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Note

Gas-liquid chromatographic analyses

XLI*. Ethyl and ω -chloroethyl esters of benzoic and monochlorobenzoic acids on SE-30 and OV-351 capillary columns

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Earlier studies with aromatic esters involved the gas chromatographic (GC) retention behaviour of saturated C_1 - C_{12} normal-chain¹ and C_3 - C_5 branched-chain esters² and unsaturated C_3 - C_6 esters³ of benzoic and monochlorobenzoic acids. Low-polarity (SE-30) and highly polar (OV-351) capillary columns with various temperature-programmed and isothermal operations were used to investigate the separations of the complex mixtures and to examine the retention indices and the retention index increments for the methylene unit and the chlorine substituents within the homologous series of esters.

Previously, the GC separation of a mixture of ethyl and ω -chloroethyl esters of aliphatic C_2 - C_{20} *n*-alkanoic acids on SE-30 and OV-351 capillary columns has been reported⁴, and more recently the retention indices and the incremental effects for the various chlorine substituents in the same series of esters have been examined⁵.

This work extends the earlier studies¹⁻⁵ to the GC retention behaviour of ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl esters of benzoic and monochlorobenzoic acids on SE-30 and OV-351 capillary columns under a variety of temperature-programmed and isothermal conditions. The relative retention data, the Kováts retention indices and the retention index increments for the chlorine substituents in either the acyl or alkyl chain of the sixteen individual esters are discussed and the results are compared with those of the earlier studies with aromatic and aliphatic esters.

EXPERIMENTAL

Materials

The ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl esters of benzoic (1-4), *o*-chlorobenzoic (*o*/1-*o*/4), *m*-chlorobenzoic (*m*/1-*m*/4) and *p*-chlorobenzoic (*p*/1-*p*/4) acids were prepared from the corresponding alcohols⁴ and acid chlorides¹ as described earlier⁶.

Mixtures of *n*-alkanes were obtained from different commercial sources.

* For Part XL, see I. O. O. Korhonen, *J. Chromatogr.*, 324 (1985) 192.

Methods

GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the following operating conditions: injection and flame ionization detection (FID) temperatures, 250°C; nitrogen carrier gas velocities for methane at 160°C, 14.0 (SE-30) and 13.1 cm sec⁻¹ (OV-351); splitting ratio, 1:20; and chart speed, 10 mm min⁻¹. The columns used were a low-polarity SE-30 vitreous silica wall-coated open-tubular (WCOT) column (25 m × 0.33 mm I.D.), supplied by SGE (North Melbourne, Australia), and a highly polar OV-351 fused silica 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, if necessary, on OV-351 at 230°C until elution of peaks had ceased. The isothermal data were determined at 140, 160, 180, 200 and 220°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 adjacent *n*-alkanes as described earlier⁷, the dead volume being determined at each isothermal temperature by the injection of methane.

The esters of the four series of aromatic acids and *n*-alkanes were chromatographed separately in turn owing to the incomplete resolution of the peaks of the monochloro isomers. The elution order of the individual components in a complex

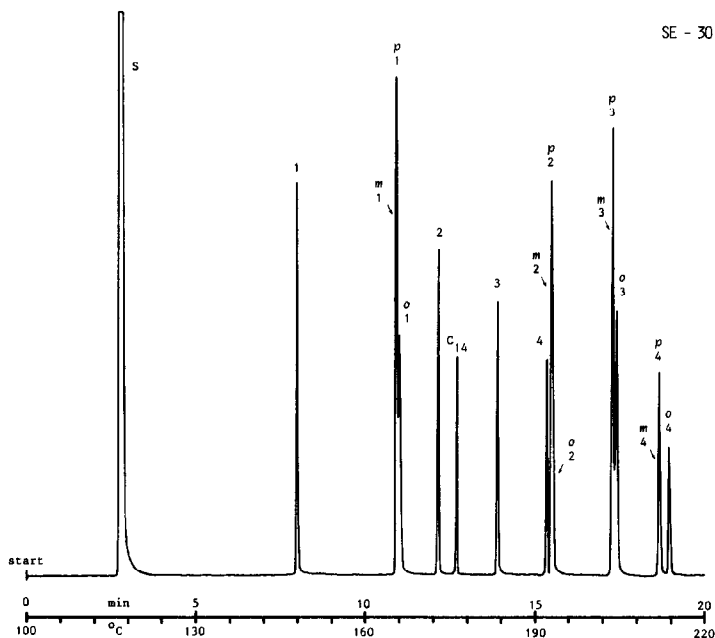


Fig. 1. Chromatogram of a mixture of ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl esters of benzoic (1-4), *o*-chlorobenzoic (*o*/1-*o*/4), *m*-chlorobenzoic (*m*/1-*m*/4) and *p*-chlorobenzoic (*p*/1-*p*/4) acids, obtained on a low-polarity SE-30 capillary column with temperature programming from 100°C at 6°C min⁻¹ until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane. Peaks are identified in Table I.

mixture shown in Figs. 1 and 2 was confirmed with the pure components added to the mixture and the increased peak responses obtained.

RESULTS AND DISCUSSION

Chromatograms of a mixture of ethyl and ω -chloroethyl esters of benzoic and monochlorobenzoic acids, separated on SE-30 and OV-351 with temperature programming, are shown in Figs. 1 and 2, respectively. The corresponding retention data are presented in Table I.

Fig. 1 shows that the isomers are eluted on a low-polarity SE-30 column in order of their degree of chlorination and that the *m*-, *p*- and *o*-chloro esters are eluted close together, as are the other esters of monochlorobenzoic acids¹⁻³. All the *m*- and *p*-isomers are coincident, but the *o*-isomers, having increased retentions, are generally resolved so that the resolution increases with increasing degree of chlorination (Fig. 1 and Table I).

On a highly polar OV-351 stationary phase the retention is increased (Table I) and the elution order between the 2,2-di- and 2,2,2-trichloroethyl esters is changed, as previously shown with the corresponding aliphatic esters^{4,5}. The separation between the isomeric compounds is better than on SE-30, *i.e.*, the peaks of the trichloroethyl esters of the *m*- and *p*-isomers are resolved and the retention of the *o*-isomers is markedly increased relative to that of the *m*- and *p*-isomers¹⁻³ (Fig. 2).

The elution order of the esters shown in Figs. 1 and 2 generally remained

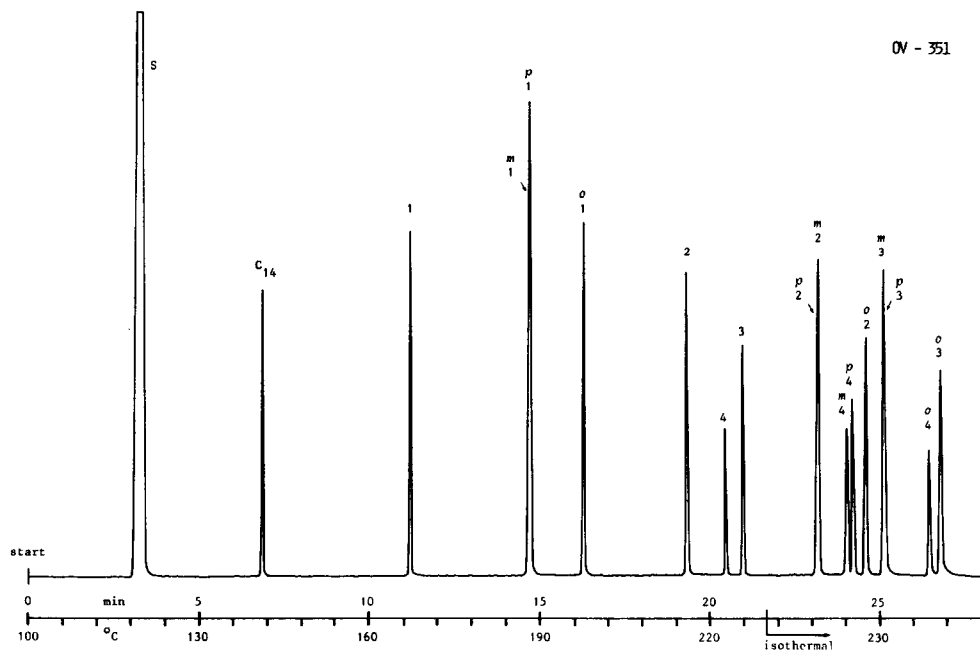


Fig. 2. Chromatogram of the same mixture as in Fig. 1, obtained on a highly polar OV-351 capillary column with temperature programming from 100 to 230°C at 6°C min⁻¹ and held at 230°C until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane. Peaks are identified in Table I.

TABLE I
RETENTION DATA FOR ETHYL AND *o*-CHLOROETHYL ESTERS OF BENZOIC AND MONOCHLOROBENZOIC ACIDS, OBTAINED ON SE-30
AND OV-351 CAPILLARY COLUMNS WITH TEMPERATURE PROGRAMMING
Conditions as in Figs. 1 and 2.

Peak No.	Compound	SE-30				OV-351				
		ART*	RRT**	RRT***	RRT§	ART*	RRT**	RRT***	RRT§	RRT§§
1	Ethyl benzoate	7.96	0.63	1.00	1.00	11.22	1.62	1.00	1.00	1.41
2	2-Chloroethyl benzoate	12.11	0.95	1.52	1.00	19.30	2.79	1.72	1.00	1.59
3	2,2-Dichloroethyl benzoate	13.89	1.09	1.74	1.00	20.96	3.03	1.87	1.00	1.51
4	2,2,2-Trichloroethyl benzoate	15.32	1.20	1.92	1.00	20.46	2.96	1.82	1.00	1.34
<i>o</i> /1	Ethyl <i>o</i> -chlorobenzoate	11.00	0.86	1.00	1.38	16.32	2.36	1.00	1.45	1.48
<i>o</i> /2	2-Chloroethyl <i>o</i> -chlorobenzoate	15.52	1.22	1.41	1.28	24.62	3.56	1.51	1.28	1.59
<i>o</i> /3	2,2-Dichloroethyl <i>o</i> -chlorobenzoate	17.40	1.37	1.58	1.25	26.86	3.89	1.65	1.28	1.54
<i>o</i> /4	2,2,2-Trichloroethyl <i>o</i> -chlorobenzoate	18.93	1.49	1.72	1.24	26.47	3.83	1.62	1.29	1.40
<i>m</i> /1	Ethyl <i>m</i> -chlorobenzoate	10.89	0.86	1.00	1.37	14.67	2.12	1.00	1.31	1.35
<i>m</i> /2	2-Chloroethyl <i>m</i> -chlorobenzoate	15.49	1.22	1.42	1.28	23.20	3.36	1.58	1.20	1.50
<i>m</i> /3	2,2-Dichloroethyl <i>m</i> -chlorobenzoate	17.29	1.36	1.59	1.24	25.13	3.64	1.71	1.20	1.45
<i>m</i> /4	2,2,2-Trichloroethyl <i>m</i> -chlorobenzoate	18.61	1.46	1.71	1.21	24.09	3.49	1.64	1.18	1.29
<i>p</i> /1	Ethyl <i>p</i> -chlorobenzoate	10.90	0.86	1.00	1.37	14.68	2.12	1.00	1.31	1.35
<i>p</i> /2	2-Chloroethyl <i>p</i> -chlorobenzoate	15.50	1.22	1.42	1.28	23.18	3.35	1.58	1.20	1.50
<i>p</i> /3	2,2-Dichloroethyl <i>p</i> -chlorobenzoate	17.31	1.36	1.59	1.25	25.15	3.64	1.71	1.20	1.45
<i>p</i> /4	2,2,2-Trichloroethyl <i>p</i> -chlorobenzoate	18.65	1.47	1.71	1.22	24.24	3.51	1.65	1.18	1.30
C ₁₄	<i>n</i> -Tetradecane	12.72	1.00	—	—	6.91	1.00	—	—	0.54

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

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

*** Relative retention time for the corresponding ethyl ester (1, *o*/1, *m*/1 and *p*/1) taken as 1.00.

§ Relative retention time for the corresponding ester of benzoic acid (1-4) taken as 1.00.

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

TABLE II

RETENTION INDICES FOR ETHYL AND ω -CHLOROETHYL ESTERS OF BENZOIC AND MONOCHLOROBENZOIC ACIDS ON SE-30

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
Ethyl benzoate	1155	1143	1154	1166	1157	1176
2-Chloroethyl benzoate	1373	1368	1380	1375	1380	1396
2,2-Dichloroethyl benzoate	1456	1459	1472	1462	1470	1485
2,2,2-Trichloroethyl benzoate	1528	1531	1542	1526	1536	1552
Ethyl <i>o</i> -chlorobenzoate	1321	1311	1320	1322	1325	1341
2-Chloroethyl <i>o</i> -chlorobenzoate	1540	1541	1552	1538	1549	1559
2,2-Dichloroethyl <i>o</i> -chlorobenzoate	1629	1637	1651	1628	1638	1653
2,2,2-Trichloroethyl <i>o</i> -chlorobenzoate	1706	1717	1732	1697	1708	1726
Ethyl <i>m</i> -chlorobenzoate	1316	1305	1316	1317	1318	1335
2-Chloroethyl <i>m</i> -chlorobenzoate	1537	1540	1551	1535	1542	1555
2,2-Dichloroethyl <i>m</i> -chlorobenzoate	1624	1632	1646	1618	1627	1643
2,2,2-Trichloroethyl <i>m</i> -chlorobenzoate	1688	1700	1715	1678	1690	1705
Ethyl <i>p</i> -chlorobenzoate	1317	1306	1316	1318	1323	1336
2-Chloroethyl <i>p</i> -chlorobenzoate	1537	1540	1551	1536	1544	1558
2,2-Dichloroethyl <i>p</i> -chlorobenzoate	1625	1633	1647	1622	1635	1647
2,2,2-Trichloroethyl <i>p</i> -chlorobenzoate	1692	1702	1717	1683	1696	1711

unchanged under various temperature-programmed and isothermal operating conditions; the variations between that of the closely related *m*- and *p*-isomers observed on OV-351 are negligible, however.

The Kováts retention indices of the aromatic esters investigated, obtained on SE-30 and OV-351 at a variety of temperatures, are presented in Tables II and III. Fig. 3 shows the retention indices on both stationary phases at 160°C, together with the retention enhancements that occurred on the polar column.

As usual, the retention increases with temperature, the effect being most pronounced on a polar column (Table III). As is evident in Fig. 3, the retention enhancement on SE-30 is linear with different levels of chlorine substitution, unlike that obtained on OV-351. The enhanced retentions on a polar column presented in Table III and Fig. 3 are 538–743 retention index units (i.u.) with benzoates, 555–784 i.u. with *p*-chlorobenzoates, 566–794 i.u. with *m*-chlorobenzoates and 640–853 i.u. with *o*-chlorobenzoates. The ethyl esters show the smallest and the mono- and dichloroethyl esters the greatest differences between the highly polar and low-polarity stationary phases (Fig. 3). The retention index ratios shown in Table III are close to 1.50, increasing for the esters in the following order: trichloroethyl < ethyl < dichloroethyl < monochloroethyl and *p*-chlorobenzoate \leq *m*-chlorobenzoate < benzoate < *o*-chlorobenzoate. The differences between the isomeric benzoates are negligible, however.

By comparing the retention behaviour of *n*-alkyl benzoates and monochlorobenzoates¹ with that of the ω -chloroethyl esters studied in this work, it was found

TABLE III
RETENTION INDICES FOR ETHYL AND *o*-CHLOROETHYL ESTERS OF BENZOIC AND MONOCHLOROBENZOIC ACIDS ON OV-351

Compound	Column (OV-351) temperature						160°C	
	Programmed from 100°C at						Isothermal at	
	2°C min ⁻¹	6°C min ⁻¹	10°C min ⁻¹	10°C min ⁻¹	160°C	180°C	200°C	220°C
Ethyl benzoate	1660	1674	1688	1688	1695	1704	1700	1692
2-Chloroethyl benzoate	2114	2138	2151	2151	2123	2146	2165	2179
2,2-Dichloroethyl benzoate	2211	2238	2252	2252	2213	2237	2258	2273
2,2,2-Trichloroethyl benzoate	2180	2208	2223	2223	2184	2210	2232	2250
Ethyl <i>o</i> -chlorobenzoate	1951	1964	1980	1980	1965	1986	2009	2018
2-Chloroethyl <i>o</i> -chlorobenzoate	2417	2442	2456	2456	2398	2425	2449	2468
2,2-Dichloroethyl <i>o</i> -chlorobenzoate	2520	2545	2559	2559	2491	2520	2544	2565
2,2,2-Trichloroethyl <i>o</i> -chlorobenzoate	2498	2528	2545	2545	2469	2501	2528	2552
Ethyl <i>m</i> -chlorobenzoate	1856	1870	1893	1893	1884	1901	1920	1935
2-Chloroethyl <i>m</i> -chlorobenzoate	2342	2368	2385	2385	2331	2359	2379	2398
2,2-Dichloroethyl <i>m</i> -chlorobenzoate	2438	2467	2483	2483	2421	2448	2470	2491
2,2,2-Trichloroethyl <i>m</i> -chlorobenzoate	2383	2416	2428	2428	2366	2397	2420	2441
Ethyl <i>p</i> -chlorobenzoate	1861	1871	1888	1888	1878	1899	1921	1939
2-Chloroethyl <i>p</i> -chlorobenzoate	2339	2367	2380	2380	2325	2354	2378	2396
2,2-Dichloroethyl <i>p</i> -chlorobenzoate	2440	2468	2484	2484	2419	2448	2472	2494
2,2,2-Trichloroethyl <i>p</i> -chlorobenzoate	2391	2423	2439	2439	2372	2404	2430	2454

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

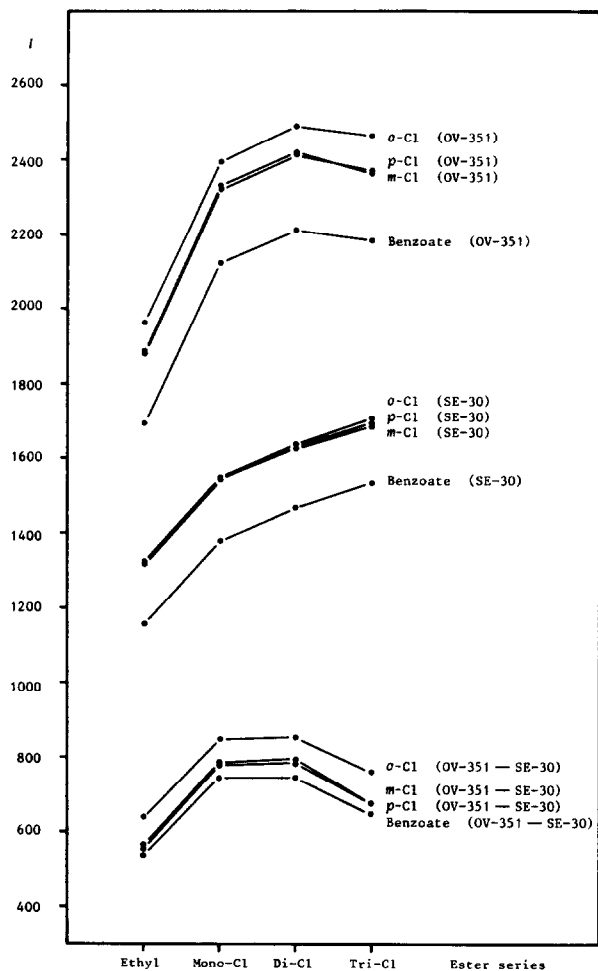


Fig. 3. Retention indices (I) for ethyl and ω -chloroethyl esters of benzoic and o -, m - and p -chlorobenzoic acids, obtained on SE-30 and OV-351 at 160°C, and the retention enhancements that occurred on the polar column, i.e., $I_{OV-351} - I_{SE-30}$ (Tables II and III).

that on SE-30 the 2-chloroethyl esters are eluted later than the butyl esters, the 2,2-di- and 2,2,2-trichloroethyl esters appearing between the pentyl and hexyl esters. Thus, one ω -chlorine substituent in the alkyl group is equivalent to *ca.* two methylene groups, 2-3 ω -chlorine atoms corresponding to *ca.* 3-4 methylene groups. On OV-351 the influence of the ω -chlorine substituents are more pronounced, *viz.*, one chlorine atom is equivalent to *ca.* 4-5 methylene groups, 2-3 chlorine atoms being equivalent to 5-6 methylene groups. The corresponding comparison between n -alkanols and ω -chloroethanols showed an even greater effect of the chlorine substituents on the polar stationary phase⁷.

The incremental effects for the chlorine substitution in both the acyl and alkyl chains of the esters are shown in Tables IV and V, obtained with one temperature-

TABLE IV
 INCREMENTAL EFFECTS FOR CHLORINE SUBSTITUTION IN THE ACYL AND ALKYL CHAINS OF THE ESTERS, OBTAINED ON SE-30 WITH
 TEMPERATURE PROGRAMMING AND ISOTHERMAL OPERATION

Compound	Isothermal at 160°C											
	Column (SE-30) temperature					Programmed from 100°C at 6°C min ⁻¹						
	ΔI^*	$\Sigma \Delta I_{mCl}^{**}$	ΔI_{Cl}^{***}	ΔI_{1Cl}^{\S}	$\Delta I_{2Cl}^{\ \S}$	$\Delta I_{3Cl}^{\ \S\ }$	ΔI^*	$\Sigma \Delta I_{mCl}^{**}$	ΔI_{Cl}^{***}	ΔI_{1Cl}^{\S}	$\Delta I_{2Cl}^{\ \S}$	$\Delta I_{3Cl}^{\ \S\ }$
Ethyl benzoate	—	—	—	—	—	—	—	—	—	—	—	—
2-Chloroethyl benzoate	—	225	225	225	—	—	—	223	223	—	—	—
2,2-Dichloroethyl benzoate	—	316	158	225	91	—	—	313	223	90	—	—
2,2,2-Trichloroethyl benzoate	—	388	129	225	91	72	—	379	223	90	66	—
Ethyl <i>o</i> -chlorobenzoate	168	—	—	—	—	—	—	168	—	—	—	—
2-Chloroethyl <i>o</i> -chlorobenzoate	173	230	230	230	—	—	—	169	224	224	—	—
2,2-Dichloroethyl <i>o</i> -chlorobenzoate	178	326	163	230	96	—	—	168	313	157	224	89
2,2,2-Trichloroethyl <i>o</i> -chlorobenzoate	186	406	135	230	96	80	—	172	383	128	224	89
Ethyl <i>m</i> -chlorobenzoate	162	—	—	—	—	—	—	161	—	—	—	—
2-Chloroethyl <i>m</i> -chlorobenzoate	172	235	235	235	—	—	—	162	224	224	—	—
2,2-Dichloroethyl <i>m</i> -chlorobenzoate	173	327	164	235	92	—	—	157	309	155	224	85
2,2,2-Trichloroethyl <i>m</i> -chlorobenzoate	169	395	132	235	92	68	—	154	372	124	224	85
Ethyl <i>p</i> -chlorobenzoate	163	—	—	—	—	—	—	166	—	—	—	—
2-Chloroethyl <i>p</i> -chlorobenzoate	172	234	234	234	—	—	—	164	221	221	—	—
2,2-Dichloroethyl <i>p</i> -chlorobenzoate	174	327	164	234	93	—	—	165	312	156	221	91
2,2,2-Trichloroethyl <i>p</i> -chlorobenzoate	171	396	132	234	93	69	—	160	373	124	221	91

* Retention index increment for the chlorine substitution in the acyl chain, *i.e.*, $I_{\text{monochlorobenzoate}} - I_{\text{benzoate}}$.
 ** Total retention index increment for the chlorine substitution in the alkyl chain, *i.e.*, $I_{\text{*o*-chloroethyl ester}} - I_{\text{ethyl ester}}$.
 *** Retention index increment per chlorine atom in the alkyl chain, *i.e.*, $\Sigma \Delta I_{mCl}$ /number of the chlorine atoms.
 § Retention index increment for the first chlorine atom, *i.e.*, $I_{\text{monochloroethyl ester}} - I_{\text{ethyl ester}}$.
 || Retention index increment for the second chlorine atom, *i.e.*, $I_{\text{dichloroethyl ester}} - I_{\text{monochloroethyl ester}}$.
 ||| Retention index increment for the third chlorine atom, *i.e.*, $I_{\text{trichloroethyl ester}} - I_{\text{dichloroethyl ester}}$.

TABLE V
INCREMENTAL EFFECTS FOR CHLORINE SUBSTITUTION IN THE ACYL AND ALKYL CHAINS OF THE ESTERS, OBTAINED ON OV-351
WITH TEMPERATURE PROGRAMMING AND ISOTHERMAL OPERATION

Compound	Column (OV-351) temperature											
	Programmed from 100°C at 6°C min ⁻¹						Isothermal at 160°C					
	ΔT^*	$\Sigma \Delta I_{\text{ac1}}^{**}$	$\Delta I_{\text{Cl}}^{***}$	$\Delta I_{\text{Cl}}^{\$}$	$\Delta I_{2\text{Cl}}^{\$}$	$\Delta I_{3\text{Cl}}^{\$}$	ΔT^*	$\Sigma \Delta I_{\text{ac1}}^{**}$	$\Delta I_{\text{Cl}}^{***}$	$\Delta I_{\text{Cl}}^{\$}$	$\Delta I_{2\text{Cl}}^{\$}$	$\Delta I_{3\text{Cl}}^{\$}$
Ethyl benzoate	—	—	—	—	—	—	—	—	—	—	—	—
2-Chloroethyl benzoate	—	464	464	464	—	—	—	428	428	428	—	—
2,2-Dichloroethyl benzoate	—	564	282	464	100	—	—	518	259	428	90	—
2,2,2-Trichloroethyl benzoate	—	534	178	464	100	-30	—	489	163	428	90	-29
Ethyl <i>o</i> -chlorobenzoate	290	—	—	—	—	—	270	—	—	—	—	—
2-Chloroethyl <i>o</i> -chlorobenzoate	304	478	478	478	—	—	275	433	433	433	—	—
2,2-Dichloroethyl <i>o</i> -chlorobenzoate	307	581	291	478	103	—	278	526	263	433	93	—
2,2,2-Trichloroethyl <i>o</i> -chlorobenzoate	320	564	188	478	103	-17	285	504	168	433	93	-22
Ethyl <i>m</i> -chlorobenzoate	196	—	—	—	—	—	189	—	—	—	—	—
2-Chloroethyl <i>m</i> -chlorobenzoate	230	498	498	498	—	—	208	447	447	447	—	—
2,2-Dichloroethyl <i>m</i> -chlorobenzoate	229	597	299	498	99	—	208	537	269	447	90	—
2,2,2-Trichloroethyl <i>m</i> -chlorobenzoate	208	546	182	498	99	-51	182	482	161	447	90	-55
Ethyl <i>p</i> -chlorobenzoate	197	—	—	—	—	—	183	—	—	—	—	—
2-Chloroethyl <i>p</i> -chlorobenzoate	229	496	496	496	—	—	202	447	447	447	—	—
2,2-Dichloroethyl <i>p</i> -chlorobenzoate	230	597	299	496	101	—	206	541	271	447	94	—
2,2,2-Trichloroethyl <i>p</i> -chlorobenzoate	215	552	184	496	101	-45	188	494	165	447	94	-47

***, ***, §, §, §, § As in Table IV.

TABLE VI

SEPARATION BETWEEN MONOCHLOROBENZOATES ON SE-30 AND OV-351 AT 160°C AND THE RETENTION INCREMENT RATIOS BETWEEN THE COLUMNS

Retention increment*	Ester series			
	Ethyl	2-Chloroethyl	2,2-Dichloroethyl	2,2,2-Trichloroethyl
<i>SE-30 column</i>				
ΔI_{o-Cl}	168	169	168	172
ΔI_{m-Cl}	161	162	157	154
ΔI_{p-Cl}	166	164	165	160
$\Delta I_{o-Cl} - \Delta I_{p-Cl}$	2	5	3	12
$\Delta I_{p-Cl} - \Delta I_{m-Cl}$	5	2	8	6
<i>OV-351 column</i>				
ΔI_{o-Cl}	270	275	278	285
ΔI_{m-Cl}	189	208	208	182
ΔI_{p-Cl}	183	202	206	188
$\Delta I_{o-Cl} - \Delta I_{p-Cl}$	87	73	72	97
$\Delta I_{p-Cl} - \Delta I_{m-Cl}$	-6	-6	-2	6
$\Delta I_{OV-351}/\Delta I_{SE-30}$				
<i>o</i> -Cl	1.61	1.63	1.65	1.66
<i>m</i> -Cl	1.17	1.28	1.32	1.18
<i>p</i> -Cl	1.10	1.23	1.25	1.18

* $\Delta I = I_{\text{monochlorobenzoate}} - I_{\text{benzoate}}$

programmed and isothermal operation on SE-30 and OV-351, respectively. Separation between monochlorobenzoates on both columns at 160°C is shown in Table VI, which also gives the retention increment ratios between the columns.

Although the retention increments are not presented at a variety of temperatures, it is evident (Tables II and III) that the increments remain fairly constant on SE-30, but increase with temperature on OV-351. It is also clear that particularly on SE-30 (Tables IV and VI) the chlorine substitution in the alkyl chain has a negligible influence on the incremental effect for the chlorine substituent in the acyl chain. The increments on SE-30 at 160°C are in the ranges 168–172 i.u. for *o*-, 154–162 i.u. for *m*- and 160–166 i.u. for *p*-chlorobenzoates. On OV-351 the corresponding increments are increased, particularly with the *o*-isomers, owing to the maximization of the polar effects¹, i.e., 270–285 i.u. for *o*-, 182–208 i.u. for *m*- and 183–206 i.u. for *p*-chlorobenzoates (Tables V and VI). The increment with the *o*-isomers increases with increasing degree of chlorination, obviously owing to the increased loss of electron density occurring in the phenyl ring. This causes the enhancement of the retention of the *o*-isomers with respect to the parent esters on a polar OV-351 phase containing electron-donating groups¹. With the *m*- and *p*-isomers the greatest effects are shown by the mono- and dichloro esters, being markedly lower with the trichloro esters. This would indicate the most electron-deficient ring of the former esters.

The incremental effects for the chlorine substituents in the alkyl chain as presented in Tables IV and V show that the acyl group has a small influence on the increments, particularly on SE-30. The increments for the first, second and third chlorine atoms on SE-30 at 160°C are in the ranges 221–224, 85–91 and 61–70 i.u.,

respectively (Table IV). As with the corresponding alcohols⁷, the effect decreases with increasing degree of chlorination, unlike with the chlorinated acetic acid esters⁸⁻¹⁰.

On a highly polar OV-351 stationary phase (Table V) the increment for the first chlorine atom is increased up to 428-447 i.u., that for the second chlorine atom being in the same range as on SE-30, *i.e.*, 90-94 i.u. Unlike 2,2,3-trichloroethanol⁷ and like the esters of trichloroacetic acid⁸⁻¹⁰, the third chlorine atom shows a reduction in the retention, *viz.*, from -22 to -55 i.u., the retention decrease being greatest with *m*-chlorobenzoate (Table V). The reductions observed are in the same range as with the acetate esters, owing to the increased influence of steric effects on the polar stationary phase⁸.

The retention increment ratios between the highly polar and low-polarity columns as presented in Table VI indicate that the polar effects are maximized with the *o*-isomers and particularly with the trichloroethyl ester. With the *m*- and *p*-isomers, however, the polar effects are maximized with the dichloroethyl esters, whereas with further chloro substitution the steric effects are the most apparent, as shown from the lower increment ratios of the trichloroethyl esters. Possible reasons for the phenomena observed are as mentioned above and in the previous papers^{1,11}.

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