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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XLVII*. RETENTION INCREMENTS OF SOME LOWER SATURATED BRANCHED-CHAIN, UNSATURATED AND CHLORINATED ESTERS OF BENZOIC, 4-NITROBENZOIC AND 3,5-DINITROBENZOIC ACIDS ON SE-30 AND OV-351 CAPILLARY COLUMNS

ILPO O. O. KORHONEN
Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10 (Finland)
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SUMMARY

The gas chromatographic retention behaviour of C_3–C_5 saturated branched-chain, C_3–C_6 unsaturated, ethyl and 2-chloro-, 2,2-dichloro- and 2,2,2-trichloroethyl esters of benzoic, 4-nitrobenzoic and 3,5-dinitrobenzoic acids on SE-30 and OV-351 capillary columns at several temperatures is reported. The Kováts retention indices for all 54 individual components are given and the retention index increments were used to examine the effects of chain branching, unsaturation and chlorine substitution in the alkyl chain and the effect of nitro substitution in the acyl chain. The results are compared with those reported earlier for the corresponding halobenzoates and *n*-alkyl nitrobenzoates.

INTRODUCTION

Previously, the influence of chain branching[1,2], unsaturation[2,3] and chlorine substitution[4–10] in the alkyl chain of various groups of aliphatic and aromatic esters was investigated by using low-polarity (SE-30) and polar (OV-351) capillary columns with temperature-programmed and/or isothermal operating conditions. The effect of halogen substitution in the acyl chain of various groups of aliphatic esters has been examined and discussed[11–13], the effect with the aromatic esters being shown only by the monochlorobenzoyl[1,3,4,14] and pentafluorobenzoyl[2,15] derivatives, however.

The gas chromatography (GC) of nitro compounds has received little attention[16,17] and the aim of previous studies was generally rather to separate the mixtures on a low-polarity stationary phase than a systematic GC study of the compounds by using both polar and low-polarity columns. The retention increments for nitro substitution with some nitrated polynuclear aromatic hydrocarbons[16] and more recently

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* For Part XLVI, see ref. 18.

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with the C_1–C_{12} *n*-alkyl esters of 4-nitro- and 3,5-dinitrobenzoic acids[17] were examined and discussed by the present author.

This paper reports the Kováts retention indices of six lower (C_3-C_5) branched-chain, eight lower (C_3–C_6) unsaturated and ethyl and 2-chloro-, 2,2-dichloro- and 2,2,2-trichloroethyl esters of benzoic, 4-nitrobenzoic and 3,5-dinitrobenzoic acids, determined on a low-polarity (SE-30) and a highly polar (OV-351) capillary column under various operating temperatures. The separation, mutual retention order and relative retention data of these esters, obtained on both columns with temperature programming, are presented elsewhere[18]. The retention index increments were used to show the effect of variation of the various structural parameters, *i.e.*, branching, unsaturation and chlorine substitution in the alkyl chain and nitro substitution in the acyl chain. The results are compared with those reported earlier for the corresponding esters of halogenated benzoic acids[1–4] and C_1–C_{12} *n*-alkyl esters of 4-nitro- and 3,5-dinitrobenzoic acids[17].

EXPERIMENTAL

Materials

Saturated branched-chain, unsaturated, ethyl and ω-chloroethyl esters of benzoic, 4-nitrobenzoic and 3,5-dinitrobenzoic acids, listed in Table I, were synthesized as described earlier[18].

Mixtures of *n*-alkanes, used as the reference components, were obtained from different commercial sources.

Methods

GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the operating conditions reported in the previous paper[18]. The column temperature with SE-30 was programmed from 100°C at 6°C min^{-1} until elution of peaks had ceased and with OV-351 from 100 to 220°C at 6°C min^{-1} and held at 220°C until elution of peaks had ceased. The isothermal data were determined between 140 and 220°C and are shown in Tables II and III.

The chromatographic data were recorded with a Hewlett-Packard Model 3390A reporting integrator, the retention times being measured from the time of sample injection. The Kováts retention indices were calculated off-line by using two appropriate *n*-alkanes as described earlier[19]. The dead volume was determined by the injection of methane.

Mixtures of (i) branched-chain, (ii) unsaturated and (iii) ethyl and ω-chloroethyl esters of benzoic, 4-nitrobenzoic and 3,5-dinitrobenzoic acids and (iv) *n*-alkanes were chromatographed at each column temperature in turn and the compounds that overlapped[18] were injected separately with the appropriate *n*-alkanes. The retention behaviour of the closely related (*E*)- and (*Z*)-3-hexenyl esters, with overlapping, is due to the lack of the pure isomers, but their elution sequence, (*E*)-isomer < (*Z*)-isomer, is assumed to remain unchanged with different structures of the acyl chain[2,3] on both the polar and low-polarity stationary phases, however.

RESULTS AND DISCUSSION

The Kováts retention indices of the aromatic esters shown in Table I, deter-

TABLE I

ESTERS INVESTIGATED

Ester	*Benzoate*	*4-Nitrobenzoate*	*3,5-Dinitrobenzoate*
Methylethyl	1	4/1	35/1
1-Methylpropyl	2	4/2	35/2
2-Methylpropyl	3	4/3	35/3
1,2-Dimethylpropyl	4	4/4	35/4
1-Methylbutyl	5	4/5	35/5
3-Methylbutyl	6	4/6	35/6
2-Propenyl	7	4/7	35/7
2-Propynyl	8	4/8	35/8
3-Butenyl	9	4/9	35/9
1-Methyl-3-butenyl	10	4/10	35/10
(*E*)-2-Butenyl	11	4/11	35/11
4-Pentenyl	12	4/12	35/12
(*E*)-3-Hexenyl	13	4/13	35/13
(*Z*)-3-Hexenyl	14	4/14	35/14
Ethyl	15	4/15	35/15
2-Chloroethyl	16	4/16	35/16
2,2-Dichloroethyl	17	4/17	35/17
2,2,2-Trichloroethyl	18	4/18	35/18

TABLE II

RETENTION INDICES FOR SATURATED BRANCHED-CHAIN, UNSATURATED AND ETHYL AND ω-CHLOROETHYL ESTERS OF BENZOIC, 4-NITROBENZOIC AND 3,5-DINITROBENZOIC ACIDS, DETERMINED ON AN SE-30 CAPILLARY COLUMN AT A VARIETY OF TEMPERATURES

*Compound**	*SE-30 column temperature*					
	*Programmed***	*E.t. (°C)***	*140°C*	*160°C*	*180°C*	*200°C*
1	1193	128.5	1223	1172	1185	1208
2	1285	137.0	1307	1276	1293	1287
3	1306	139.1	1331	1308	1319	1312
4	1356	144.2	1375	1355	1368	1386
5	1370	145.7	1389	1371	1380	1395
6	1413	150.3	1429	1414	1428	1438
4/1	1528	163.2	1540	1536	1551	1561
4/2	1628	174.6	1633	1634	1652	1668
4/3	1649	176.9	1653	1657	1671	1685
4/4	1708	183.3	1705	1710	1726	1741
4/5	1724	185.1	1721	1724	1740	1753
4/6	1764	189.5	1759	1765	1781	1797
35/1	1785	191.9	1783	1788	1800	1816
35/2	1883	201.9	1872	1878	1891	1905
35/3	1903	204.0	1889	1897	1910	1925
35/4	1953	209.0	1933	1940	1955	1973
35/5	1971	210.9	1955	1961	1974	1989
35/6	2015	215.3	1995	2003	2018	2034

(Continued on p. 66)

TABLE II (*continued*)

*Compound**	*SE-30 column temperature*					
	*Programmed***	*E.t. (°C)***	*140°C*	*160°C*	*180°C*	*200°C*
7	1243	133.1	1254	1221	1263	1261
8	1252	133.9	1262	1235	1265	1261
9	1334	141.9	1343	1327	1352	1361
10	1361	144.8	1370	1355	1380	1395
11	1364	145.1	1375	1359	1381	1395
12	1444	153.8	1447	1442	1463	1476
13	1541	164.7	1540	1536	1553	1557
14	1552	165.9	1549	1547	1563	1568
4/7	1577	168.9	1580	1586	1601	1614
4/8	1586	169.9	1587	1593	1603	1614
4/9	1678	180.1	1675	1681	1698	1711
4/10	1708	183.4	1706	1716	1728	1742
4/11	1709	183.5	1706	1716	1728	1742
4/12	1791	192.5	1783	1793	1804	1820
4/13	1904	204.0	1884	1897	1907	1925
4/14	1905	204.2	1885	1897	1907	1925
35/7	1842	197.8	1833	1844	1851	1865
35/8	1857	199.3	1846	1857	1862	1873
35/9	1938	207.6	1920	1934	1942	1958
35/10	1962	209.9	1940	1951	1961	1978
35/11	1970	210.8	1948	1956	1967	1986
35/12	2054	218.9	2025	2040	2049	2064
35/13	2156	228.5	2119	2134	2144	2160
35/14	2158	228.6	2119	2134	2144	2160
15	1149	125.3	1174	1147	1169	1100
16	1366	145.3	1381	1375	1394	1361
17	1453	154.8	1465	1462	1482	1476
18	1523	162.6	1530	1533	1551	1552
4/15	1491	159.0	1501	1501	1521	1517
4/16	1736	186.5	1725	1732	1753	1764
4/17	1826	196.2	1809	1821	1841	1853
4/18	1891	202.7	1867	1875	1897	1916
35/15	1761	189.3	1752	1762	1777	1783
35/16	2014	215.1	1992	1992	2015	2029
35/17	2104	223.5	2073	2074	2099	2111
35/18	2149	227.8	2105	2116	2136	2152

* Compounds are listed in Table I.

** From 100°C at 6°C min^{-1} until elution of peaks had ceased; E.t. = elution temperature.

mined on the SE-30 and OV-351 capillary columns at a variety of temperatures, are presented in Tables II and III, respectively. Fig. 1 shows the retention index plots for the three series of esters, obtained on both columns at 180°C.

The separations of the mixtures of the esters studied were examined previously on SE-30 and OV-351 with temperature programming[18]; the elution orders reported generally remain unchanged under isothermal conditions, although the mutual sep-

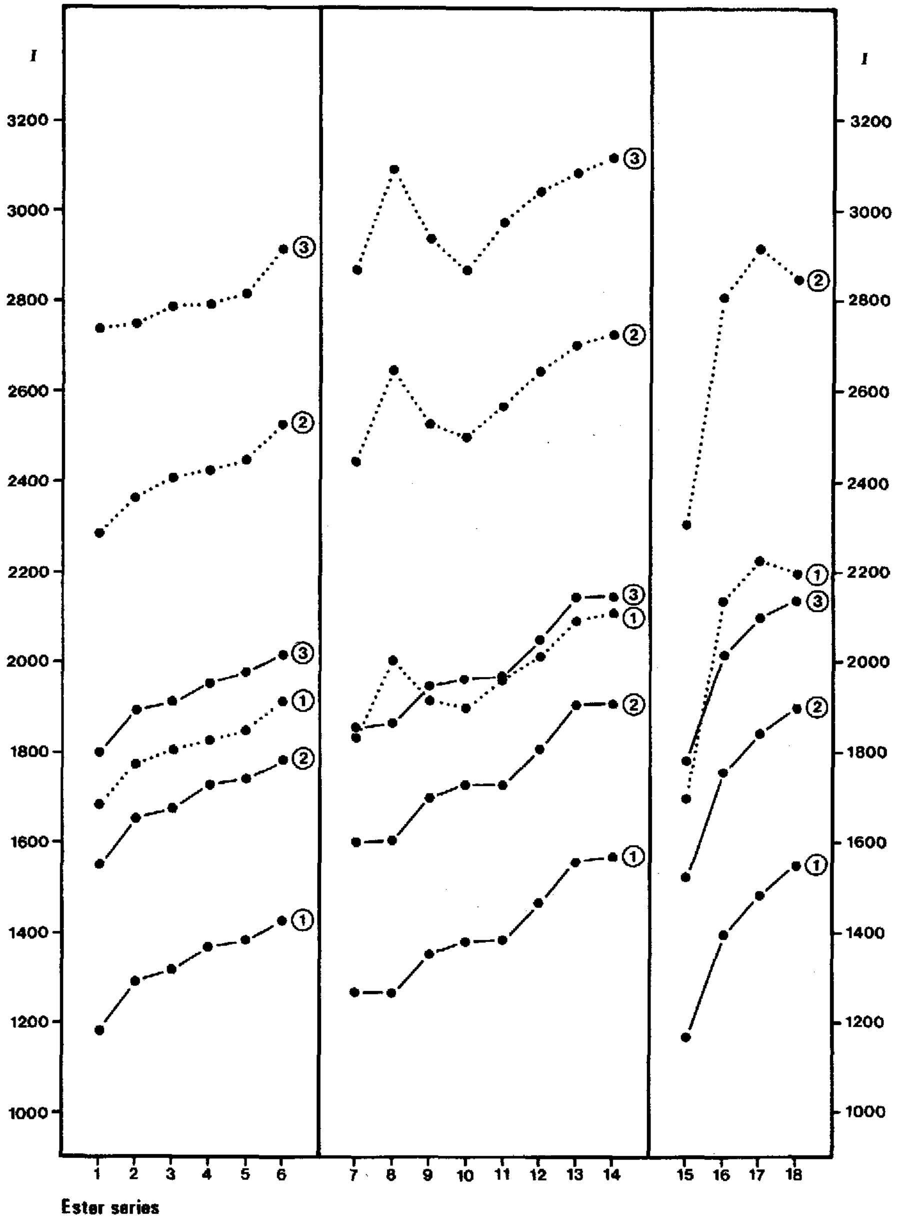

Fig. 1. Plots showing retentions (*I*, i.u.) of saturated branched-chain (1–6), unsaturated (7–14) and ethyl and ω-chloroethyl (15–18) esters of benzoic (curve 1), 4-nitrobenzoic (curve 2) and 3,5-dinitrobenzoic (curve 3) acids, analysed on SE-30 (●—●) and OV-351 (●····●) capillary columns at 180°C (Tables II and III). Esters 1–18 are listed in Table I.

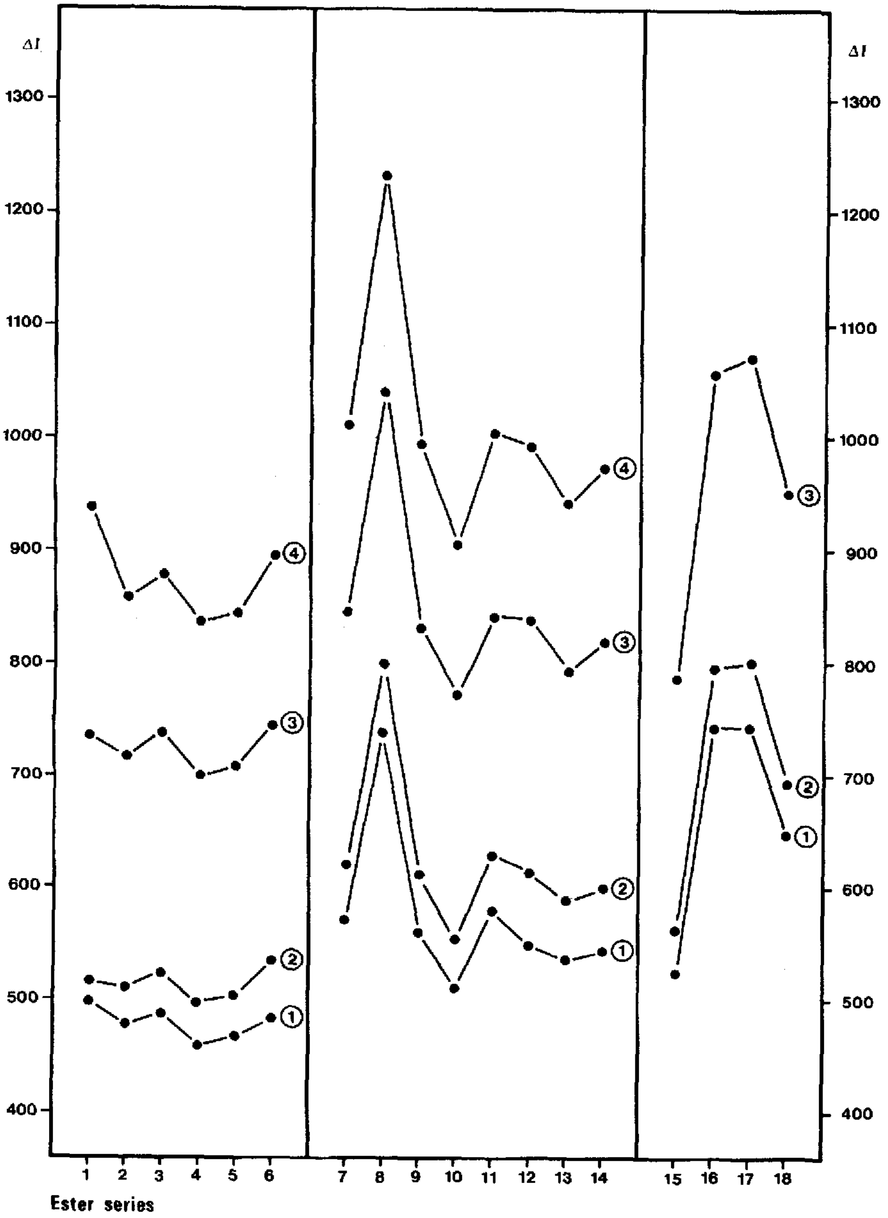

Fig. 2. Retention enhancements of the three series of esters of benzoic (curve 1), 4-chlorobenzoic (curve 2), 4-nitrobenzoic (curve 3) and 3,5-dinitrobenzoic (curve 4) acids on a highly polar column at 180°C. $\Delta I = I_{\text{OV-351}} - I_{\text{SE-30}}$ (Table III). Esters 1–18 are listed in Table I.

aration between the isomers, particularly with the 3,5-dinitro isomers on OV-351, would have been changed.

The enhanced retentions of the esters that occurred on the highly polar OV-

TABLE III

RETENTION INDICES FOR SATURATED BRANCHED-CHAIN, UNSATURATED AND ETHYL AND ω-CHLOROETHYL ESTERS OF BENZOIC, 4-NITROBENZOIC AND 3,5-DINITROBENZOIC ACIDS, DETERMINED ON AN OV-351 CAPILLARY COLUMN AT A VARIETY OF TEMPERATURES

*Compound**	*OV-351 column temperature*					$I_{OV\text{-}351} - I_{SE\text{-}30}$*** *(180°C)*
	*Programmed***	*E.t.(°C)***	*180°C*	*200°C*	*220°C*	
1	1649	124.0	1684	–	–	499
2	1741	131.0	1771	–	–	478
3	1776	134.0	1806	–	–	487
4	1801	136.1	1827	–	–	459
5	1824	138.2	1848	–	–	468
6	1891	144.3	1911	–	–	483
4/1	2256	178.5	2287	2300	2339	736
4/2	2353	186.9	2368	2382	2413	716
4/3	2395	190.7	2409	2424	2454	738
4/4	2413	192.3	2425	2440	2465	699
4/5	2438	194.4	2448	2463	2490	708
4/6	2522	201.5	2526	2547	2567	745
35/1	2746	219/8	2738	2759	2781	938
35/2	2757	220.0	2748	2764	2785	857
35/3	2805	220.0	2788	2804	2825	878
35/4	2806	220.0	2790	2805	2827	835
35/5	2835	220.0	2818	2834	2855	844
35/6	2943	220.0	2913	2934	2954	895
7	1791	135.2	1834	–	–	571
8	1981	152.9	2003	–	–	738
9	1876	143.0	1912	–	–	560
10	1857	141.2	1892	–	–	512
11	1931	148.1	1961	–	–	580
12	1986	153.4	2012	–	–	549
13	2069	161.0	2089	–	–	536
14	2088	162.8	2107	–	–	544
4/7	2428	193.5	2446	2458	2486	845
4/8	2644	211.5	2644	2661	2672	1041
4/9	2522	201.4	2529	2547	2570	831
4/10	2484	198.2	2498	2511	2538	770
4/11	2562	204.8	2569	2586	2606	841
4/12	2638	211.0	2642	2662	2684	838
4/13	2706	216.5	2701	2718	2739	794
4/14	2734	218.8	2725	2745	2768	818
35/7	2880	220.0	2863	2879	2900	1012
35/8	3119	220.0	3094	3105	3125	1232
35/9	2956	220.0	2935	2953	2974	993
35/10	2890	220.0	2866	2883	2905	905
35/11	2997	220.0	2972	2989	3009	1005
35/12	3073	220.0	3042	3060	3085	993
35/13	3116	220.0	3084	3104	3125	940
35/14	3147	220.0	3117	3134	3158	973
15	1654	124.4	1693	1689	1705	524
16	2101	164.0	2137	2137	2159	743

(Continued on p. 70)

TABLE III (*continued*)

Compound[*]	*OV-351 column temperature*					$I_{OV\text{-}351} - I_{SE\text{-}30}$[***] *(180°C)*
	Programmed[*]	*E.t.(°C)*[**]	*180°C*	*200°C*	*220°C*	
17	2192	173.0	2226	2231	2267	744
18	2159	169.7	2199	2205	2239	648
4/15	2275	180.1	2307	2326	2351	786
4/16	2821	220.0	2808	2831	2860	1055
4/17	2940	220.0	2913	2938	2965	1072
4/18	2867	220.0	2847	2873	2904	950
35/15	2749	220.0	2753	2774	2792	976
35/16[§]	—	—	—	—	—	—
35/17[§]	—	—	—	—	—	—
35/18[§]	—	—	—	—	—	—

[*] Compounds are listed in Table I.

[**] From 100 to 220°C at 6°C min^{-1} and held at 220°C until elution of peaks had ceased; E.t. = elution temperature.

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

[§] Compounds are not eluted on OV-351.

351 capillary column are shown in Table III and Fig. 2, and a comparison between the retention enhancements of the saturated and unsaturated esters is presented in Table IV. Lower enhancements are shown by the saturated esters, being increased with olefinic and particularly with acetylenic unsaturation and with chlorine substitution in the alkyl chain following the order benzoate < 4-chlorobenzoate < 4-nitrobenzoate < 3,5-dinitrobenzoate, as is evident in Fig. 2. Earlier results with monochlorobenzoates[1,3,4] showed that the disparity between the enhancements of the 4-nitro and 4-chloro esters are fairly constant with saturated branched-chain (1–6) and olefinic (7, 9–14) esters, *i.e.*, in the range 202–224 retention index units (i.u.), being increased to 242 i.u. with the acetylenic esters (8) and to 257–271 i.u. with the ω-chloroethyl esters (16–18). The corresponding disparities between the 3,5-dinitro and 4-nitro esters are lower, as is evident in Fig. 2. The effect of four different acyl groups on the disparity between the olefinic and saturated homologues is negligible, that between a single acetylenic and saturated ester increasing with increasing size of the acyl group, however (Table IV).

The retention increments for the methylene units and the effects of unsaturation presented in Table V indicate in general the same trends as shown previously with the corresponding esters of monochlorobenzoic acids[1,3]. The increments of the 4-nitro and 4-chloro esters are similar, generally decreasing with the 3,5-dinitro esters, particularly on the highly polar column (Table V).

The effects of chlorine substituents in the alkyl chain are shown in Tables VI (SE-30) and VII (OV-351). The influence of the acyl group on the increments is more pronounced with nitro than chloro substitution[4], particularly on OV-351. Trends from the isothermal data obtained on SE-30 are as follows: (i) the increment for the first chlorine atom increases slightly in the series benzoate → 4-nitrobenzoate → 3,5-dinitrobenzoate (225 → 232 → 238 i.u.); (ii) that for the second chlorine atom

TABLE IV

COMPARISON BETWEEN RETENTION ENHANCEMENTS OF SATURATED AND UNSATURATED ESTERS ON OV-351 AT 180°C

Ester series	*Benzoate*		*4-Chlorobenzoate***		*4-Nitrobenzoate*			*3,5-Dinitrobenzoate*		
	ΔI_1***	ΔI_2§	ΔI_1***	ΔI_2§	ΔI_1***	ΔI_2§	ΔI_3§§	ΔI_1***	ΔI_2§	ΔI_4§§§
Propyl*	543	–	546	–	774	–	228	931	–	157
2-Propenyl	571	28	621	75	845	71	224	1012	81	167
2-Propynyl	738	195	799	253	1041	267	242	1232	301	191
Butyl*	527	–	545	–	768	–	223	923	–	155
3-Butenyl	560	33	612	67	831	63	219	993	70	162
(*E*)-2-Butenyl	580	53	629	84	841	73	212	1005	82	164
Pentyl*	517	–	544	–	767	–	223	922	–	155
4-Pentenyl	549	32	613	69	838	71	225	993	71	155
Hexyl*	514	–	542	–	764	–	222	921	–	157
(*E*)-3-Hexenyl	536	22	588	46	794	30	206	940	19	146
(*Z*)-3-Hexenyl	544	30	600	58	818	54	218	973	52	155
1-Methylbutyl	468	–	503	–	708	–	205	844	–	136
1-Methyl-3-butenyl	512	44	554	51	770	62	216	905	61	135

* From ref. 17.

** From refs. 1, 3 and 14.

*** $\Delta I_1 = I_{\text{OV-351}} - I_{\text{SE-30}}$.

§ $\Delta I_2 = \Delta I_1$ (unsaturated ester) $- \Delta I_1$ (saturated ester).

§§ $\Delta I_3 = \Delta I_1$ (4-nitro ester) $- \Delta I_1$ (4-chloro ester).

§§§ $\Delta I_4 = \Delta I_1$ (3,5-dinitro ester) $- \Delta I_1$ (4-nitro ester).

TABLE V

RETENTION INCREMENTS FOR METHYLENE UNITS AND EFFECTS OF UNSATURATION ON SE-30 AND OV-351 AT 180°C

*Compound**	*Stationary phase*									
	SE-30					*OV-351*				
	ΔI_{CH_2}**	$\Delta I_{\alpha\text{-}CH_2}$***	$\Delta I_{\beta\text{-}CH_2}$***	$\Delta I_{\gamma\text{-}CH_2}$***	ΔI_U§	ΔI_{CH_2}**	$\Delta I_{\alpha\text{-}CH_2}$***	$\Delta I_{\beta\text{-}CH_2}$***	$\Delta I_{\gamma\text{-}CH_2}$***	ΔI_U§
1	—	43	—			—	−22	—		
2	108	45	108	—		87	−20	87	—	
3	134	—	71			122	—	15		
4		49	75				21	56		
5	87	28		87		77	−31		77	
6	109			76		105			32	
4/1	—	50	—			—	−11	—		
4/2	101	50	101	—		81	−8	81	—	
4/3	120	—	69			122	—	33		
4/4		55	74				16	57		
4/5	88	36		88		80	−24		80	
4/6	110			77		117			54	
35/1	—	40	—			—	−1	—		
35/2	91	38	91	—		10	−36	10	—	
35/3	110	—	57			50	—	4		
35/4		45	64				2	42		
35/5	83	24		83		70	−55		70	
35/6	108			68		125			40	

7	–		15	–		43
8			17			212
9	89	–	0	78	–	33
10		28	0		−20	44
11	118		29	127		82
12	111		9	100		41
13			−2			20
14			8			38
4/7	–		−1	–		70
4/8			1			268
4/9	97	–	−6	83	–	57
4/10		30	−12		−31	50
4/11	127		24	123		97
4/12	106		−1	113		70
4/13			0			30
4/14			0			54
35/7	–		−2	–		79
35/8			9			310
35/9	91	–	−8	72	–	62
35/10		19	−13		−69	48
35/11	116		17	109		99
35/12	107		2	107		73
35/13			−2			17
35/14			−2			50

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* Compounds are listed in Table I.

** Obtained from series 1 → 2 → 5, 1 → 3 → 6, 7 → 9 → 12 and 7 → 11.

*** Obtained by replacement of α-hydrogen atom (ethyl ester[17] → 1, *n*-propyl ester[17] → 2, *n*-butyl ester[17] → 5, 3 → 4, 9 → 10), β-hydrogen atom (*n*-propyl ester[17] → 3, 1 → 2, 2 → 4) and γ-hydrogen atom (*n*-butyl ester[17] → 6, 2 → 5) by a methyl group in three series of esters.

§ Deviation due to the unsaturation, *i.e.*, I (unsaturated compound) − I (saturated compound[17]).

TABLE VI

RETENTION INCREMENTS FOR CHLORINE SUBSTITUTION IN THE ALKYL CHAIN OF THE ESTERS, OBTAINED ON SE-30 AT A VARIETY OF TEMPERATURES

*Compound**	*SE-30 column temperature*									
	*Programmed***					*180°C*				
	$\Sigma\Delta I_{nCl}$***	ΔI_{Cl}§	ΔI_{1Cl}§§	ΔI_{2Cl}§§§	ΔI_{3Cl}†	$\Sigma\Delta I_{nCl}$***	ΔI_{Cl}§	ΔI_{1Cl}§§	ΔI_{2Cl}§§§	ΔI_{3Cl}†
16	217	217	217	–	–	225	225	225	–	–
17	304	152	217	87	–	313	157	225	88	–
18	374	125	217	87	70	382	127	225	88	69
4/16	245	245	245	–	–	232	232	232	–	–
4/17	335	168	245	90	–	320	160	232	88	–
4/18	400	133	245	90	65	376	125	232	88	56
35/16	253	253	253	–	–	238	238	238	–	–
35/17	343	172	253	90	–	322	161	238	84	–
35/18	388	129	253	90	45	359	120	238	84	37

* Compounds are listed in Table I.

** From 100°C at 6°C min^{-1} until elution of peaks had ceased.

*** Total retention index increment for the chlorine substitution, *i.e.*, *I* (ω-chloroethyl ester) – *I* (ethyl ester).

§ Retention index increment per chlorine atom, *i.e.*, $\Sigma\Delta I_{nCl}$/number of the chlorine atoms.

§§ Retention index increment for the first chlorine atom, *i.e.*, *I* (monochloroethyl ester) – *I* (ethyl ester).

§§§ Retention index increment for the second chlorine atom, *i.e.*, *I* (dichloroethyl ester) – *I* (monochloroethyl ester).

† Retention index increment for the third chlorine atom, *i.e.*, *I* (trichloroethyl ester) – *I* (dichloroethyl ester).

TABLE VII

RETENTION INCREMENTS FOR CHLORINE SUBSTITUTION IN THE ALKYL CHAIN OF THE ESTERS, OBTAINED ON OV-351 AT A VARIETY OF TEMPERATURES

*Compound**	*OV-351 column temperature*									
	*Programmed***					*180°C*				
	$\Sigma\Delta I_{nCl}$***	ΔI_{Cl}§	ΔI_{1Cl}§§	ΔI_{2Cl}§§§	ΔI_{3Cl}†	$\Sigma\Delta I_{nCl}$***	ΔI_{Cl}§	ΔI_{1Cl}§§	ΔI_{2Cl}§§§	ΔI_{3Cl}†
16	447	447	447	–	–	444	444	444	–	–
17	538	269	447	91	–	533	267	444	89	–
18	505	168	447	91	–33	506	169	444	89	–27
4/16	546	546	546	–	–	521	521	521	–	–
4/17	665	333	546	119	–	606	303	521	85	–
4/18	592	197	546	119	–73	540	180	521	85	–66

*,***, §, §§, §§§, † As in Table VI.

** From 100 to 220°C at 6°C min^{-1} and held at 220°C until elution of peaks had ceased.

TABLE VIII

RETENTION INCREMENTS FOR NITRO SUBSTITUTION ON SE-30 AT VARIOUS COLUMN TEMPERATURES

*Compound**	*SE-30 column temperature*				
	*Programmed***	*140°C*	*160°C*	*180°C*	*200°C*
4/1	335	317	364	366	353
4/2	343	326	358	359	381
4/3	343	322	349	352	373
4/4	352	330	355	358	355
4/5	354	332	353	360	358
4/6	351	330	351	353	359
Average	346	326	355	358	363
4/7	334	326	365	338	353
4/8***	334***	325***	358***	338***	353***
4/9	344	332	354	346	350
4/10	347	336	361	348	347
4/11	345	331	357	347	347
4/12	347	336	351	341	344
4/13	363	344	361	354	368
4/14	353	336	350	344	357
Average	348	334	357	345	352
4/15	342	327	354	352	417
4/16	370	344	357	359	403
4/17	373	344	359	359	377
4/18	368	337	342	346	364
Average	363	338	353	354	390
35/1	592	560	616	615	608
35/2	598	565	602	598	618
35/3	597	558	589	591	613
35/4	597	558	585	587	587
35/5	601	566	590	594	594
35/6	602	566	589	590	596
Average	598	562	595	596	603
35/7	599	579	623	588	604
35/8***	605***	584***	622***	597***	612***
35/9	604	577	607	590	597
35/10	601	570	596	581	583
35/11	606	573	597	586	591
35/12	610	578	598	586	588
35/13	615	579	598	591	603
35/14	606	570	587	581	592
Average	606	575	601	586	594
35/15	612	578	615	608	683
35/16	648	611	617	621	668
35/17	651	608	612	617	635
35/18	626	575	583	585	600
Average	634	593	607	608	647

* Compounds are listed in Table I.

** From 100°C at 6°C min^{-1} until elution peaks had ceased.

*** A single acetylenic ester, not included in average values.

TABLE IX

RETENTION INCREMENTS FOR NITRO SUBSTITUTION ON OV-351 AT VARIOUS COLUMN TEMPERATURES AND INCREMENT RATIOS BETWEEN HIGHLY POLAR AND LOW-POLARITY STATIONARY PHASES

Compound[*]	*OV-351 column temperature*		*OV-351/SE-30*[***]	
	Programmed[**]	*180°C*	*(Programmed)*	*(180°C)*
4/1	607	603	1.81	1.65
4/2	612	597	1.78	1.66
4/3	619	603	1.80	1.71
4/4	612	598	1.74	1.67
4/5	614	600	1.73	1.67
4/6	631	615	1.80	1.74
Average	616	603	1.78	1.68
4/7	637	612	1.91	1.81
4/8[§]	663[§]	641[§]	1.99[§]	1.90[§]
4/9	646	617	1.88	1.78
4/10	627	606	1.81	1.74
4/11	631	608	1.83	1.75
4/12	652	630	1.88	1.85
4/13	637	612	1.75	1.73
4/14	646	618	1.83	1.80
Average	639	615	1.84	1.78
4/15	621	614	1.82	1.74
4/16	720	671	1.95	1.87
4/17	748	687	2.01	1.91
4/18	708	648	1.92	1.87
Average	699	655	1.93	1.85
35/1	1097	1054	1.85	1.71
35/2	1016	977	1.70	1.63
35/3	1029	982	1.72	1.66
35/4	1005	963	1.68	1.64
35/5	1011	970	1.68	1.63
35/6	1052	1002	1.75	1.70
Average	1035	991	1.73	1.66
35/7	1089	1029	1.82	1.75
35/8[§]	1138[§]	1091[§]	1.88[§]	1.83[§]
35/9	1080	1023	1.79	1.73
35/10	1033	974	1.72	1.68
35/11	1066	1011	1.76	1.73
35/12	1087	1030	1.78	1.76
35/13	1047	995	1.70	1.68
35/14	1059	1010	1.75	1.74
Average	1066	1010	1.76	1.72
35/15	1095	1060	1.79	1.74
35/16[§§]	–	–	–	–
35/17[§§]	–	–	–	–
35/18[§§]	–	–	–	–

[*] Compounds are listed in Table I.

[**] From 100 to 220°C at 6°C min^{-1} and held at 220°C until elution of peaks had ceased.

[***] For the retention increments on SE-30, see Table VIII.

[§] A single acetylenic ester, not included in average values.

[§§] Compounds are not eluted on OV-351.

shows a slight decreasing tendency (88 → 88 → 84 i.u.); and (iii) the decrease for the third chlorine atom with nitro substitution is more appreciable (69 → 56 → 37 i.u.). On the highly polar column, where data for the 3,5-dinitro esters are regrettably lacking[18], the effects observed are more pronounced, *i.e.*, (i) 444 → 521 i.u., (ii) 89 → 85 i.u. and (iii) −27 → −66 i.u., as shown in Table VII.

The retention increments of nitro substitution presented in Tables VIII (SE-30) and IX (OV-351) are generally in the same ranges as for the corresponding *n*-alkyl esters[17], the disparity between the increments of three groups of the esters investigated varying with SE-30 column temperature, *i.e.*, at low temperature the saturated branched-chain esters show lower increments than the olefinic esters, but when the column temperature increases the trend becomes opposite. The ω-chloroethyl esters generally show the highest increments with both groups of the nitro esters studied, similarly to the esters of the monochlorobenzoic acids[4]. On the polar column the incremental effects between the three groups of esters are accentuated, as expected, the increments increasing with the series saturated branched-chain < olefinic < acetylenic < ω-chloroethyl esters (Table IX).

The retention increment ratios between the highly polar and low-polarity stationary phases are presented in Table IX. Owing to the proximity of the methyl and carbonyl groups, the values for the branched-chain esters generally are lower than those for the straight-chain esters[17]. The ratios increase with olefinic and particularly acetylenic unsaturation and ω-chlorine substitution owing to the increase in the polar effects, this increase being more pronounced than with the monochlorinated benzoates[1,3,4]. The polar effects are maximized with the 4-nitro derivatives and 2-propynyl and 2,2-dichloroethyl esters. The slightly lower values for the 3,5-dinitro esters might be consistent with increased steric effects due to the bulky NO_2 substituents.

The effect on retention of the individual configurations of the various alkyl groups of aliphatic[12,20] and aromatic chloro esters[1,3,4] have been studied and discussed previously, and it is evident that the same trends are also apparent with the esters investigated in this work. The increased polar effects of nitrobenzoates, relative to chlorobenzoates[1,3,4], might be due to their more electron-deficient ring, which gives rise to an increased interaction between the electron-donating groups of the polar stationary phase[14], shown from the relatively higher retention times on OV-351.

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