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Note

Gas chromatography of homologous esters

XXVI*. Capillary column studies of the chloromethyl esters of C_5–C_{12} *n*-carboxylic acids

J. K. HAKEN* and B. G. MADDEN
Department of Polymer Science and Industrial Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)
and
I. O. O. KORHONEN
Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10 (Finland)
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The gas chromatography (GC) of the chloromethyl esters of aliphatic *n*-acids has not been extensively studied. However, the separation of the isomeric chloromethyl esters of C_5–C_{12} *n*-carboxylic acids on capillary columns coated with SE-30 and Carbowax 20M with temperature programming to optimise the separations has recently been reported[1], while Komarék *et al.*[2] have described studies on an OV-101 capillary column at 80°C for the lower esters and 200°C for higher esters.

The present work shows the effect on retention of the position of chlorine substitution in the alkyl chain of C_5–C_{12} *n*-carboxylic acids. Incremental effects in terms of retention indices are shown on a non-polar (SE-30) and a polar (Carbowax 20M) capillary column. A comparison of the incremental effects is shown with *n*-alkyl and 2-chloroalkyl esters, all determined at temperatures between 100 and 200°C.

EXPERIMENTAL

The esters were prepared and characterised in the laboratory as previously reported[1].

GC analyses were carried out on a Varian Model 2400 gas chromatograph and on a Perkin-Elmer Sigma 3 instrument under the following operating conditions: a glass capillary column (22 m × 0.30 mm I.D.) coated with 3% Carbowax 20M; a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.22 mm I.D.), supplied by SGE (North Melbourne, Australia); injector and detector temperatures, 275°C; splitting ratio, 1:20, nitrogen carrier gas flow-rate, 1 ml/min. Retention data were recorded with a Hewlett-Packard Model 3390A Reporting Integrator.

The retention times were measured from the time of sample injection and the retention indices were determined off-line using a Vector M2 microprocessor system,

* For Part XXV, see ref. 5.

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the dead volume being first determined by regression analysis from a series of *n*-alkanes by the procedure of Grobler and Balizs[3].

TABLE I.

RETENTION INDICES OF CHLOROMETHYL ESTERS OF *n*-C_5–C_{12} MONOCHLOROACIDS ON SE-30 AND CARBOWAX 20M

Chloromethyl	*SE-30*					*Carbowax 20M*				
	100°C	*120°C*	*140°C*	*160°C*	*180°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*
Pentanoate	989	967	953	997		1374	1376	1396	1417	
2-Chloro	1113	1986	1108	1108		1606	1619	1628	1646	
3-Chloro	1142	1126	1136	1133		1694	1709	1721	1735	
4-Chloro	1166	1153	1160	1153		1730	1749	1760	1780	
5-Chloro	1227	1225	1228	1214		1851	1867	1882	1904	
Hexanoate	1069	1051	1072	1084			1477	1493	1513	
2-Chloro	1194	1204	1207	1199			1704	1713	1733	
3-Chloro	1214	1227	1229	1220			1775	1786	1807	
4-Chloro	1246	1264	1262	1253			1822	1837	1863	
5-Chloro	1259	1277	1275	1265			1867	1883	1905	
6-Chloro	1320	1341	1337	1327			1961	1979	2002	
Heptanoate		1197	1195	1164	1181		1565	1582	1603	1609
2-Chloro		1328	1307	1293	1316		1787	1807	1820	1820
3-Chloro		1348	1328	1313	1334		1854	1875	1894	1894
4-Chloro		1373	1352	1340	1360		1886	1910	1933	1935
5-Chloro		1394	1376	1365	1388		1939	1964	1988	1988
6-Chloro		1406	1387	1376	1395		1964	1988	2012	2018
7-Chloro		1457	1442	1443	1452		2045	2070	2096	2105
Octanoate			1278	1263	1286			1684	1700	1719
2-Chloro			1406	1394	1417			1907	1918	1919
3-Chloro			1425	1414	1434			1969	1984	1988
4-Chloro			1451	1443	1458			2002	2020	2031
5-Chloro			1464	1456	1470			2039	2058	2068
6-Chloro			1487	1481	1494			2075	2096	2107
7-Chloro			1491	1484	1498			2086	2108	2121
8-Chloro			1545	1545	1555			2167	2191	2206
Nonanoate			1380	1364	1380			1776	1798	1796
2-Chloro			1508	1501	1509			1996	2014	2013
3-Chloro			1526	1521	1529			2059	2081	2084
4-Chloro			1551	1549	1556			2090	2115	2122
5-Chloro			1562	1561	1567			2123	2149	2160
6-Chloro			1576	1578	1582			2144	2171	2182
7-Chloro			1591	1594	1597			2166	2195	2207
8-Chloro			1594	1599	1601			2178	2207	2220
9-Chloro			1647	1657	1654			2255	2286	2302

(Continued on p. 152)

TABLE I *(continued)*

Chloromethyl	*SE-30*					*Carbowax 20M*				
	120°C	*140°C*	*160°C*	*180°C*	*200°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*
Decanoate		1479	1470	1483	1481		1872	1889	1895	1898
2-Chloro		1608	1613	1610	1615		2091	2108	2114	2118
3-Chloro		1625	1636	1628	1636		2155	2173	2185	2189
4-Chloro		1650	1664	1654	1658		2193	2212	2227	2233
5-Chloro		1659	1675	1663	1672		2216	2239	2255	2258
6-Chloro		1672	1690	1678	1684		2234	2257	2276	2277
7-Chloro		1679	1698	1686	1691		2241	2265	2285	2287
8-Chloro		1693	1716	1701	1707		2264	2289	2311	2311
9-Chloro		1696	1719	1704	1709		2274	2299	2321	2320
10-Chloro		1747	1775	1755	1761		2349	2376	2401	2403
Undecanoate		1581	1581	1585	1592			1990	1996	2008
2-Chloro		1709	1722	1712	1715			2206	2207	2224
3-Chloro		1726	1746	1730	1736			2273	2287	2290
4-Chloro		1750	1773	1755	1761			2326	2344	2348
5-Chloro		1758	1783	1764	1771			2335	2353	2360
6-Chloro		1770	1796	1775	1783			2350	2369	2373
7-Chloro		1775	1802	1781	1789			2355	2374	2379
8-Chloro		1781	1809	1787	1795			2362	2382	2388
9-Chloro		1795	1824	1801	1811			2384	2406	2312
10-Chloro		1796	1825	1802	1811			2393	2416	2422
11-Chloro		1847	1885	1856	1861			2471	2499	2502
Dodecanoate		1682	1694	1684	1691			2089	2087	2102
2-Chloro		1809	1840	1817	1826			2305	2315	2320
3-Chloro		1826	1860	1834	1837			2371	2387	2391
4-Chloro		1850	1888	1859	1863			2424	2444	2448
5-Chloro		1858	1897	1867	1872			2432	2452	2457
6-Chloro		1870	1910	1878	1882			2447	2470	2464
7-Chloro		1874	1915	1882	1886			2448	2470	2474
8-Chloro		1878	1919	1887	1891			2453	2476	2481
9-Chloro		1882	1925	1892	1896			2459	2482	2488
10-Chloro		1895	1940	1905	1910			2480	2506	2512
11-Chloro		1896	1941	1906	1911			2490	2516	2521
12-Chloro		1947	2005	1958	1960			2567	2597	2601

RESULTS AND DISCUSSION

The retention indices of the n-C_5–C_{12} chloromethyl monochloroesters determined on both SE-30 and Carbowax 20M capillary columns are shown in Table I. Tables II and III show the retention increments on both columns for a chlorine substituent at each position along the acyl chain. Considerable enhancement of retention due to a terminal chlorine substituent is evident as occurs with the simple monochloro esters [4,5] and with unsaturation[6].

The individual contribution of a particular position of unsaturation tends to decrease slightly as the acyl chain length is increased. This situation and the relative constant increase of the terminal position are in agreement with the behaviour of the monochloro esters. Comparison of the relative increases with those of the mono-

TABLE II

INCREMENTAL EFFECT OF MONOCHLORO SUBSTITUTION AT EACH POSITION ALONG THE CHAIN OF CHLOROMETHYL ESTERS ON SE-30

Chloromethyl alkanoate	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
100°C								
2-Chloro	124	125						
3-Chloro	153	145						
4-Chloro	177	177						
5-Chloro	238	190						
6-Chloro		251						
120°C								
2-Chloro	119	153	131					
3-Chloro	159	176	151					
4-Chloro	186	213	175					
5-Chloro	258	226	196					
6-Chloro		290	209					
7-Chloro			260					
140°C								
2-Chloro	155	135	132	128	128	129	128	127
3-Chloro	183	157	153	147	146	146	145	144
4-Chloro	207	190	177	173	171	171	169	168
5-Chloro	275	203	201	186	182	180	177	176
6-Chloro		265	212	209	196	193	189	188
7-Chloro			267	213	211	200	194	192
8-Chloro				267	214	214	200	196
9-Chloro					267	217	214	200
10-Chloro						268	215	213
11-Chloro							266	214
12-Chloro								265
160°C								
2-Chloro	111	115	129	131	137	143	141	146
3-Chloro	136	136	149	151	157	166	165	166
4-Chloro	156	169	176	180	185	194	192	194
5-Chloro	217	181	201	193	197	205	202	203
6-Chloro		243	212	218	214	220	215	216
7-Chloro			279	221	230	228	221	221
8-Chloro				282	235	246	228	225
9-Chloro					293	249	243	231
10-Chloro						305	244	246
11-Chloro							304	247
12-Chloro								311
180°C								
2-Chloro			135	131	129	127	127	133
3-Chloro			153	148	149	145	145	150
4-Chloro			179	172	176	171	170	175
5-Chloro			207	184	187	180	179	183
6-Chloro			214	208	202	195	190	194
7-Chloro			271	212	217	203	196	198

(Continued on p. 154)

TABLE II *(continued)*

Chloromethyl alkanoate	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
8-Chloro				269	221	218	202	203
9-Chloro					274	221	216	208
10-Chloro						272	217	221
11-Chloro							271	222
12-Chloro								274
200°C								
2-Chloro						134	123	135
3-Chloro						155	144	146
4-Chloro						177	169	172
5-Chloro						191	179	181
6-Chloro						203	191	191
7-Chloro						210	196	195
8-Chloro						226	203	201
9-Chloro						228	219	206
10-Chloro						280	219	219
11-Chloro							269	220
12-Chloro								269

TABLE III

INCREMENTAL EFFECT OF MONOCHLORO SUBSTITUTION AT EACH POSITION ALONG THE CHAIN OF CHLOROMETHYL ESTERS ON CARBOWAX 20M

Chloromethyl alkanoate	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
100°C								
2-Chloro	232							
3-Chloro	320							
4-Chloro	356							
5-Chloro	477							
120°C								
2-Chloro	243	227	222					
3-Chloro	333	298	289					
4-Chloro	373	345	321					
5-Chloro	491	390	374					
6-Chloro		484	399					
7-Chloro			480					
140°C								
2-Chloro	232	220	225	223	220	219		
3-Chloro	325	293	293	295	283	283		
4-Chloro	364	344	328	318	314	321		
5-Chloro	486	390	382	355	347	344		
6-Chloro		486	406	391	368	362		
7-Chloro			488	402	390	369		
8-Chloro				483	402	392		

TABLE III *(continued)*

Chloromethyl alkanoate	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
9-Chloro					479	402		
10-Chloro						477		
160°C								
2-Chloro	229	220	217	218	216	219	216	216
3-Chloro	318	294	291	284	283	284	283	282
4-Chloro	363	350	330	320	317	323	336	335
5-Chloro	487	392	385	358	351	350	345	343
6-Chloro		489	409	396	373	368	360	358
7-Chloro			493	408	397	376	365	359
8-Chloro				491	409	400	372	364
9-Chloro					488	410	394	370
10-Chloro						487	403	391
11-Chloro							481	401
12-Chloro								478
180°C								
2-Chloro			211	200	217	219	211	228
3-Chloro			285	269	290	291	300	300
4-Chloro			326	312	326	332	348	357
5-Chloro			379	349	364	360	357	365
6-Chloro			409	388	386	381	373	383
7-Chloro			496	402	411	390	378	383
8-Chloro				487	424	416	386	389
9-Chloro					506	426	410	395
10-Chloro						506	420	419
11-Chloro							503	429
12-Chloro								510
200°C								
2-Chloro						220	216	218
3-Chloro						291	282	289
4-Chloro						335	340	346
5-Chloro						360	352	355
6-Chloro						379	365	372
7-Chloro						389	371	372
8-Chloro						413	380	379
9-Chloro						422	404	386
10-Chloro						505	414	410
11-Chloro							494	419
12-Chloro								499

chloroesters[5] shows that similar increases occur with both ester series, indicating that chlorine substitution to a methyl ester or a chloromethyl ester is not markedly different.

The data in Tables II and III are summarised in Table IV where the incremental effects of chlorine substitution at the 2- and the terminal (ω) position are shown together with the difference between these two positions.

While retention on SE-30 is expectedly higher with the chloromethyl esters due to the greater molecular size, the effects of a chlorine substituent at the 2-position is

TABLE IV

SUMMARY OF INCREMENTAL EFFECTS ON SE-30 AND CARBOWAX 20M

Position of chlorine substitution	*Temp. (°C)*	*SE-30*								*Carbowax 20M*								*Average increments*	
		C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	*SE-30*	*Carbowax 20M*
2	100	124	125							232								125	232
ω		238	251							477								245	477
ω−2		114	126							245								120	245
2	120	119	153	131						243	227	222						134	231
ω		258	290	260						491	484	480						269	485
ω−2		139	137	129						248	257	258						135	254
2	140	155	135	132	128	128	129	128	127	232	220	225	223	220	219			133	223
ω		275	265	267	267	267	268	266	265	486	486	488	483	379	477			267	483
ω−2		120	130	135	139	139	139	138	138	254	266	263	260	259	258			135	260
2	180			135	131	129	127	127	133			211	200	217	219	211	228	130	214
ω				271	269	274	272	271	274			496	487	506	506	503	510	272	501
ω−2				136	138	145	145	144	141			285	287	289	287	292	282	142	287
2	200						134	123	135						220	216	218	131	218
ω							280	269	269						505	494	499	272	499
ω−2							146	146	134						285	278	281	142	281

lower with the chloromethyl esters. This effect is shown in Fig. 1 where the increase in retention with the methyl 2-chloro esters (plot 2) and the methyl esters (plot 1) is greater than between the plots of chloromethyl 2-chloro esters (plot 4) and the chloromethyl alkanoates (plot 3) with both stationary phases. On the polar phase (Fig. 2), both of the separations are increased. The effect of terminal substitution is very similar with both series and accordingly the increased retention between the 2- and

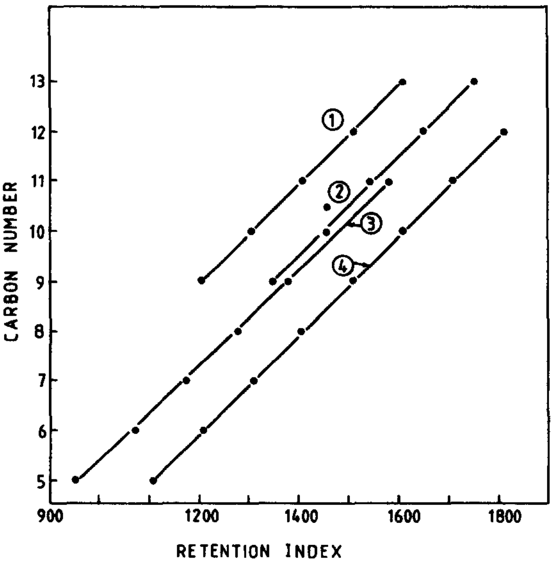

Fig. 1. Plot showing retention indices and carbon number on SE-30 of (1) methyl alkanoates; (2) methyl 2-chloroalkanoates; (3) chloromethyl alkanoates; (4) chloromethyl 2-chloroalkanoates.

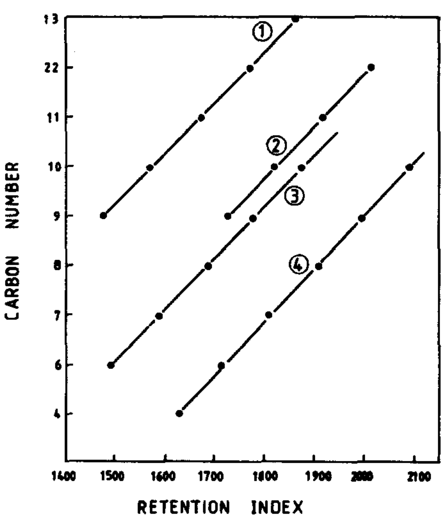

Fig. 2. Plot showing retention indices and carbon number on Carbowax 20M of (1) methyl alkanoates; (2) methyl 2-chloroalkanoates; (3) chloromethyl alkanoates; (4) chloromethyl 2-chloroalkanoates.

TABLE V

COMPARISON OF INCREMENTAL VALUES FOR METHYL AND CHLOROMETHYL MONOCHLORO ESTERS

	Methyl monochloro esters (C_5–C_{18})		*Chloromethyl monochloro esters* (C_5–C_{12})	
	SE-30	*Carbowax 20M*	*SE-30*	*Carbowax 20M*
Average 2-Cl	151	278	131	224
Average ω-Cl	272	505	265	489
Average (ω-Cl)−(2-Cl)	121	227	135	265
Ratio CW 20M/SE-30				
2-Cl	1.84		1.71	
ω-Cl	1.86		1.85	
(ω-Cl)−(2-Cl)	1.88		1.96	

3-chloro esters is higher with the chloromethyl esters. The effect may be explained due to the chloromethyl esters with two acceptor chlorine atoms adjacent to the donor carboxyl group having a marked effect on the retention due to the proximity and (or) interaction with the carboxyl group, which is reduced as the chlorine atoms move along the acyl chain and tends to simulate the performance of the ω-substituted monochloro esters.

With the Carbowax 20M column the same effects are evident although the individual values are very much higher than on the non-polar column where polar interactions between the solvent and solutes are experienced.

It is evident, however, that retention ratios of the components with positions of substitution at the 2- and ω-carbon atoms and of the quantity $\omega-2$, as shown in Table V, are virtually identical for the methyl monochloro esters and the chloromethyl esters. This shows that the effects of steric hindrance are not apparent. If these effects with the chloromethyl monochloro esters were operative, lower values of the ratios, particularly for the ω-positions of substitution would be observed as has previously been reported with some series of hindered aliphatic esters[7,8].

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REFERENCES

1 I. O. O. Korhonen, *J. Chromatogr.*, 219 (1981) 306.
2 K. Komárek, L. Hornová and J. Churáček, *J. Chromatogr.*, 252 (1982) 293.
3 A. Grobler and G. Balizs, *J. Chromatogr. Sci.*, 12 (1974) 57.
4 J. K. Haken, *J. Chromatogr.*, 243 (1982) 9.
5 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 298 (1984) 89.
6 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 62 (1971) 39.
7 J. K. Haken, J. R. Chrétien and C. Lion, *J. Chromatogr.*, 217 (1981) 125.
8 J. R. Chrétien, J. E. Dubois and J. K. Haken, *Proceedings of the 3rd Danube Symposium on Chromatography, Siófok, August 31–September 3, 1981*, H5.282.