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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XXVIII*. RETENTION INCREMENTS OF ALIPHATIC C_1–C_{18} *n*-ALKYL ESTERS OF BUTANOIC ACID AND ITS MONOCHLORO DERIVATIVES ON SE-30 AND OV-351 CAPILLARY COLUMNS

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SUMMARY

The retention behaviour of C_1–C_{18} *n*-alkyl esters of butanoic and 2-, 3- and 4-chlorobutanoic acids was examined isothermally at several temperatures on SE-30 and OV-351 capillary columns. Retention increments showing the effects of each position of chlorine substitution are presented. The considerable enhancement of terminal chlorine substitution is discussed together with the corresponding behaviour of the monochloropropanoate esters.

INTRODUCTION

In earlier work[1] are considered the retention enhancement of propanoyl and 2- and 3-chloropropanoyl derivatives of primary C_1–C_{18} alcohols on SE-30 and OV-351 capillary columns operated isothermally at a series of temperatures.

On the non-polar column the 2-chloropropanoyl derivatives showed retention enhancement of approximately 140 and 160 retention index units at 120 and 220°C compared with the corresponding propanoyl derivatives, while the 3-chloro derivatives showed increased retention of 207 and 232 index units. With the polar stationary phase the increases due to the 2- and 3-chloro substitutions were 240 and 270 index units for the first derivative and 391 and 426 index units for the 3-chloro derivative on both series at 120 and 220°C. In previous studies we considered the methyl esters of mono- and dichlorobutanoic acids at several temperatures on a non-polar OV-101 stationary phase[2], while programmed gas chromatography of aliphatic monochloro esters on SE-30 and OV-351 has been reported to maximize the practical separation

* For part XXVII, see ref. 1.

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of the homologues[3]. Complete separation was achieved on the non-polar column, whereas some overlapping occurred on the polar column. The studies allowed the elution orders of the series to be established.

In this work we examined the gas chromatographic retention behaviour of the C_1–C_{18} *n*-alkyl butanoates and their 2-, 3- and 4-monochlorinated derivatives. Retention index increments are considered for the isomers at several temperatures on SE-30 and OV-351 capillary columns, and retention index ratios indicate the influence of polar effects.

EXPERIMENTAL

Materials

Primary C_1–C_{18} alkanols were commercial products (Fluka, Buchs, Switzerland). *n*-Alkyl butanoates and the corresponding monochlorinated isomers were synthesized from aliphatic alcohols and acid chlorides as described earlier[4]. Butanoyl chloride was prepared by the reaction of benzoyl chloride with commercial butanoic acid (Fluka)[5], 2-chlorobutanoyl chloride by chlorination of butanoyl chloride[6] and 3-chlorobutanoyl chloride from the corresponding acid[7] and thionyl chloride. 4-Chlorobutanoyl chloride was a commercial product (Merck-Schuchardt, F.R.G.) and was used after redistillation.

Gas chromatography

Analyses were performed on a Perkin-Elmer Sigma 3 instrument using the following operating conditions: injector and flame ionization detector temperatures, 280°C; nitrogen carrier gas flow-rate, 1 ml min $^{-1}$; splitting ratio, 1:30; and chart speed, 10 mm min^{-1}. The columns used were a vitreous silica SE-30 wall-coated open-tabular (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 columns were operated isothermally at temperatures between 80 and 260°C as shown in Tables I and II. The chromatographic data were recorded using a Hewlett-Packard Model 3390A reporting integrator. Retention times were measured from the time of sample injection and the retention indices were determined off-line using a Vector MZ microprocessor system, the dead volume first being determined by regression analysis on a series of *n*-alkanes, using the procedure of Grobler and Balizs[8].

RESULTS AND DISCUSSION

The retention data of the compounds studied are presented in Tables I and II, and plots for the butanoate esters and their chlorinated homologues are shown in Figs. 1 and 2 for determinations on SE-30 and OV-351 at 120°C.

Retention index increments for methylene groups of the homologous series, measured at 120 and 220°C on both stationary phases, are shown in Table III. It is evident that as with the propanoate esters[1], increments near 100 retention index units occur and again a chlorine substituent in the acyl chain has little influence on the alkyl chain length. Also, the values at 220°C are again marginally greater than those at 120°C. Comparison with earlier work[1] shows little difference between the propa-

TABLE I

RETENTION INDICES OF C_1 C_{18} *n*-ALKYL ESTERS OF BUTANOIC AND MONOCHLOROBUTANOIC ACIDS ON SE-30

Compounds	*Carbon No.*	*Temperature (°C)*								
		80	*100*	*120*	*140*	*160*	*180*	*200*	*220*	*240*
n-Alkyl butanoates	C_1	710	723	706	663	681				
	C_2	792	802	783	757	747	689			
	C_3	888	896	885	863	845	835			
	C_4	985	991	982	964	957	937	951	897	
	C_5	1083	1088	1084	1067	1058	1048	1056	1020	
	C_6	1182	1187	1185	1166	1160	1152	1157	1125	1111
	C_7	1279	1287	1286	1267	1260	1254	1258	1243	1234
	C_8		1387	1388	1367	1362	1359	1364	1347	1345
	C_9			1489	1466	1464	1461	1463	1452	1445
	C_{10}			1590	1566	1564	1565	1565	1557	1548
	C_{11}				1665	1664	1666	1666	1660	1653
	C_{12}				1763	1765	1767	1768	1761	1754
	C_{14}				1959	1965	1969	1967	1964	1961
	C_{16}						2169	2165	2165	2164
	C_{18}							2362	2363	2363
n-Alkyl 2-chloro-butanoates	C_1	867	875	865	845	845	835			
	C_2	937	945	936	911	904	923	922		
	C_3	1029	1037	1032	1018	1014	1007	1010		
	C_4	1124	1131	1131	1117	1112	1105	1115	1070	1084
	C_5	1220	1228	1228	1215	1211	1209	1216	1172	1188
	C_6	1315	1327	1330	1314	1313	1309	1318	1305	1306
	C_7		1427	1431	1413	1412	1410	1419	1409	1402
	C_8			1530	1512	1513	1516	1522	1513	1505
	C_9			1631	1611	1613	1618	1622	1616	1613
	C_{10}				1709	1713	1718	1722	1719	1716
	C_{11}				1807	1813	1820	1823	1822	1818
	C_{12}				1905	1913	1920	1922	1922	1922
	C_{14}						2120	2120	2123	2127
	C_{16}							2317	2322	2324
	C_{18}								2519	2524
n-Alkyl 3-chloro-butanoates	C_1	873	881	870	848	845	835			
	C_2	948	955	947	935	926	923	922	848	
	C_3	1043	1050	1045	1030	1026	1014	1016	987	
	C_4	1139	1145	1145	1130	1126	1117	1133	1102	1084
	C_5	1235	1244	1244	1230	1227	1223	1229	1196	1202
	C_6	1331	1343	1346	1330	1328	1325	1334	1315	1320
	C_7		1443	1446	1429	1428	1428	1436	1425	1417
	C_8			1547	1528	1529	1531	1538	1531	1521
	C_9				1627	1629	1633	1638	1634	1628
	C_{10}				1725	1729	1734	1738	1736	1732
	C_{11}				1823	1829	1836	1839	1838	1834
	C_{12}				1921	1929	1936	1939	1938	1938
	C_{14}						2137	2137	2139	2142
	C_{16}							2333	2338	2342
	C_{18}								2535	2541

(Continued on p. 328)

TABLE I (*continued*)

Compounds	*Carbon No.*	*Temperature (°C)*								
		80	*100*	*120*	*140*	*160*	*180*	*200*	*220*	*240*
n-Alkyl 4-chloro-butanoates	C_1	941	990	941	924	920	923	922	848	
	C_2	1015	1022	1018	1002	995	989	982	930	
	C_3	1110	1117	1117	1102	1100	1093	1099	1042	1084
	C_4	1208	1215	1216	1202	1199	1194	1202	1162	1174
	C_5	1303	1314	1317	1301	1299	1295	1308	1286	1294
	C_6		1417	1418	1401	1401	1401	1409	1397	1390
	C_7			1518	1500	1501	1503	1510	1499	1493
	C_8			1619	1599	1601	1607	1611	1605	1605
	C_9				1698	1702	1708	1711	1710	1708
	C_{10}				1796	1802	1809	1812	1811	1809
	C_{11}				1894	1902	1909	1912	1913	1911
	C_{12}				1991	2001	2010	2012	2014	2016
	C_{14}						2211	2210	2214	2218
	C_{16}							2406	2412	2417
	C_{18}								2608	2616

TABLE II

RETENTION INDICES OF C_1–C_{18} *n*-ALKYL ESTERS OF BUTANOIC AND MONOCHLORO-BUTANOIC ACIDS ON OV-351

Compounds	*Carbon No.*	*Temperature (°C)*							
		80	*100*	*120*	*140*	*160*	*180*	*200*	*220*
n-Alkyl butanoates	C_1	984	989	1036					
	C_2	1030	1048	1085					
	C_3	1114	1146	1169	1227	1233			
	C_4	1209	1237	1262	1294	1300	1272		
	C_5	1305	1333	1352	1375	1382	1382		
	C_6	1403	1425	1441	1460	1467	1456		
	C_7	1500	1516	1525	1547	1550	1550	1540	
	C_8	1599	1609	1614	1642	1645	1643	1656	
	C_9	1696	1704	1702	1738	1740	1740	1784	
	C_{10}		1800	1790	1835	1838	1843	1884	
	C_{11}			1881	1933	1936	1943	1894	1903
	C_{12}			1973	2032	2035	2042	2004	2002
	C_{14}				2229	2234	2241	2215	2216
	C_{16}				2426	2432	2440	2425	2423
	C_{18}					2629	2636	2628	2629
n-Alkyl 2-chlorobutanoates	C_1	1263	1292	1317	1345	1354	1341		
	C_2	1294	1322	1344	1368	1382	1382		
	C_3	1371	1396	1414	1439	1441	1425		
	C_4	1460	1479	1495	1520	1524	1519		
	C_5	1552	1565	1576	1603	1611	1611		

TABLE II (*continued*)

Compounds	*Carbon No.*	*Temperature (°C)*							
		80	*100*	*120*	*140*	*160*	*180*	*200*	*220*
	C_6	1647	1656	1661	1695	1703	1706	1634	1620
	C_7		1750	1748	1791	1798	1802	1746	1746
	C_8		1844	1837	1888	1896	1904	1853	1853
	C_9			1927	1986	1993	2004	1960	1969
	C_{10}			2020	2084	2093	2106	2071	2072
	C_{11}			2112	2183	2190	2203	2177	2183
	C_{12}				2281	2291	2301	2285	2286
	C_{14}					2489	2500	2493	2493
	C_{16}					2687	2699	2698	2703
	C_{18}						2894	2903	2906
n-Alkyl 3-chlorobutanoates	C_1	1305	1333	1352	1375	1382	1382		
	C_2	1343	1370	1390	1413	1419	1411		
	C_3	1428	1450	1466	1489	1497	1478		
	C_4	1518	1533	1546	1570	1574	1574	1527	
	C_5	1613	1623	1630	1660	1667	1672	1600	1569
	C_6		1716	1716	1756	1763	1769	1705	1711
	C_7		1810	1804	1852	1858	1865	1813	1812
	C_8			1895	1950	1955	1965	1926	1924
	C_9			1986	2047	2054	2066	2030	2033
	C_{10}			2078	2147	2154	2165	2137	2134
	C_{11}				2245	2252	2264	2243	2246
	C_{12}				2343	2352	2364	2348	2347
	C_{14}					2550	2562	2554	2552
	C_{16}						2760	2757	2765
	C_{18}							2959	2966
n-Alkyl 4-chlorobutanoates	C_1	1421	1445	1462	1489	1497	1478		
	C_2	1460	1479	1495	1520	1524	1519		
	C_3	1541	1555	1568	1599	1607	1611		
	C_4	1634	1646	1652	1690	1699	1706	1634	1620
	C_5		1744	1738	1784	1794	1802	1745	1746
	C_6		1842	1827	1880	1889	1900	1853	1853
	C_7			1917	1978	1985	2000	1960	1969
	C_8			2009	2075	2086	2098	2071	2072
	C_9			2101	2174	2185	2200	2177	2183
	C_{10}				2272	2285	2298	2284	2286
	C_{11}				2371	2385	2397	2387	2391
	C_{12}					2484	2497	2492	2493
	C_{14}					2682	2696	2696	2702
	C_{16}						2892	2901	2905
	C_{18}							3100	3107

noate and butanoate esters. With previous studies of *n*-alkyl esters[9] it was shown that values near 100 index units were observed, although the range of alcohol chain lengths considered was much smaller.

Table IV shows the incremental effect of substitution along the butanoic acid chain on SE-30 at 120 and 220°C. At the lower temperature the enhanced retention with the 2-chloro position adjacent to the carbonyl group is approximately 150 re-

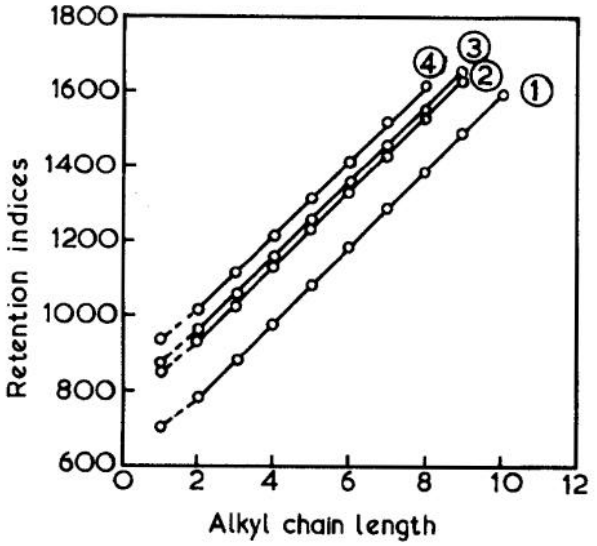

Fig. 1. Retention plots for alkyl butanoates and monochlorobutanoates on SE-30 at 120°C. (1) *n*-Alkyl butanoates; (2) *n*-alkyl 2-chlorobutanoates; (3) *n*-alkyl 3-chlorobutanoates; (4) *n*-alkyl 4-chlorobutanoates.

TABLE III

METHYLENE INCREMENTS FOR HOMOLOGOUS ALCOHOLS AND ESTERS AT 120 AND 220°C ON SE-30 AND OV-351

Alkyl chain length	*n-Alkanols**				*n-Alkyl butanoates*				*n-Alkyl 2-chloro-*	
	SE-30		*OV-351*		*SE-30*		*OV-351*		*SE-30*	
	120°C	*220°C*	*120°C*	*220°C*	*120°C*	*220°C*	*120°C*	*220°C*	*120°C*	*220°C*
2	42**		37**		77**		49**		71**	
3	62**		16**		102		84		96	
4	74**		93		97		93		99	123
5	99		114		102	123	90		97	105
6	97		94		101	105	89		102	118
7	105		95		101	118	84		101	104
8	99		101		102	104	89	141	99	104
9	98		99		101	105	88	126	101	103
10	100		99	103	101	105	88	117		103
11	100	83**	100	103		103	91	114		103
12	101	103	98	93		101	92	99		100
14	99	106		99		102		107		100
16		104		99		101		104		100
18		102		99		99		103		99
Σ	100	104	99	99	101	106	89	114	99	105

* From ref. 1.
** Not included in average values.

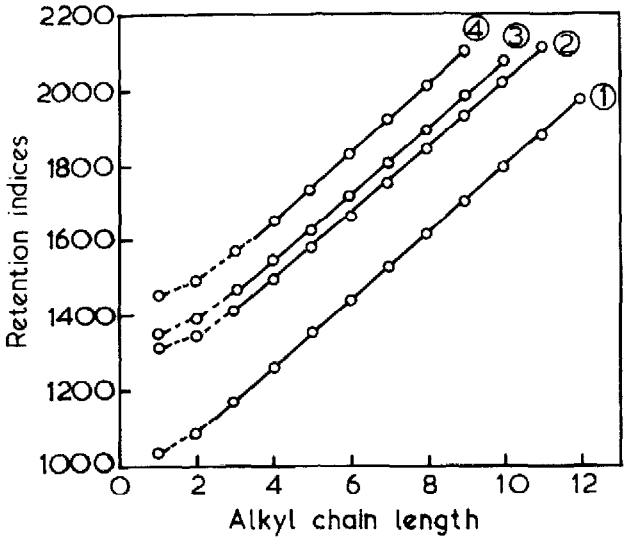

Fig. 2. Retention plots for alkyl butanoates and monochlorobutanoates on OV-351 at 120°C. (1) *n*-Alkyl butanoates; (2) *n*-alkyl 2-chlorobutanoates; (3) *n*-alkyl 3-chlorobutanoates; (4) *n*-alkyl 4-chlorobutanoates.

butanoates		*n-Alkyl 3-chlorobutanoates*				*n-Alkyl 4-chlorobutanoates*			
OV-351		*SE-30*		*OV-351*		*SE-30*		*OV-351*	
120°C	*220°C*	*120°C*	*220°C*	*120°C*	*220°C*	*120°C*	*220°C*	*120°C*	*220°C*
27**		77**		38**		77**	82**	33**	100
70**		98	139**	76**		99	112	73**	116
81		100	115	80**	158**	99	120	84	124
81	116	99	94	84	131	101	124	86	126
85	124	102	119	86	142	101	111	89	107
87	126	100	110	88	101	100	102	90	116
89	107	101	106	91	112	101	106	92	103
90	116		103	91	109		105	92	111
93				92	101		101		103
92	111		102		112		102		105
	103		100		101		101		102
	104		101		103		100		105
	105		100		106		99		102
	102		99		101		98		101
87	111	100	104	89	111	100	106	89	109

TABLE IV

INCREMENTAL EFFECT OF CHLORINE SUBSTITUENT ON BUTANOATE ESTERS, DETERMINED ON SE-30 AT 120 AND 220°C

Alkyl chain length	*120°C*			*220°C*		
	*Δ2-ClB − ΔB**	*Δ3-ClB − ΔB**	*Δ4-ClB − ΔB**	*Δ2-ClB − ΔB**	*Δ3-ClB − ΔB**	*Δ4-ClB − ΔB**
1	159	164	235			
2	153	164	135			
3	147	160	232			
4	149	163	234	173	205**	265
5	144	160	233	152	176	266
6	145	161	233	180	190	272
7	145	160	232	166	182	256
8	142	159	231	166	184	258
9	142			164	182	258
10				162	179	254
11				162	178	253
12				161	177	253
14				159	175	250
16				157	173	247
18				156	172	245
Σ	147	161	233	163	179	256

* Δ2-ClB, Δ3-ClB, Δ4Cl-B and ΔB = retention indices of the 2-chloro, 3-chloro, 4-chloro and parent butanoate esters, respectively.

** Not included in average values.

TABLE V

INCREMENTAL EFFECT OF POSITION OF CHLORINE SUBSTITUENT IN CHLOROBUTANOATE ESTERS, OBTAINED ON OV-351 AT 120 AND 220°C

Alkyl chain length	*120°C*			*220°C*		
	*Δ2-ClB − ΔB**	*Δ3-ClB − ΔB**	*Δ4-ClB − ΔB**	*Δ2-ClB − ΔB**	*Δ3-ClB − ΔB**	*Δ4-ClB − ΔB**
1	281**	316**	426**			
2	259	305	410			
3	245	297	399			
4	233	284	390			
5	224	278	386			
6	220	275	386			
7	223	279	392	341**	407**	564**
8	223	281	395	307	378	526
9	225	284	399	297	361	511
10	230	288		283	345	497
11	231			280	343	488
12				284	345	491
14				277	336	486
16				280	342	482
18				277	337	478
Σ	231	286	395	286	348	495

* Δ2-ClB, Δ3-ClB, Δ4Cl-B and ΔB = retention indices of the 2-chloro, 3-chloro, 4-chloro and parent butanoate esters, respectively.

** Not included in average values.

TABLE VI

INCREMENTAL SEPARATION BETWEEN HOMOLOGOUS 2-CHLORO-, 3-CHLORO- AND 4-CHLOROBUTANOATES AT 120 AND 220°C AND RETENTION INCREMENT RATIOS

Temperature (°C)	*SE-30*					*OV-351*					*ΔOV-351 / ΔSE-30*		
	2-Cl	*3-Cl*	*4-Cl*	*Δ(3-Cl−2-Cl)*	*Δ(4-Cl−3-Cl)*	*2-Cl*	*3-Cl*	*4-Cl*	*Δ(3-Cl−2-Cl)*	*Δ(4-Cl−3-Cl)*	*2-Cl*	*3-Cl*	*4-Cl*
120	147	161	233	14	72	231	286	395	55	109	1.57	1.78	170
220	163	179	256	16	77	286	348	495	62	147	1.75	1.94	1.93

tention index units at 120°C, the increment increasing slightly to approximately 160 index units for the 3-chloro- position and increasing substantially for the 4-chloro or terminal position to approximately 230 index units. The trend is as previously observed[1], *viz.*, the slight increase in retention for the 3-chloro position is due to the slightly greater separation of two adjacent pendant groups, and the marked enhancement for the substituent at the chain extremity is due to its vulnerable position. At 220°C the relative increases on substitution are maintained, all of the values increasing slightly.

The corresponding incremental increases on the OV-351 column are shown in Table V, where it is apparent that all of the values have increased relative to the retention on the non-polar column. The enhancements for the 2-, 3- and 4-chloro esters at 120°C are 231, 286 and 395 retention index units, respectively, and increase to a greater extent than on SE-30, *i.e.*, to 286, 348 and 495 retention index units at 220°C.

Retention increment ratios as presented in Table VI show that the 3-chloro ester ratio is higher than that for the 2-chloro homologues, the higher ratio indicating the influence of polar effects. The lower ratio for the 2-chloro esters shows the increasing influence of steric effects due to the proximity of the carbonyl group and the chlorine substituent. The 4-chloro esters show a higher ratio than the 2-chloro homologues, the ratio being very similar to but slightly lower than that for the 3-chloro esters. This possibly indicates that the longer acyl chain allows the substituent at the terminal position to move closer to the carbonyl group.

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