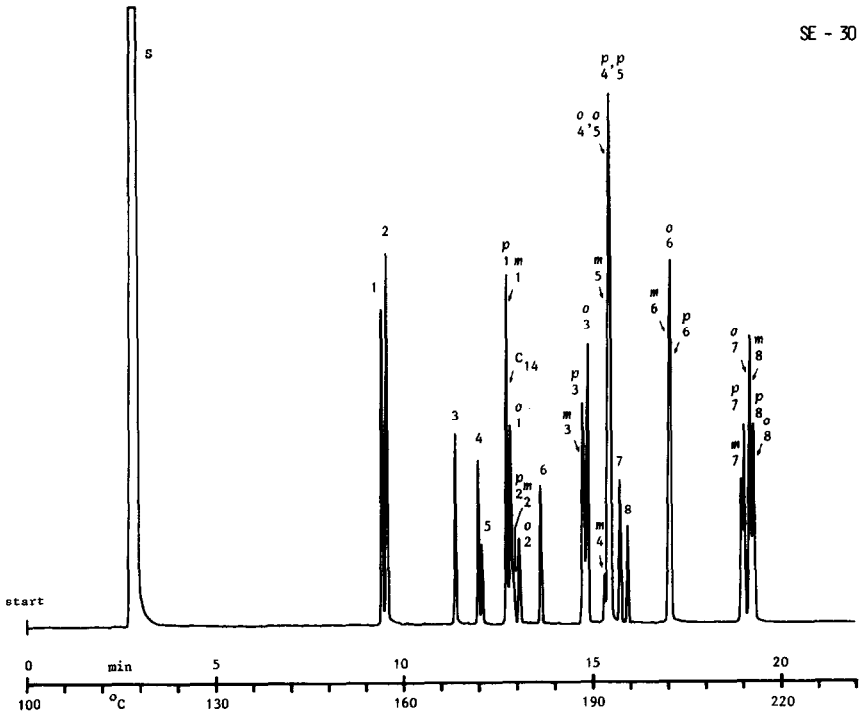

Fig. 1. Chromatogram of a mixture of the unsaturated esters of benzoic (1–8), *o*-chlorobenzoic (*o*/1–*o*/8), *m*-chlorobenzoic (*m*/1–*m*/8) and *p*-chlorobenzoic (*p*/1–*p*/8) acids, separated on an SE-30 quartz capillary column with temperature programming from 100°C at 6°C min^{-1} until elution of peaks had ceased. S = Solvent; C_{14} = *n*-tetradecane; peaks are listed in Table I.

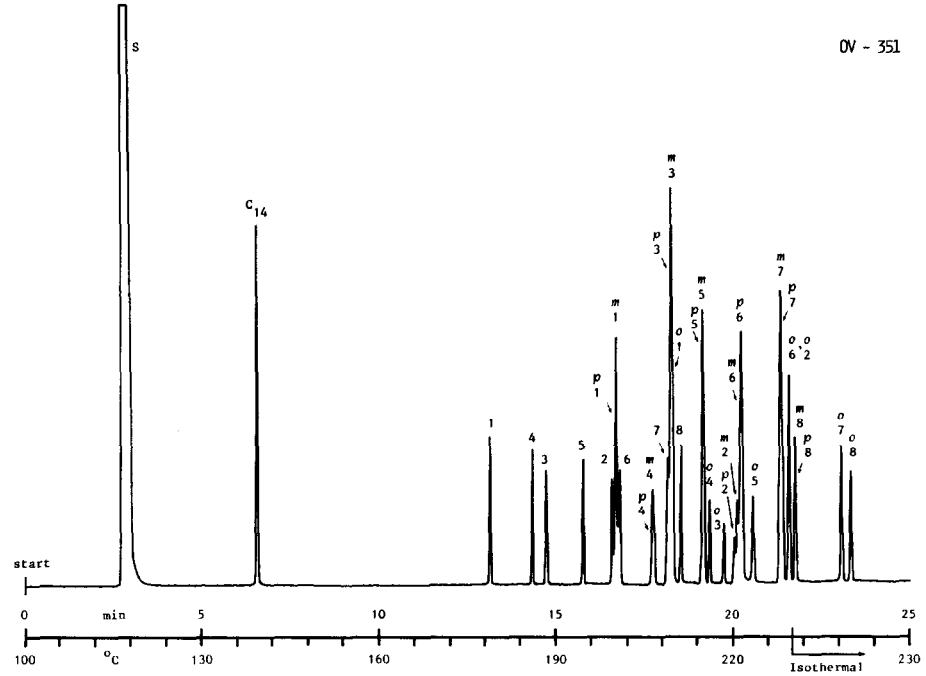

Fig. 2. Chromatogram of the same mixture as in Fig. 1, obtained on an OV-351 quartz capillary column with temperature programming from 100 to 230°C at 6°C min^{-1} and maintained at the final temperature until elution of peaks had ceased. S = Solvent; C_{14} = *n*-tetradecane; peaks are listed in Table I.

benzoic acid esters on a packed SE-30 column[16]. The esters in this work were prepared by using a mixture of 3-hexen-1-ols (*E:Z* isomer = 60:40) and the observed peak areas of the esters show that the aromatic esters are eluted in the same order as the alcohols, as also are the aliphatic esters[3–6].

On OV-351 the 2-propynyl and 4-pentenyl esters are eluted closer together, and generally in the reverse order to the corresponding aliphatic esters[3–6], the ace-

TABLE II

RETENTION INDICES FOR UNSATURATED ESTERS OF BENZOIC, *o*-CHLOROBENZOIC, *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	1231	1236	1239	1241	1248	1260
2	1241	1245	1247	1249	1254	1263
3	1327	1335	1337	1334	1341	1348
4	1357	1365	1366	1363	1368	1374
5	1362	1369	1371	1366	1373	1376
6	1436	1445	1447	1439	1447	1452
7	1535	1545	1546	1536	1544	1549
8	1544	1554	1558	1544	1553	1558
o/1	1396	1403	1407	1399	1410	1420
o/2	1409	1414	1422	1410	1420	1429
o/3	1491	1498	1505	1494	1505	1513
o/4	1522	1529	1533	1522	1535	1540
o/5	1522	1529	1533	1522	1536	1540
o/6	1598	1609	1613	1595	1607	1614
o/7	1703	1714	1721	1696	1707	1715
o/8	1707	1719	1727	1700	1712	1720
m/1	1390	1400	1402	1396	1404	1414
m/2	1401	1408	1411	1404	1411	1420
m/3	1485	1494	1499	1488	1498	1505
m/4	1514	1524	1528	1517	1526	1533
m/5	1519	1528	1533	1521	1530	1536
m/6	1595	1606	1612	1593	1604	1612
m/7	1691	1702	1712	1686	1696	1704
m/8	1701	1715	1724	1695	1706	1715
p/1	1391	1398	1401	1395	1404	1414
p/2	1400	1405	1408	1402	1410	1418
p/3	1488	1495	1501	1490	1500	1508
p/4	1518	1530	1534	1519	1529	1539
p/5	1522	1531	1534	1522	1532	1539
p/6	1600	1610	1614	1596	1606	1616
p/7	1697	1706	1713	1689	1699	1709
p/8	1707	1719	1726	1699	1709	1720

* Compounds are listed in Table I.

tylenic esters being eluted first. The (*E*)-2-butenyl esters are eluted between the 3-butenyl and 2-propynyl esters (Fig. 2).

Tables II and III show the retention indices of the components, obtained at six column temperatures on SE-30 and OV-351, respectively. The retention indices of the esters on both columns at 160°C are illustrated in Fig. 3. The retention enhancements on a polar column, *i.e.*, $I_{OV\text{-}351} - I_{SE\text{-}30}$, are presented in Fig. 4 and

TABLE III

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

*Compound**	*Column (OV-351) 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	1806	1805	1828	1820	1836	1848
2	2003	2004	2026	2004	2017	2026
3	1895	1897	1921	1902	1917	1933
4	1874	1876	1896	1883	1896	1911
5	1951	1956	1981	1956	1973	1986
6	2008	2016	2042	2009	2028	2042
7	2088	2095	2120	2083	2100	2115
8	2108	2117	2144	2101	2116	2136
o/1	2094	2106	2127	2086	2104	2125
o/2	2302	2310	2331	2283	2298	2313
o/3	2183	2196	2217	2167	2186	2209
o/4	2159	2171	2191	2145	2163	2183
o/5	2232	2244	2266	2212	2231	2254
o/6	2295	2309	2329	2269	2290	2313
o/7	2384	2397	2414	2351	2371	2392
o/8	2396	2411	2430	2360	2382	2404
m/1	2004	2012	2034	2001	2020	2039
m/2	2208	2214	2231	2194	2207	2222
m/3	2088	2104	2119	2082	2101	2122
m/4	2065	2073	2091	2057	2074	2093
m/5	2147	2158	2174	2133	2152	2172
m/6	2208	2219	2239	2187	2208	2229
m/7	2282	2293	2312	2255	2276	2296
m/8	2306	2318	2335	2276	2298	2319
p/1	2000	2006	2035	1999	2019	2035
p/2	2203	2207	2231	2190	2204	2217
p/3	2090	2099	2126	2083	2102	2120
p/4	2065	2070	2096	2059	2077	2093
p/5	2143	2152	2178	2131	2150	2168
p/6	2208	2221	2248	2190	2211	2229
p/7	2282	2293	2319	2258	2279	2297
p/8	2305	2318	2342	2277	2299	2320

* Compounds are listed in Table I.

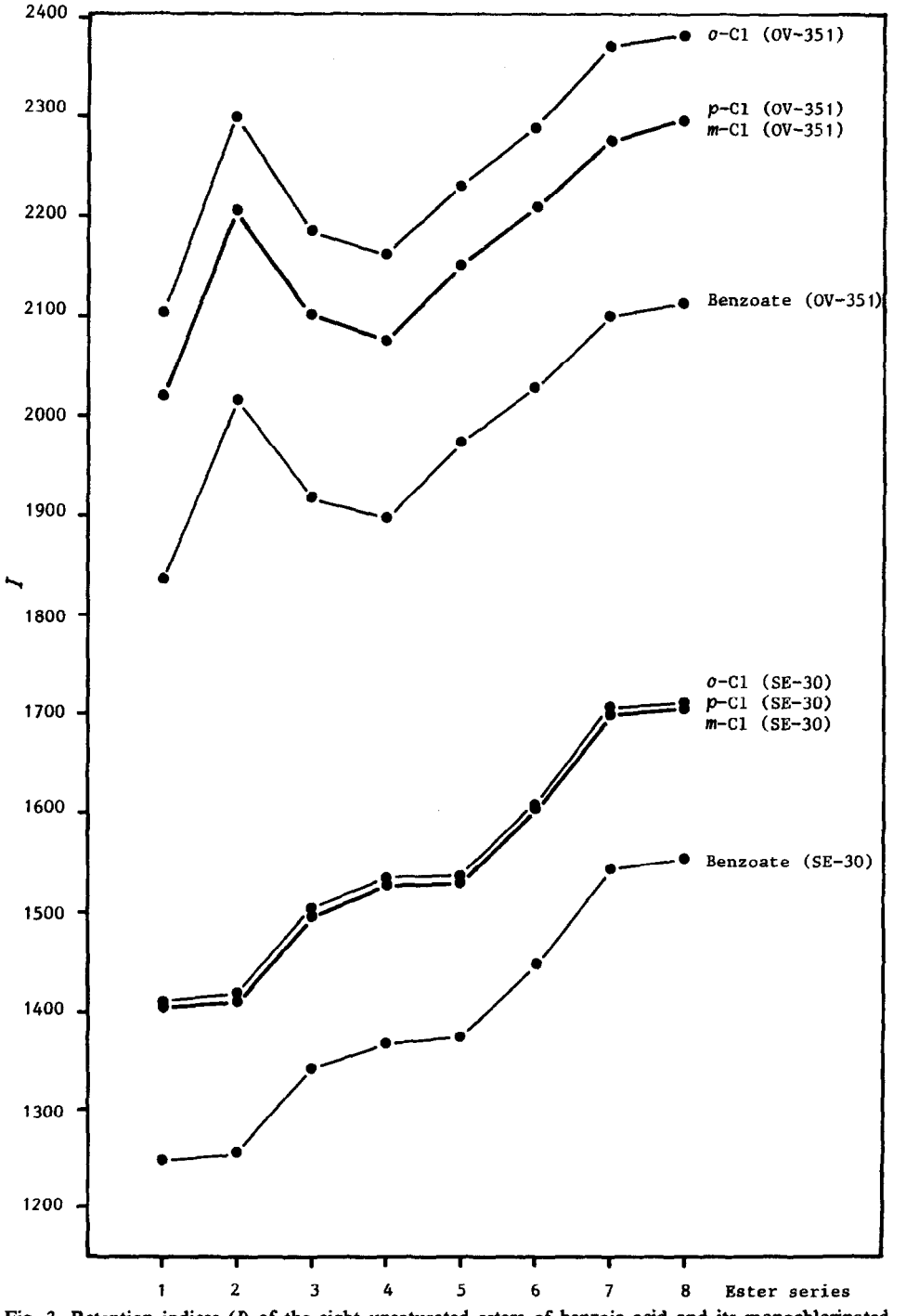

Fig. 3. Retention indices (I) of the eight unsaturated esters of benzoic acid and its monochlorinated derivatives, obtained on SE-30 and OV-351 at 160°C. For identification of the esters (1–8), see Table I.

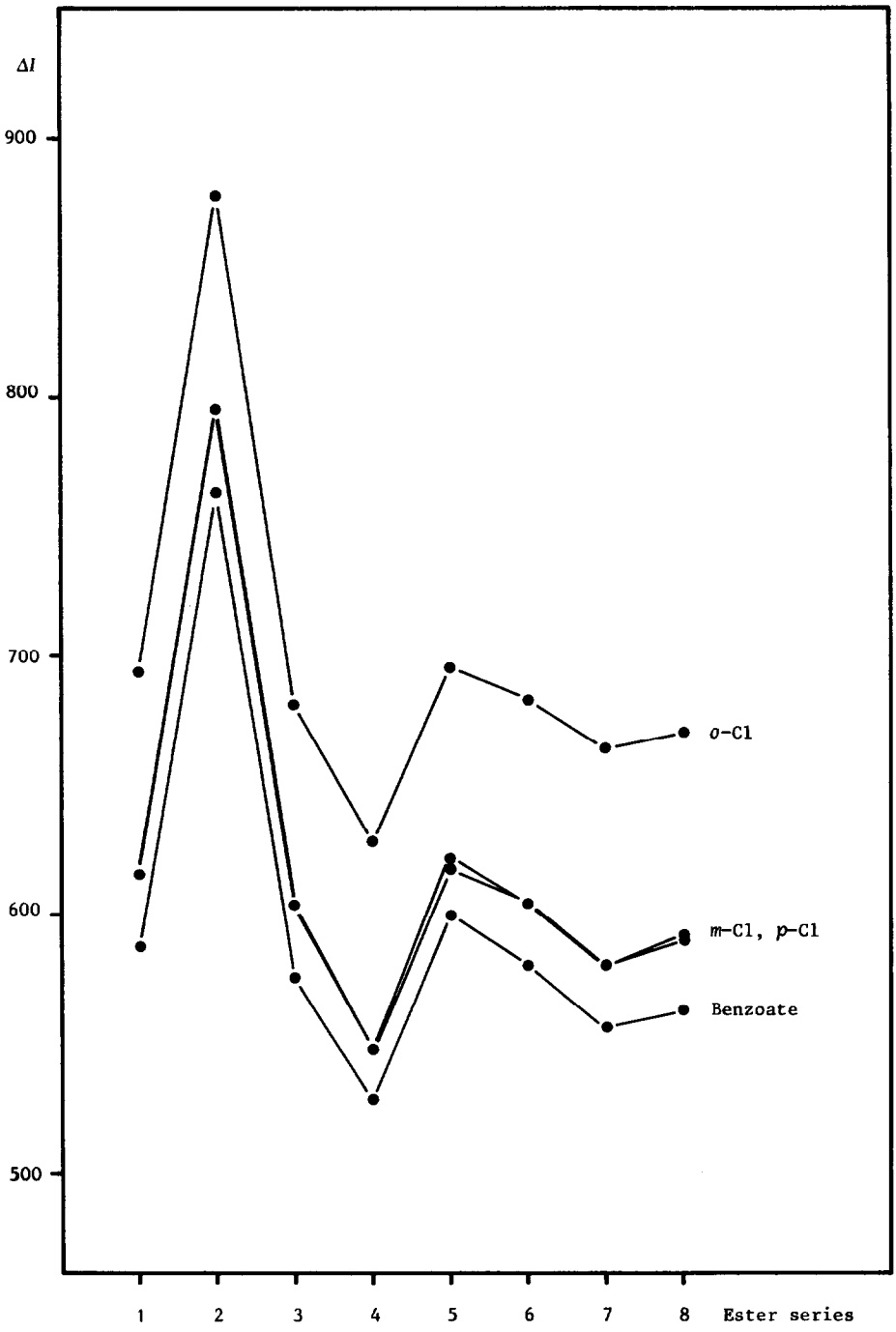

Fig. 4. Retention enhancements of the four series of aromatic esters on a polar column at 160°C. $\Delta I = I_{OV\text{-}351} - I_{SE\text{-}30}$ (Table IV). Esters (1–8) are listed in Table I.

Table IV compares the retention enhancements of the unsaturated esters and their saturated homologues.

On both columns the retention increases with increasing temperature and the elution order of the isomers remains unchanged on SE-30. On OV-351, however, the retention order of the closely related 2-propynyl and 4-pentenyl esters of *m*- (*m*/2, *m*/6) and *p*-chlorobenzoic acids (*p*/2, *p*/6) is changed, *viz.*, at higher temperature the acetylenic esters are eluted first (Table III). The retention order between the isomeric *m*- and *p*-chloro esters seems to vary with temperature and also with the ester series; the variations are more pronounced on a polar column.

TABLE IV

COMPARISON BETWEEN RETENTION ENHANCEMENTS OF SATURATED AND UNSATURATED ESTERS, OCCURRED ON A POLAR COLUMN AT 160°C

Ester series	*Benzoate*		*o-Chlorobenzoate*		*m-Chlorobenzoate*		*p-Chlorobenzoate*	
	ΔI_1***	ΔI_2§	ΔI_1***	ΔI_2§	ΔI_1***	ΔI_2§	ΔI_1***	ΔI_2§
Propyl*	513	–	633	–	547	–	551	–
2-Propenyl	588	75	694	61	616	69	615	64
2-Propynyl	763	250	878	245	796	249	794	243
Butyl*	519	–	624	–	540	–	547	–
3-Butenyl	576	57	681	57	603	63	602	55
(*E*)-2-Butenyl	600	81	695	71	622	82	618	71
Pentyl*	516	–	623	–	539	–	542	–
4-Pentenyl	581	65	683	60	604	65	605	63
Hexyl*	515	–	621	–	537	–	538	–
(*E*)-3-Hexenyl	556	41	664	43	580	43	580	42
(*Z*)-3-Hexenyl	563	48	670	49	592	55	590	52
1-Methylbutyl**	473	–	577	–	495	–	496	–
1-Methyl-3-butenyl	528	55	628	51	548	53	548	52

* From ref. 11.
** From ref. 12.
*** $\Delta I_1 = I_{OV\text{-}351} - I_{SE\text{-}30}$.
§ $\Delta I_2 = \Delta I_1$ (unsaturated ester) $- \Delta I_1$ (saturated ester).

The retention enhancements on a polar column presented in Fig. 4 are highest with the 2-propynyl series (2), being due to the acetylenic and terminal unsaturation[3] and, as expected[12], lowest with a single 1-methyl-3-butenyl (4) branced-chain ester series studied. The disparity between the columns increases with chlorine substitution in the order *p*-Cl $\leqslant$ *m*-Cl $<$ *o*-Cl (Fig. 4). As is evident in Table IV, the unsaturated esters always show higher disparities than their saturated homologues, *viz.*, the alkenyl esters 41–82 retention index units (i.u.) and the most polar 2-propynyl esters 243–250 i.u. The chlorine substitution on the alkyl chain seems to have a negligible effect on the values.

TABLE V

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*
o/1	165	167	168	158	162	160
o/2	168	169	175	161	166	166
o/3	164	163	168	160	164	165
o/4	165	164	167	159	167	166
o/5	160	160	162	156	163	164
o/6	162	164	166	156	160	162
o/7	168	169	175	160	163	166
o/8	163	165	169	156	159	162
Average	164	165	169	158	163	164
m/1	159	164	163	155	156	154
m/2	160	163	164	155	157	157
m/3	158	159	162	154	157	157
m/4	157	159	162	154	158	159
m/5	157	159	162	155	157	160
m/6	159	161	165	154	157	160
m/7	156	157	166	150	152	155
m/8	157	161	166	151	153	157
Average	159	160	164	154	156	157
p/1	160	162	162	154	156	154
p/2	159	160	161	153	156	155
p/3	161	160	164	156	159	160
p/4	161	165	168	156	161	165
p/5	160	162	163	156	159	163
p/6	164	165	167	157	159	164
p/7	162	161	167	153	155	160
p/8	163	165	168	155	156	162
Average	161	163	165	155	158	160

* Compounds are listed in Table I.

The retention increments of chlorine substitution presented in Tables V (SE-30) and VI (OV-351) are in the same ranges as previously reported for the normal-chain[11] and branched-chain[12] homologues, showing minimal enhancement with unsaturation, however. Also, the retention increment ratios between the columns given in Tables VI and VII seem to increase with increasing unsaturation and especially with acetylenic unsaturation (Table VI). This indicates the increased polar effects, as shown previously with the aliphatic esters[5,6].

Series 1 → 3 → 6 and 1 → 5 permit consideration of the retention index increase for the methylene unit, shown in Table VIII. The values are in the ranges 93–128 (SE-30) and 81–137 i.u. (OV-351), again showing little enhancement with unsaturation[11]. The same trend is also found by the replacement of an α-hydrogen

TABLE VI

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

*Compound**	*Column (OV-351) temperature*						$\frac{\Delta I_{OV\text{-}351}}{\Delta I_{SE\text{-}30}}$ at 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*	
o/1	288	301	299	266	268	277	1.65
o/2	299	306	305	279	281	287	1.69
o/3	288	299	296	265	269	276	1.64
o/4	285	295	295	262	267	272	1.60
o/5	281	288	285	256	258	268	1.58
o/6	287	293	287	260	262	271	1.64
o/7	296	302	294	268	271	277	1.66
o/8	288	294	286	259	266	268	1.67
Average	289	297	293	264	268	275	1.64
m/1	198	207	206	181	184	191	1.18
m/2	205	210	205	190	190	196	1.21
m/3	193	207	198	180	184	189	1.17
m/4	191	197	195	174	178	182	1.13
m/5	196	202	193	177	179	186	1.14
m/6	200	203	197	178	180	187	1.15
m/7	194	198	192	172	176	181	1.16
m/8	198	201	191	175	182	183	1.19
Average	197	203	197	178	182	187	1.17
p/1	194	201	207	179	183	187	1.17
p/2	200	203	205	186	187	191	1.20
p/3	195	202	205	181	185	187	1.16
p/4	191	194	200	176	181	182	1.12
p/2	192	196	197	175	177	182	1.11
p/6	200	205	206	181	183	187	1.15
p/7	194	198	199	175	179	182	1.15
p/8	197	201	198	176	183	184	1.17
Average	195	200	202	179	182	185	1.15

* Compounds are listed in Table I.
** For the retention increments on SE-30, see Table III.

atom in the ester series 3 by a methyl group (3 → 4), with respect to the saturated esters[12]. From Table VIII it is also apparent that on SE-30 the retention decreases with increasing unsaturation, while on OV-351 the trend is opposite. The (*E*)-2-butenyl esters on SE-30 are anomalous in this respect, however. These findings are comparable to those of the aliphatic esters studied previously[3].

The effects of chlorine substitution with benzoic acid esters[11,12] and unsaturation with aliphatic esters[3–6] have been examined and discussed previously and it is apparent that the same trends are also evident with the unsaturated aromatic esters studied in this work.

TABLE VII

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

Temperature	*Column*										$\frac{\Delta I_{OV\text{-}351}}{\Delta I_{SE\text{-}30}}$		
	SE-30					*OV-351*							
	$\Delta I_{o\text{-}Cl}$	$\Delta I_{m\text{-}Cl}$	$\Delta I_{p\text{-}Cl}$	$\Delta I_{o\text{-}Cl}-\Delta I_{p\text{-}Cl}$	$\Delta I_{p\text{-}Cl}-\Delta I_{m\text{-}Cl}$	$\Delta I_{o\text{-}Cl}$	$\Delta I_{m\text{-}Cl}$	$\Delta I_{p\text{-}Cl}$	$\Delta I_{o\text{-}Cl}-\Delta I_{p\text{-}Cl}$	$\Delta I_{p\text{-}Cl}-\Delta I_{m\text{-}Cl}$	*o-Cl*	*m-Cl*	*p-Cl*
Programmed from 100°C at:													
2°C min^{-1}	164	159	161	3	2	289	197	195	94	−2	1.76	1.24	1.21
6°C min^{-1}	165	160	163	2	3	297	203	200	97	−3	1.80	1.27	1.23
10°C min^{-1}	169	164	165	4	1	293	197	202	91	5	1.73	1.20	1.22
Isothermal at:													
140°C	158	154	155	3	1	264	178	179	85	1	1.67	1.16	1.15
160°C	163	156	158	5	2	268	182	182	86	0	1.64	1.17	1.15
180°C	164	157	160	4	3	275	187	185	90	−2	1.68	1.19	1.16

TABLE VIII

RETENTION INCREMENTS FOR METHYLENE UNITS AND EFFECTS OF UNSATURATION ON SE-30 AND OV-351 AT 160°C

*Compound**	*Stationary phase*					
	SE-30			*OV-351*		
	ΔI_{CH_2}**	$\Delta I_{\alpha\text{-}CH_2}$***	$\Delta I^{\S}$	ΔI_{CH_2}**	$\Delta I_{\alpha\text{-}CH_2}$***	$\Delta I^{\S}$
1	–		−16	–		59
2			−10			240
3	93	–	−19	81	–	38
4		27	−13		−21	42
5	125		13	137		94
6	106		−11	111		54
7			−14			27
8			−5			43
o/1	–		−12	–		49
o/2			−2			243
o/3	95	–	−15	82	–	42
o/4		30	−7		−23	44
o/5	126		16	127		87
o/6	102		−10	104		50
o/7			−10			33
o/8			−5			44
m/1	–		−14	–		55
m/2			−7			242
m/3	94	–	−19	81	–	44
m/4		28	−12		−27	41
m/5	126		13	132		95
m/6	106		−10	107		55
m/7			−18			25
m/8			−8			47
p/1	–		−15	–		49
p/2			−9			234
p/3	96	–	−18	83	–	37
p/4		29	−11		−25	41
p/5	128		14	131		85
p/6	106		−10	109		53
p/7			−17			25
p/8			−7			45

* Compounds are listed in Table I.

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

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

§ Deviation due to the unsaturation, *i.e.*, $I_{\text{Unsaturated compound}} - I_{\text{Saturated compound}}$[11,12].

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