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GAS-LIQUID CHROMATOGRAPHIC ANALYSES

XXXV*. CAPILLARY COLUMN STUDIES OF C₁-C₁₂ n-ALKYL ESTERS OF BENZOIC AND MONOCHLOROBENZOIC ACIDS

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SUMMARY

The gas chromatographic retention behaviour of C₁-C₁₂ n-alkyl esters of benzoic acid and monochlorobenzoic acids was studied on low-polarity (SE-30) and polar (OV-351) capillary columns under various isothermal and temperature-programmed operating conditions. The relative retention data, the retention indices and the retention index increments for the methylene unit and the chlorine substituents were determined and the retention order of the individual components in the mixture is discussed. The results are compared with those reported previously for aromatic esters.

INTRODUCTION

The gas chromatographic (GC) retention behaviour of various homologous series of aliphatic esters has been extensively studied, the correlations between retention, structure and boiling point and the effect of varying polarity of the stationary phase being variously examined¹. Same effects of various halogenated esters with substitution in both the acyl and alkyl chains have been investigated by Haken and Korhonen², Komárek *et al.*³ and Korhonen⁴.

Unlike aliphatic esters, there have been few studies on the GC retention behaviour of aromatic esters, as previously reviewed by Haken *et al.*¹. The halogenated aromatic esters analysed by GC have most frequently been the acetate esters of chlorinated aromatics, *viz.*, chlorophenols⁵⁻⁷, chloroguaiacols⁸ and chlorinated 4-hydroxybenzaldehydes⁹. Halogenated benzoic acid isomers have been analysed as their more volatile derivatives, *i.e.*, methyl esters¹⁰⁻¹², and also as the free components^{13,14}. Their retention indices have not been previously reported, however.

In this work we studied the retention behaviour of C₁-C₁₂ n-alkyl esters of benzoic, and *o*-, *m*- and *p*-chlorobenzoic acids on low-polarity (SE-30) and polar (OV-351) capillary columns under various isothermal and temperature-programmed

* For Part XXXIV, see *J. Chromatogr.*, 322 (1985) 71.

conditions. The relative retention data for all 48 individual compounds are given and their elution order on both stationary phases is discussed. The Kováts retention indices were determined, together with the retention index increments due to the methylene unit and the position of chlorine substitution. The results are compared with those reported previously for aromatic esters^{1,6}.

EXPERIMENTAL

Materials

n-Alkyl benzoates and chlorobenzoates were synthesized from the C₁-C₁₂ *n*-alkanols (Fluka, Buchs, Switzerland) and acid chlorides. Benzoyl chloride was a commercial product (Merck-Schuchardt, Darmstadt, F.R.G.), whereas *o*-, *m*- and *p*-chlorobenzoyl chlorides were obtained by the reaction of thionyl chloride (Fluka) with commercial *o*-chlorobenzoic acid (Fluka) and synthetic *m*-¹⁵ and *p*-chlorobenzoic acid¹⁶. The mixture analysed contained suitable amounts of the individual components for the sensitivity of the flame-ionization detector.

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

Methods

GC analyses were performed on a Perkin-Elmer Sigma 3 gas chromatograph. 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 following operating conditions were used: injection and flame-ionization detection temperatures, 275°C; nitrogen (SE-30) and hydrogen (OV-351) carrier gas velocities for methane at 160°C, 14 and 46 cm sec⁻¹, respectively; splitting ratio, 1:30; and chart speed, 10 mm min⁻¹. The column temperature was programmed from 100 to 320°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 the final temperature until elution of peaks had ceased. The isothermal data were obtained at 160, 180 and 200°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*-alkanes¹⁷; the dead volumes for the isothermal runs were determined by the injection of methane.

RESULTS AND DISCUSSION

Chromatograms of a mixture of C₁-C₁₂ *n*-alkyl esters of benzoic (1-12), 2-(*o*-) (2/1-2/12), 3-(*m*-) (3/1-3/12) and 4-(*p*-)chlorobenzoic (4/1-4/12) acids are illustrated in Figs. 1 and 2, separated on SE-30 and OV-351 with temperature programming, respectively. Table I gives the absolute and relative retention times of all 48 individual compounds relative to *n*-tetradecane and relative to the parent esters (= 1.00). The retentions are also expressed as the ratios of the retention times of the compounds on OV-351 divided by those on SE-30.

Fig. 1 shows that on a low-polarity column all alkyl benzoates (1-12) are resolved from the chlorinated isomers, the retention order being C_{*n*}-alkyl *m*-chlorobenzoate ≤ C_{*n*}-alkyl *p*-chlorobenzoate ≤ C_{*n*}-alkyl *o*-chlorobenzoate < C_{*n*+2}-alkyl

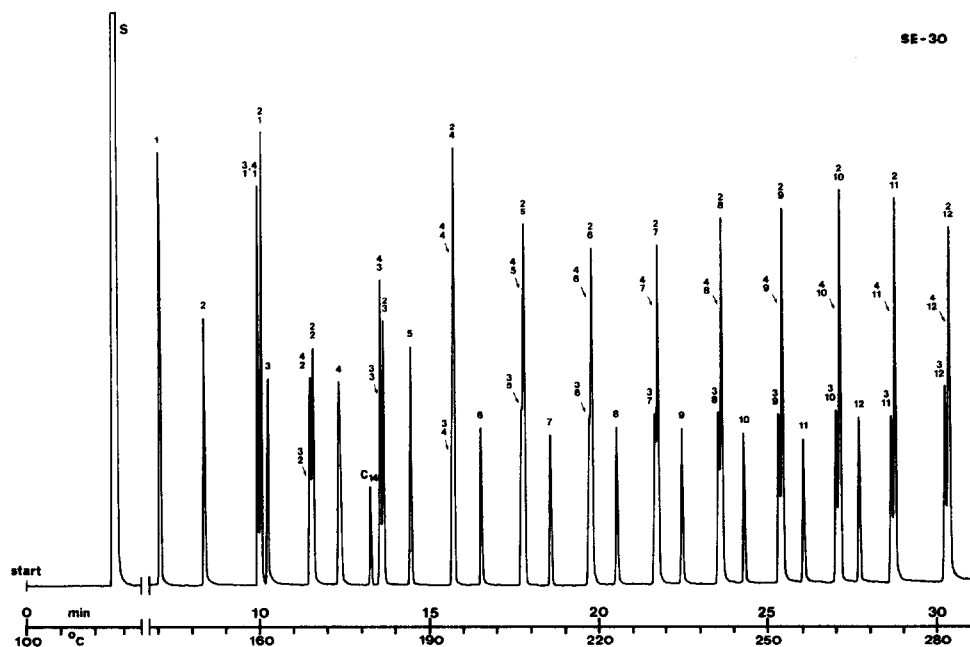


Fig. 1. Chromatogram of a mixture of C_1 - C_{12} *n*-alkyl esters of benzoic (1-12), 2-(*o*-)chlorobenzoic (2/1-2/12), 3-(*m*-)chlorobenzoic (3/1-3/12) and 4-(*p*-)chlorobenzoic (4/1-4/12) acids, separated on an SE-30 quartz capillary column with temperature programming from 100°C at 6°C min⁻¹ until elution of peaks had ceased. S = Solvent; C_{14} = *n*-tetradecane; peaks are identified in Table I.

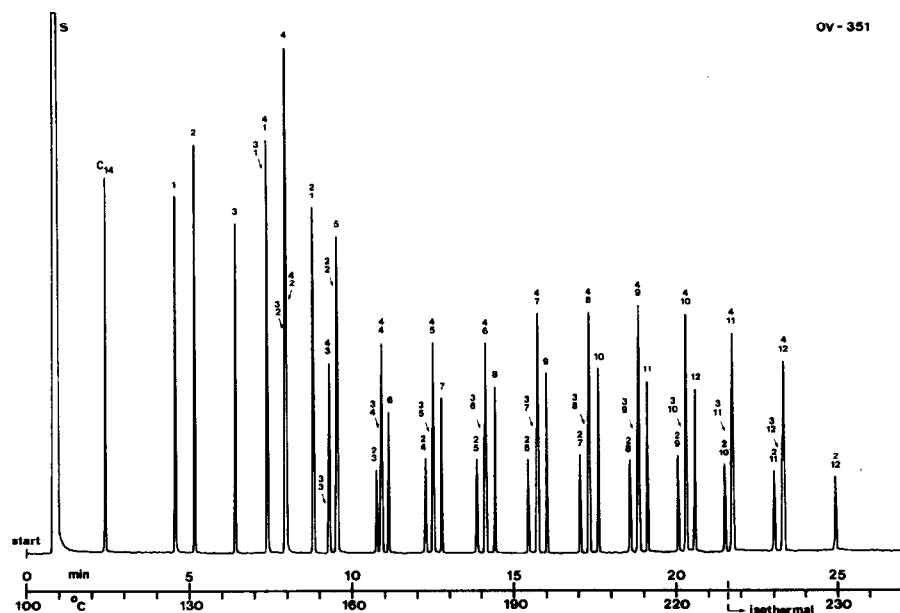


Fig. 2. Chromatogram of the same mixture as in Fig. 1, separated on an OV-351 quartz capillary column with temperature programming from 100 to 230°C at 6°C min⁻¹ and held at the final temperature until elution of peaks had ceased. S = Solvent; C_{14} = *n*-tetradecane; peaks are identified in Table I.

TABLE I

RETENTION DATA FOR C₁-C₁₂ *n*-ALKYL ESTERS OF BENZOIC, *o*-CHLOROBENZOIC, *m*-CHLOROBENZOIC AND *p*-CHLOROBENZOIC ACIDS, DETERMINED 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	Methyl benzoate	7.10	0.53	1.00	4.60	1.88	1.00	0.65
2	Ethyl benzoate	8.40	0.63	1.00	5.22	2.13	1.00	0.62
3	Propyl benzoate	10.29	0.77	1.00	6.46	2.64	1.00	0.63
4	Butyl benzoate	12.37	0.93	1.00	8.00	3.27	1.00	0.65
5	Pentyl benzoate	14.49	1.09	1.00	9.60	3.92	1.00	0.66
6	Hexyl benzoate	16.55	1.24	1.00	11.13	4.54	1.00	0.67
7	Heptyl benzoate	18.60	1.40	1.00	12.79	5.22	1.00	0.69
8	Octyl benzoate	20.57	1.55	1.00	14.42	5.89	1.00	0.70
9	Nonyl benzoate	22.59	1.70	1.00	16.02	6.54	1.00	0.71
10	Decyl benzoate	24.32	1.83	1.00	17.61	7.19	1.00	0.72
11	Undecyl benzoate	26.07	1.96	1.00	19.12	7.80	1.00	0.73
12	Dodecyl benzoate	27.73	2.08	1.00	20.58	8.40	1.00	0.74
2/ 1	Methyl <i>o</i> -chlorobenzoate	10.17	0.76	1.43	8.85	3.61	1.92	0.87
2/ 2	Ethyl <i>o</i> -chlorobenzoate	11.60	0.87	1.38	9.58	3.91	1.84	0.83
2/ 3	Propyl <i>o</i> -chlorobenzoate	13.61	1.02	1.32	10.79	4.40	1.67	0.79
2/ 4	Butyl <i>o</i> -chlorobenzoate	15.75	1.18	1.27	12.29	5.02	1.54	0.78
2/ 5	Pentyl <i>o</i> -chlorobenzoate	17.82	1.34	1.23	13.88	5.67	1.45	0.78
2/ 6	Hexyl <i>o</i> -chlorobenzoate	19.81	1.49	1.20	15.47	6.31	1.39	0.78
2/ 7	Heptyl <i>o</i> -chlorobenzoate	21.78	1.64	1.17	17.05	6.96	1.33	0.78
2/ 8	Octyl <i>o</i> -chlorobenzoate	23.68	1.78	1.15	18.59	7.59	1.29	0.79
2/ 9	Nonyl <i>o</i> -chlorobenzoate	25.45	1.91	1.13	20.08	8.20	1.25	0.79
2/10	Decyl <i>o</i> -chlorobenzoate	27.16	2.04	1.12	21.51	8.78	1.22	0.79
2/11	Undecyl <i>o</i> -chlorobenzoate	28.79	2.16	1.10	23.05	9.41	1.21	0.80
2/12	Dodecyl <i>o</i> -chlorobenzoate	30.39	2.28	1.10	24.94	10.18	1.21	0.92
3/ 1	Methyl <i>m</i> -chlorobenzoate	10.06	0.76	1.42	7.48	3.05	1.63	0.74
3/ 2	Ethyl <i>m</i> -chlorobenzoate	11.52	0.87	1.37	7.99	3.26	1.53	0.69
3/ 3	Propyl <i>m</i> -chlorobenzoate	13.59	1.02	1.32	9.30	3.80	1.44	0.68
3/ 4	Butyl <i>m</i> -chlorobenzoate	15.70	1.18	1.27	10.90	4.45	1.36	0.69
3/ 5	Pentyl <i>m</i> -chlorobenzoate	17.77	1.34	1.23	12.49	5.10	1.30	0.70
3/ 6	Hexyl <i>m</i> -chlorobenzoate	19.75	1.48	1.19	14.10	5.76	1.27	0.71
3/ 7	Heptyl <i>m</i> -chlorobenzoate	21.71	1.63	1.17	15.70	6.41	1.23	0.72
3/ 8	Octyl <i>m</i> -chlorobenzoate	23.58	1.77	1.15	17.29	7.06	1.20	0.73
3/ 9	Nonyl <i>m</i> -chlorobenzoate	25.35	1.91	1.12	18.80	7.67	1.17	0.74
3/10	Decyl <i>m</i> -chlorobenzoate	27.04	2.03	1.11	20.28	8.28	1.15	0.75
3/11	Undecyl <i>m</i> -chlorobenzoate	28.67	2.16	1.10	21.70	8.86	1.13	0.76
3/12	Dodecyl <i>m</i> -chlorobenzoate	30.27	2.28	1.09	23.28	9.50	1.13	0.77
4/ 1	Methyl <i>p</i> -chlorobenzoate	10.08	0.76	1.42	7.50	3.06	1.63	0.74
4/ 2	Ethyl <i>p</i> -chlorobenzoate	11.55	0.87	1.38	8.00	3.27	1.53	0.69
4/ 3	Propyl <i>p</i> -chlorobenzoate	13.62	1.02	1.32	9.32	3.80	1.44	0.68
4/ 4	Butyl <i>p</i> -chlorobenzoate	15.74	1.18	1.27	10.92	4.46	1.37	0.69
4/ 5	Pentyl <i>p</i> -chlorobenzoate	17.79	1.34	1.23	12.52	5.11	1.30	0.70
4/ 6	Hexyl <i>p</i> -chlorobenzoate	19.80	1.49	1.20	14.15	5.78	1.27	0.71
4/ 7	Heptyl <i>p</i> -chlorobenzoate	21.73	1.63	1.17	15.77	6.44	1.23	0.73

TABLE I (continued)

Peak No.	Compound	Column						
		SE-30			OV-351			
		ART*	RRT**	RRT***	ART*	RRT**	RRT***	RRT [§]
4/ 8	Octyl <i>p</i> -chlorobenzoate	23.60	1.77	1.15	17.33	7.07	1.20	0.73
4/ 9	Nonyl <i>p</i> -chlorobenzoate	25.39	1.91	1.12	18.88	7.71	1.18	0.74
4/10	Decyl <i>p</i> -chlorobenzoate	27.10	2.04	1.11	20.32	8.29	1.15	0.75
4/11	Undecyl <i>p</i> -chlorobenzoate	28.74	2.16	1.10	21.76	8.88	1.14	0.76
4/12	Dodecyl <i>p</i> -chlorobenzoate	30.36	2.28	1.09	23.34	9.53	1.13	0.77
C ₁₄	<i>n</i> -Tetradecane	13.30	1.00	—	2.45	1.00	—	0.18

* 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 *n*-alkyl benzoate (1-12) taken as 1.00.

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

benzoate. The chloro isomers generally overlap owing to the close proximity of their boiling points. The C₁-C₃ *o*-chloro esters are resolved from the corresponding *m*- and *p*-chloro isomers, which overlapped, the poorer resolution occurring with the butyl esters. Thereafter, with increasing chain length, the *m*- and *p*-isomers gradually separated, whereas the peaks of the *p*- and *o*-isomers overlapped (Fig. 1). The relative retention times, relative to the parent esters, decrease with increasing chain length, viz., from about 1.40 (methyl esters) to about 1.10 (dodecyl esters); the retentions, relative to *n*-tetradecane, are in the range 0.53-2.08 for alkyl benzoates and 0.76-2.28 for alkyl monochlorobenzoates (Table I).

The earlier elutions of polar components from a polar column are due to the relatively higher carrier gas velocity used (owing to the lower thermal stability of OV-351 with respect to SE-30), the relative retentions increasing, however (Table I). As shown in Fig. 2, *n*-tetradecane is eluted first, and three lower alkyl benzoates appear earlier than the first eluted methyl *m*- and *p*-chlorobenzoates. All the *m*- and *p*-isomers overlap, but the *o*-isomers, having clearly increased retentions, are separable, except for the ethyl ester, which overlaps with pentyl benzoate. Four isomers are in general eluted close together, viz., C_{*n*}-alkyl *o*-chlorobenzoate < C_{*n*+1}-alkyl *m*-chlorobenzoate ≤ C_{*n*+1}-alkyl *p*-chlorobenzoate < C_{*n*+3}-alkyl benzoate (*n* ≥ 3).

It has been previously shown¹¹ that a column packed with 5% Bentone 34 (dimethyldioctadecylammonium bentonite) and 5% trimer acid on acid-washed Chromosorb W separated methyl *m*- and *p*-chlorobenzoates completely, the components being coincident on several polar and low-polarity stationary phases, i.e., Carbowax 20M, SE-30 silicone rubber, neopentyl glycol succinate and Reoplex 400, as they also are in this work on both SE-30 and OV-351 capillary columns.

Retention indices determined on SE-30 and OV-351 at three isothermal and temperature-programmed conditions are presented in Tables II and III, respectively, and plots of the retention of the four homologous series at 160°C on both phases are shown in Fig. 3. Tables IV and V give the incremental effects for the methylene units and chlorine substitution, and the separations between plots of the *o*-, *m*- and *p*-

TABLE II

RETENTION INDICES FOR C₁-C₁₂ *n*-ALKYL 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		
	2°C min ⁻¹	6°C min ⁻¹	10°C min ⁻¹	160°C	180°C	200°C
Methyl benzoate	1071	1078	1081	1097	1100	1101
Ethyl benzoate	1145	1153	1154	1164	1176	1179
Propyl benzoate	1247	1252	1257	1264	1272	1276
Butyl benzoate	1346	1355	1358	1360	1367	1373
Pentyl benzoate	1448	1457	1459	1458	1467	1474
Hexyl benzoate	1550	1558	1565	1558	1566	1573
Heptyl benzoate	1653	1662	1668	1657	1665	1673
Octyl benzoate	1756	1766	1772	1756	1764	1772
Nonyl benzoate	1859	1870	1875	1856	1864	1873
Decyl benzoate	1960	1973	1980	1955	1964	1972
Undecyl benzoate	2064	2075	2085	2055	2063	2071
Dodecyl benzoate	2168	2181	2189	2155	2163	2172
Methyl <i>o</i> -chlorobenzoate	1240	1246	1252	1258	1265	1278
Ethyl <i>o</i> -chlorobenzoate	1309	1317	1321	1327	1334	1342
Propyl <i>o</i> -chlorobenzoate	1408	1417	1423	1422	1432	1437
Butyl <i>o</i> -chlorobenzoate	1509	1518	1527	1520	1529	1540
Pentyl <i>o</i> -chlorobenzoate	1611	1622	1630	1617	1627	1637
Hexyl <i>o</i> -chlorobenzoate	1715	1725	1735	1717	1726	1736
Heptyl <i>o</i> -chlorobenzoate	1818	1831	1841	1816	1826	1836
Octyl <i>o</i> -chlorobenzoate	1922	1936	1941	1915	1925	1936
Nonyl <i>o</i> -chlorobenzoate	2027	2039	2048	2014	2024	2035
Decyl <i>o</i> -chlorobenzoate	2131	2144	2155	2114	2123	2133
Undecyl <i>o</i> -chlorobenzoate	2237	2250	2260	2213	2223	2234
Dodecyl <i>o</i> -chlorobenzoate	2342	2353	2365	2313	2323	2333
Methyl <i>m</i> -chlorobenzoate	1231	1241	1245	1253	1262	1275
Ethyl <i>m</i> -chlorobenzoate	1305	1314	1318	1323	1331	1340
Propyl <i>m</i> -chlorobenzoate	1404	1414	1418	1418	1427	1434
Butyl <i>m</i> -chlorobenzoate	1507	1516	1522	1517	1526	1536
Pentyl <i>m</i> -chlorobenzoate	1608	1619	1626	1614	1624	1632
Hexyl <i>m</i> -chlorobenzoate	1712	1722	1731	1714	1723	1732
Heptyl <i>m</i> -chlorobenzoate	1814	1827	1834	1812	1822	1831
Octyl <i>m</i> -chlorobenzoate	1917	1930	1938	1911	1920	1931
Nonyl <i>m</i> -chlorobenzoate	2021	2033	2043	2010	2019	2029
Decyl <i>m</i> -chlorobenzoate	2125	2136	2147	2109	2118	2128
Undecyl <i>m</i> -chlorobenzoate	2230	2242	2253	2208	2218	2228
Dodecyl <i>m</i> -chlorobenzoate	2334	2345	2362	2308	2317	2327
Methyl <i>p</i> -chlorobenzoate	1234	1241	1246	1254	1262	1275
Ethyl <i>p</i> -chlorobenzoate	1306	1315	1320	1324	1331	1340
Propyl <i>p</i> -chlorobenzoate	1406	1415	1420	1419	1428	1434
Butyl <i>p</i> -chlorobenzoate	1508	1518	1524	1518	1528	1539
Pentyl <i>p</i> -chlorobenzoate	1610	1621	1628	1616	1626	1635
Hexyl <i>p</i> -chlorobenzoate	1714	1725	1734	1716	1726	1735
Heptyl <i>p</i> -chlorobenzoate	1817	1828	1838	1815	1825	1835
Octyl <i>p</i> -chlorobenzoate	1921	1931	1939	1914	1924	1935
Nonyl <i>p</i> -chlorobenzoate	2025	2035	2045	2013	2023	2035
Decyl <i>p</i> -chlorobenzoate	2129	2140	2152	2113	2122	2133
Undecyl <i>p</i> -chlorobenzoate	2234	2246	2257	2212	2222	2233
Dodecyl <i>p</i> -chlorobenzoate	2339	2351	2363	2312	2322	2333

TABLE III

RETENTION INDICES FOR C₁-C₁₂ *n*-ALKYL 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		
	2°C min ⁻¹	6°C min ⁻¹	10°C min ⁻¹	160°C	180°C	200°C
Methyl benzoate	1627	1607	1632	1643	1657	1700
Ethyl benzoate	1668	1655	1676	1685	1709	1725
Propyl benzoate	1753	1745	1757	1777	1791	1818
Butyl benzoate	1847	1849	1856	1879	1884	1913
Pentyl benzoate	1946	1953	1955	1974	1976	2003
Hexyl benzoate	2033	2051	2070	2073	2081	2107
Heptyl benzoate	2142	2158	2176	2174	2184	2207
Octyl benzoate	2249	2266	2284	2273	2287	2304
Nonyl benzoate	2357	2375	2387	2374	2385	2406
Decyl benzoate	2464	2486	2494	2475	2488	2506
Undecyl benzoate	2574	2594	2601	2576	2590	2607
Dodecyl benzoate	2683	2701	2710	2677	2691	2709
Methyl <i>o</i> -chlorobenzoate	1884	1906	1916	1937	1936	1970
Ethyl <i>o</i> -chlorobenzoate	1929	1952	1964	1971	1971	2007
Propyl <i>o</i> -chlorobenzoate	2008	2029	2046	2055	2058	2095
Butyl <i>o</i> -chlorobenzoate	2108	2126	2147	2144	2153	2184
Pentyl <i>o</i> -chlorobenzoate	2211	2229	2248	2240	2249	2283
Hexyl <i>o</i> -chlorobenzoate	2318	2338	2353	2338	2349	2379
Heptyl <i>o</i> -chlorobenzoate	2425	2446	2459	2438	2452	2475
Octyl <i>o</i> -chlorobenzoate	2532	2556	2566	2539	2555	2575
Nonyl <i>o</i> -chlorobenzoate	2642	2665	2676	2639	2657	2676
Decyl <i>o</i> -chlorobenzoate	2751	2771	2787	2740	2756	2778
Undecyl <i>o</i> -chlorobenzoate	2861	2882	2897	2841	2858	2880
Dodecyl <i>o</i> -chlorobenzoate	2972	2993	3002	2943	2963	2983
Methyl <i>m</i> -chlorobenzoate	1801	1816	1834	1854	1864	1886
Ethyl <i>m</i> -chlorobenzoate	1832	1850	1863	1887	1893	1909
Propyl <i>m</i> -chlorobenzoate	1913	1934	1947	1965	1967	1999
Butyl <i>m</i> -chlorobenzoate	2015	2036	2056	2057	2070	2100
Pentyl <i>m</i> -chlorobenzoate	2121	2139	2160	2153	2166	2195
Hexyl <i>m</i> -chlorobenzoate	2225	2244	2264	2251	2263	2295
Heptyl <i>m</i> -chlorobenzoate	2334	2353	2370	2354	2365	2392
Octyl <i>m</i> -chlorobenzoate	2440	2463	2477	2453	2466	2489
Nonyl <i>m</i> -chlorobenzoate	2549	2571	2586	2553	2569	2590
Decyl <i>m</i> -chlorobenzoate	2658	2679	2692	2653	2669	2689
Undecyl <i>m</i> -chlorobenzoate	2766	2786	2802	2753	2768	2792
Dodecyl <i>m</i> -chlorobenzoate	2875	2898	2911	2854	2870	2893
Methyl <i>p</i> -chlorobenzoate	1799	1815	1834	1849	1859	1891
Ethyl <i>p</i> -chlorobenzoate	1830	1849	1863	1885	1893	1917
Propyl <i>p</i> -chlorobenzoate	1912	1934	1948	1970	1974	2001
Butyl <i>p</i> -chlorobenzoate	2017	2038	2057	2065	2073	2102
Pentyl <i>p</i> -chlorobenzoate	2124	2141	2162	2158	2170	2198
Hexyl <i>p</i> -chlorobenzoate	2229	2248	2266	2254	2268	2297
Heptyl <i>p</i> -chlorobenzoate	2338	2358	2372	2356	2369	2394
Octyl <i>p</i> -chlorobenzoate	2444	2466	2479	2456	2470	2493
Nonyl <i>p</i> -chlorobenzoate	2552	2577	2587	2555	2572	2594
Decyl <i>p</i> -chlorobenzoate	2661	2682	2696	2656	2672	2694
Undecyl <i>p</i> -chlorobenzoate	2770	2790	2805	2755	2772	2796
Dodecyl <i>p</i> -chlorobenzoate	2880	2902	2914	2856	2874	2898

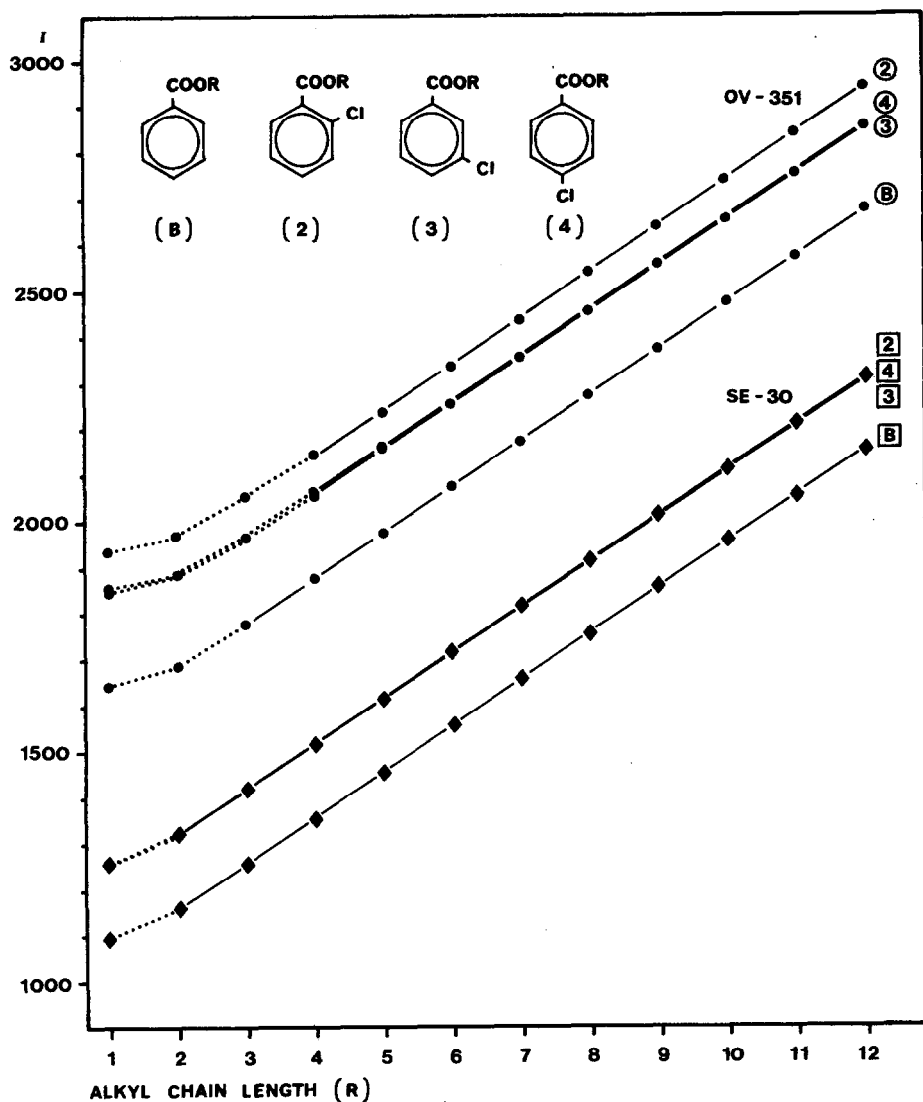


Fig. 3. Retention plots of C_1 - C_{12} *n*-alkyl benzoates (B), 2-(*o*-)chlorobenzoates (2), 3-(*m*-)chlorobenzoates (3) and 4-(*p*-)chlorobenzoates (4) on SE-30 and OV-351 capillary columns at 160°C. *I* = Retention index units.

chloro isomers on both columns, with the retention increment ratios, are shown in Table VI.

On both columns the retention generally increases with increasing temperature and the elution order of the individual components mentioned above remains unchanged. The retention is noticeably increased on OV-351 with respect to SE-30 (Fig. 3); for example at 160°C 513-546 retention index units (i.u.) with *n*-alkyl benzoates, 621-679 i.u. with *n*-alkyl *o*-chlorobenzoates, 537-601 i.u. with *n*-alkyl *m*-chlorobenzoates and 538-595 i.u. with *n*-alkyl *p*-chlorobenzoates (Tables II and III). The re-

TABLE IV

INCREMENTAL EFFECTS FOR METHYLENE UNITS AND CHLORINE SUBSTITUTION ON SE-30 AT VARIOUS COLUMN TEMPERATURES

<i>n</i> -Alkyl ester chain length	Column (OV-351) temperature											
	Programmed from 100°C at						Isothermal					
	2°C min ⁻¹		6°C min ⁻¹		10°C min ⁻¹		160°C		180°C		200°C	
	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}
Benzoate												
C ₁	—	—	—	—	—	—	—	—	—	—	—	—
C ₂	74**	—	75**	—	73**	—	67**	—	76**	—	78**	—
C ₃	102	99	103	99	103	100	100	96	96	95	97	97
C ₄	99	103	103	103	101	96	96	95	95	95	97	97
C ₅	102	102	102	102	101	98	98	100	100	100	101	101
C ₆	102	101	101	101	106	100	100	99	99	99	99	99
C ₇	103	104	104	104	103	99	99	99	99	99	100	100
C ₈	103	104	104	104	104	99	99	99	99	99	99	99
C ₉	103	104	104	104	103	100	100	100	100	100	101	101
C ₁₀	101	103	103	103	105	99	99	100	100	100	99	99
C ₁₁	104	102	102	102	105	100	100	99	99	99	99	99
C ₁₂	104	106	106	106	104	100	100	100	100	100	101	101
C ₁ -C ₁₂	102*	—	103*	—	104*	—	99*	—	99*	—	99*	—
<i>o</i>-Chlorobenzoate												
C ₁	—	169	—	168	—	171	—	161	—	165	—	177**
C ₂	69**	164	71**	164	69*	167	69**	163	69**	158	64**	163
C ₃	99	161	100	165	102	166	95	158	98	160	95	161
C ₄	101	163	101	163	104	169	98	160	97	162	103	167
C ₅	102	163	104	165	103	171	97	159	98	160	97	163
C ₆	104	165	103	167	105	170	100	159	99	160	99	163
C ₇	103	165	106	169	106	173	99	159	100	161	100	163
C ₈	104	166	105	170	100	169	99	159	99	161	100	164
C ₉	105	168	103	169	107	173	99	158	99	160	99	162
C ₁₀	104	171	105	171	107	175	100	159	99	159	98	161
C ₁₁	106	173	106	175	105	175	99	158	100	160	101	163
C ₁₂	105	174	103	172	105	176	100	158	100	160	99	161
C ₁ -C ₁₂	103*	167*	104*	168*	104*	171*	99*	159*	99*	161*	99*	163*
<i>m</i>-Chlorobenzoate												
C ₁	—	160	—	163	—	164	—	156	—	162	—	174
C ₂	74**	160	73**	161	73*	164	70**	159	69**	155	65**	161
C ₃	99	157	100	162	100	161	95	154	96	155	94	158
C ₄	103	161	102	161	104	164	99	157	99	159	102	163
C ₅	101	160	103	162	104	167	97	156	98	157	96	158
C ₆	104	162	103	164	105	166	100	156	99	157	100	159
C ₇	102	161	105	165	103	166	98	155	99	157	99	158
C ₈	103	161	103	164	104	166	99	155	98	156	100	159
C ₉	104	162	103	163	105	168	99	154	99	155	98	156
C ₁₀	104	165	103	163	104	167	99	154	99	154	99	156
C ₁₁	105	166	106	167	106	168	99	153	100	155	100	157
C ₁₂	104	166	103	164	109	173	100	153	99	154	99	155
C ₁ -C ₁₂	103*	162*	103*	163*	104*	166*	99*	155*	99*	156*	99*	158*

(Continued on p. 92)

TABLE IV (continued)

<i>n</i> -Alkyl ester chain length	Column (OV-351) temperature											
	Programmed from 100°C at						Isothermal					
	2°C min ⁻¹		6°C min ⁻¹		10°C min ⁻¹		160°C		180°C		200°C	
	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}
<i>p</i> -Chlorobenzoate												
C ₁	—	163	—	163	—	165	—	157	—	162	—	174**
C ₂	72**	161	74**	162	74**	166	70**	160	69**	155	65**	161
C ₃	100	159	100	163	100	163	95	155	97	156	94	158
C ₄	102	162	103	163	104	166	99	158	100	161	105	166
C ₅	102	162	103	164	104	169	98	158	98	159	96	161
C ₆	104	164	104	167	106	169	100	158	100	160	100	162
C ₇	103	164	103	166	104	170	99	158	99	160	100	162
C ₈	104	165	103	165	101	167	99	158	99	160	100	163
C ₉	104	166	104	165	106	170	99	157	99	159	100	162
C ₁₀	104	169	105	167	107	172	100	158	99	158	98	161
C ₁₁	105	170	106	171	105	172	99	157	100	159	100	162
C ₁₂	105	171	106	170	106	174	100	157	100	159	100	161
C ₁ -C ₁₂	103*	165*	104*	166*	104*	169*	99*	158*	99*	159*	99*	162*

* Average value.

** Not included in average values.

tention index increase effected by phase polarity is much larger for aromatic esters than for aliphatic esters¹⁸ with the same molecular weight, the same trend having been previously reported with the pair *n*-butyl hexanoate and *n*-propyl benzoate¹.

The retention indices of non-chlorinated benzoates obtained on SE-30 are in good agreement with those reported earlier on packed columns coated with SE-30^{1,19}; the values for C₁-C₁₀ *n*-alkyl benzoates at 160°C vary only 0-3 i.u. from the values of Pías and Gascó¹⁹ obtained at 140°C. The retention indices of C₁-C₄ esters on OV-351 vary more, being between the values obtained by Haken *et al.*¹ on packed columns coated with QF-1 and Silar-10C acceptor stationary phases.

The retention index increments for methylene groups in all four series are close to 100 i.u. on both columns, as is evident from Tables IV and V. The temperature-programmed runs show about 5 i.u. higher increments than the isothermal runs and it is evident that the chlorine substitution in the acid group has a negligible effect on the alkyl chain.

The incremental effects of chlorine substitution generally increase with increasing temperature, the programmed runs showing the highest average increments (Tables IV-VI). On the low-polarity SE-30 phase the retention enhancement is approximately 160 i.u. and the disparity between the monochloro isomers is only about 5 i.u. at most. On polar OV-351 the elution order of the isomeric esters remained unchanged and it is apparent that the increments are increased, *viz.*, under isothermal conditions by about 30 i.u. for the *m*- and *p*-chloro isomers and approximately 110 i.u. for the *o*-chloro isomers. The disparity between the *m*- and *p*-isomers is small on both OV-351 and on SE-30. The retention of the corresponding *o*-isomers is markedly

TABLE V

INCREMENTAL EFFECTS FOR METHYLENE UNITS AND CHLORINE SUBSTITUTION ON OV-351 AT VARIOUS COLUMN TEMPERATURES

<i>n</i> -Alkyl ester chain length	Column (SE-30) temperature											
	Programmed from 100°C at						Isothermal					
	2°C min ⁻¹		6°C min ⁻¹		10°C min ⁻¹		160°C		180°C		200°C	
	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}	ΔI_{CH_2}	ΔI_{Cl}
Benzoate												
C ₁	—	—	—	—	—	—	—	—	—	—	—	—
C ₂	41**	—	48**	—	44**	—	42**	—	52**	—	25**	—
C ₃	85	—	90	—	81	—	92	—	82	—	93	—
C ₄	94	—	104	—	99	—	102	—	93	—	95	—
C ₅	99	—	104	—	99	—	95	—	92	—	90	—
C ₆	87	—	98	—	115	—	99	—	105	—	104	—
C ₇	109	—	107	—	106	—	101	—	103	—	100	—
C ₈	107	—	108	—	108	—	99	—	103	—	97	—
C ₉	108	—	109	—	103	—	101	—	98	—	102	—
C ₁₀	107	—	111	—	107	—	101	—	103	—	100	—
C ₁₁	110	—	108	—	107	—	101	—	102	—	101	—
C ₁₂	109	—	107	—	109	—	101	—	101	—	102	—
C ₁ -C ₁₂	102*	—	105*	—	103*	—	99*	—	98*	—	98*	—
<i>o</i>-Chlorobenzoate												
C ₁	—	257	—	299	—	284	—	294	—	279	—	270
C ₂	45**	261	46**	297	48**	288	34**	286	35**	262	37*	282
C ₃	79	255	77	284	82	289	84	278	87	267	88	277
C ₄	100	261	97	277	101	291	89	265	95	269	89	271
C ₅	103	265	103	276	101	293	96	266	96	273	99	280
C ₆	107	285	109	287	105	283	98	265	100	268	96	272
C ₇	107	283	108	288	106	283	100	264	103	268	96	268
C ₈	107	283	110	290	107	282	101	266	103	268	100	271
C ₉	110	285	109	290	110	289	100	265	102	272	101	270
C ₁₀	109	287	106	285	111	293	101	265	99	268	102	272
C ₁₁	110	287	111	288	110	296	101	265	102	268	102	273
C ₁₂	111	289	111	292	105	292	102	266	105	272	103	274
C ₁ -C ₁₂	104*	275*	104*	288*	104*	289*	97*	270*	99*	270*	98*	273*
<i>m</i>-Chlorobenzoate												
C ₁	—	174	—	209	—	202	—	211	—	207	—	186
C ₂	31**	164	34**	195	29**	187	33**	202	29**	184	23**	184
C ₃	81	160	84	189	84	190	78	188	74	176	90	181
C ₄	102	168	102	187	109	200	92	178	103	186	101	187
C ₅	106	175	103	186	104	205	96	179	96	190	95	192
C ₆	104	192	105	193	104	194	98	178	97	182	100	188
C ₇	109	192	109	195	106	194	103	180	102	181	97	185
C ₈	106	191	110	197	107	193	99	180	101	179	97	185
C ₉	109	192	108	196	109	199	100	179	103	184	101	184
C ₁₀	109	194	108	193	106	198	100	178	100	181	99	183
C ₁₁	108	192	107	192	110	201	100	177	99	178	103	185
C ₁₂	109	192	112	197	109	201	101	177	102	179	101	184
C ₁ -C ₁₂	104*	182*	105*	194*	105*	197*	97*	184*	98*	184*	98*	185*

(Continued on p. 94)

TABLE V (continued)

<i>n</i> -Alkyl ester chain length	Column (SE-30) temperature											
	Programmed from 100°C at						Isothermal					
	2°C min ⁻¹		6°C min ⁻¹		10°C min ⁻¹		160°C		180°C		200°C	
	ΔI_{CB_2}	ΔI_{Cl}	ΔI_{CB_2}	ΔI_{Cl}	ΔI_{CB_2}	ΔI_{Cl}	ΔI_{CB_2}	ΔI_{Cl}	ΔI_{CB_2}	ΔI_{Cl}	ΔI_{CB_2}	ΔI_{Cl}
<i>p</i> -Chlorobenzoate												
C ₁	—	172	—	208	—	202	—	206	—	202	—	191
C ₂	31**	162	34**	194	29**	187	36**	200	34**	184	26**	192
C ₃	82	159	85	189	85	191	85	193	81	183	84	183
C ₄	105	170	104	189	109	201	95	186	99	189	101	189
C ₅	107	178	103	188	105	207	93	184	97	194	96	195
C ₆	105	196	107	197	104	196	96	181	98	187	99	190
C ₇	109	196	110	200	106	196	102	182	101	185	97	187
C ₈	106	195	108	200	107	195	100	183	101	183	99	189
C ₉	108	195	111	202	108	200	99	181	102	187	101	188
C ₁₀	109	197	105	196	109	202	101	181	100	184	100	188
C ₁₁	109	196	108	196	109	204	99	179	100	182	102	189
C ₁₂	110	197	112	201	109	204	101	179	102	183	102	189
C ₁ -C ₁₂	105*	184*	105*	197*	105*	199*	97*	186**	98*	187*	98*	189*

* Average value.

** Not included in average values.

increased, however, owing to the maximization of the polar effects, shown from the relatively higher retention increment ratios given in Table VI. This behaviour can be explained on the basis of electromerism¹. The decrease in electron density occurring in the phenyl ring with *o*-substitution is more pronounced than that with *m*- and *p*-substitution, the increased interaction between this more electron-deficient ring and the electron-donating groups of the phase giving rise to the relatively higher retentions of the *o*-chloro isomers on OV-351. This effect with the *m*- and *p*-chloro isomers seems to be similar, *i.e.*, the retention behaviour between the isomeric esters remains unchanged with increasing column polarity.

It has been previously reported¹ that on low-polarity SE-30 and OV-25 stationary phases benzoate esters, probably owing to their increased polar character, exhibit higher retention than the isomeric phenyl esters with the same total carbon number. However, the esters are eluted from the polar QF-1 and Silar-10C acceptor phases in the reverse order for reasons explained¹. The same trend is shown in Table VII, where a comparison of the retention indices of methyl benzoates and phenyl acetates⁶ is presented. The difference between the esters on SE-30 is in the range 51–89 i.u., in general being lower on the polar column. However, the highest disparity (108 i.u.) between the retention behaviour of methyl *o*-chlorobenzoate and *o*-chlorophenyl acetate obtained on OV-351 is probably due to the maximization of the electromerism¹, *i.e.*, the most electron-deficient ring of methyl *o*-chlorobenzoate and the most electron-rich ring of *o*-chlorophenyl acetate. This results in the highest disparity between the isomers on the donor OV-351 stationary phase. The reversed elution order between methyl *p*-chlorobenzoate and *p*-chlorophenyl acetate would, on the other hand, indicate minimization of the electromerism mentioned. This is particularly true with *p*-chlorophenyl acetate compared with the corresponding *m*-isomer.

TABLE VI
SEPARATION BETWEEN PLOTS OF *o*-, *m*- AND *p*-CHLORO ESTERS AT VARIOUS TEMPERATURES WITH RETENTION INCREMENT RATIOS

Temperature	Column											$\frac{\Delta I_{OV-351}}{\Delta I_{SE-30}}$			
	SE-30						OV-351					<i>o</i> -Cl	<i>m</i> -Cl	<i>p</i> -Cl	
	ΔI_{o-Cl}	ΔI_{m-Cl}	ΔI_{p-Cl}	$\Delta I_{p-Cl} - \Delta I_{m-Cl}$	$\Delta I_{o-Cl} - \Delta I_{p-Cl}$		ΔI_{o-Cl}	ΔI_{m-Cl}	ΔI_{p-Cl}	$\Delta I_{p-Cl} - \Delta I_{m-Cl}$	$\Delta I_{o-Cl} - \Delta I_{p-Cl}$				
Programmed from 100°C at:															
2°C min ⁻¹	167	162	165	3		2	275	182	184	2		91	1.65	1.12	1.12
6°C min ⁻¹	168	163	166	3		2	288	194	197	3		91	1.71	1.19	1.19
10°C min ⁻¹	171	166	169	3		2	289	197	199	2		90	1.69	1.19	1.18
Isothermal:															
160°C	159	155	158	3		1	270	184	186	2		84	1.70	1.19	1.18
180°C	161	156	159	3		2	270	184	187	3		83	1.68	1.18	1.18
200°C	163	158	162	4		1	273	185	189	4		84	1.67	1.17	1.17

TABLE VII

COMPARISON OF RETENTION INDICES OF METHYL BENZOATES AND PHENYL ACETATES, OBTAINED ON SE-30 AND OV-351 AT 160°C

Compound	Column			
	SE-30		OV-351	
	I^*	ΔI^{**}	I^*	ΔI^{**}
Methyl benzoate	1097		1643	
Phenyl acetate	1008	89	1633	10
Methyl <i>o</i> -chlorobenzoate	1258		1937	
<i>o</i> -Chlorophenyl acetate	1173	85	1829	108
Methyl <i>m</i> -chlorobenzoate	1253		1854	
<i>m</i> -Chlorophenyl acetate	1198	55	1848	6
Methyl <i>p</i> -chlorobenzoate	1254		1849	
<i>p</i> -Chlorophenyl acetate	1203	51	1870	-21

* For the retention indices of phenyl acetates, see ref. 6.

** $\Delta I = I_{\text{Benzoate}} - I_{\text{Phenyl acetate}}$.

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