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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XXXIII*. CAPILLARY CHROMATOGRAPHY OF MONOCHLORINATED C_1–C_8 *n*-ALKYL ACETATES, CHLOROACETATES, DICHLOROACETATES AND TRICHLOROACETATES

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SUMMARY

The effect on retention of the pattern of chlorination in *n*-C_1–C_8 monochlorinated acetates, chloroacetates, dichloroacetates and trichloroacetates has been studied at temperatures between 100 and 200°C on a low-polarity (SE-30) and a polar (OV-351) capillary column. The work extends earlier studies and shows the effect of the degree and position of chlorination in both the acyl and alkyl chains.

INTRODUCTION

The relative incremental effects of the chain parameters, *i.e.*, length and some substituents, have been studied with a wide variety of alkanoic esters and it has been established that a particular effect of a variable on retention is greater in the alkyl rather than in the acyl chain[1,2]. The retention behaviour and incremental effect of the methyl esters of the isomeric monochlorinated C_5–C_{18} monocarboxylic acids[3] has shown the influence on retention of the position of a chlorine substituent in the acyl chain, and the influence of the same substituent in the alkyl chain was shown by a study of the isomeric monochlorinated C_1–C_{18} *n*-alkyl acetates[4]. The elution of C_1–C_8 *n*-alkyl acetates with mono-, di- and trichlorination on SE-30 and OV-351 capillary columns has been reported[5]. The C_1–C_5 and C_6–C_{16} esters have also been separated at 80°C and 200°C, respectively, on an OV-101 capillary column[6].

In this work we studied the C_1–C_8 *n*-alkyl acetates, chloroacetates, dichloroacetates and trichloroacetates with monochlorination at each position along the alkyl chain on SE-30 and OV-351 capillary columns at temperatures between 80 and 200°C, extending the data obtained previously with temperature programming[7]. The effect

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TABLE I

RETENTION INDICES OF C_1–C_8 MONOCHLORINATED *n*-ALKYL ACETATES ON SE-30 AND OV-351

Isomeric acetate	*SE-30*								*OV-351*						
	60°C	*80°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*60°C*	*80°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*
Methyl	509	505	505						823	839	844	877			
Chloro	691	680	674						1181	1180	1164	1174			
Ethyl	613	577	607						881	880	875	908			
1-Chloro	744	724	726						1150	1153	1123	1130	1202		
2-Chloro	817	801	796						1315	1319	1297	1299	1354		
Propyl	711	685	676	696					981	978	943	992	1075		
1-Chloro	838	821	806	805					1217	1222	1198	1207	1278		
2-Chloro	864	848	835	831					1296	1304	1283	1289	1348		
3-Chloro	924	916	902	895					1418	1425	1414	1419	1470		
Butyl		810	786	774	781				1080	1079	1053	1064	1154		
1-Chloro		930	906	895	912				1292	1298	1278	1279	1342		
2-Chloro		964	944	930	951				1377	1384	1370	1375	1425		
3-Chloro		981	961	949	972				1424	1432	1422	1427	1478		
4-Chloro		1038	1021	1008	1033				1523	1539	1533	1540	1585		
Pentyl		912	885	867	879						1195	1182	1212	1232	
1-Chloro		1026	1006	990	1011						1401	1387	1419	1408	
2-Chloro		1051	1033	1017	1041						1469	1460	1492	1497	
3-Chloro		1078	1062	1048	1072						1528	1525	1558	1562	
4-Chloro		1089	1073	1058	1084						1563	1564	1594	1594	
5-Chloro		1143	1129	1116	1142						1652	1657	1687	1691	

Hexyl	1008	972	993	1000					1277	1255	1286	1295	1277
1-Chloro	1117	1086	1108	1114					1472	1457	1492	1500	1485
2-Chloro	1147	1121	1143	1151					1540	1532	1576	1574	1575
3-Chloro	1166	1143	1166	1173					1581	1578	1627	1629	1628
4-Chloro	1186	1163	1187	1194					1626	1627	1679	1679	1686
5-Chloro	1194	1171	1194	1202					1647	1650	1700	1703	1711
6-Chloro	1247	1227	1249	1257					1747	1737	1789	1796	1802
Heptyl	1095	1070	1086	1090	1093				1385	1372	1401	1400	1385
1-Chloro	1211	1191	1211	1215	1212				1582	1578	1602	1607	1615
2-Chloro	1235	1217	1239	1244	1242				1647	1647	1673	1673	1675
3-Chloro	1254	1238	1260	1266	1262				1686	1691	1718	1720	1725
4-Chloro	1266	1251	1273	1278	1276				1717	1723	1753	1757	1759
5-Chloro	1284	1269	1292	1297	1295				1749	1756	1787	1791	1797
6-Chloro	1291	1276	1298	1303	1299				1767	1775	1806	1809	1818
7-Chloro	1342	1329	1350	1354	1354				1846	1857	1889	1894	1904
Octyl	1194	1165	1188	1189	1190	1178			1468	1454	1490	1486	1485
1-Chloro	1306	1287	1312	1314	1315	1310			1659	1658	1702	1704	1711
2-Chloro	1328	1312	1338	1343	1344	1340			1722	1724	1771	1771	1775
3-Chloro	1345	1331	1358	1362	1364	1364			1758	1764	1814	1819	1824
4-Chloro	1355	1342	1369	1373	1373	1375			1787	1794	1845	1850	1856
5-Chloro	1365	1352	1379	1384	1385	1384			1802	1811	1862	1867	1874
6-Chloro	1382	1370	1396	1402	1405	1404			1830	1840	1893	1899	1909
7-Chloro	1385	1372	1399	1403	1405	1404			1842	1852	1905	1912	1922
8-Chloro	1435	1425	1451	1456	1458	1459			1918	1932	1987	1994	2006

TABLE II

RETENTION INDICES OF MONOCHLORINATED C_1–C_8 *n*-ALKYL CHLOROACETATES ON SE-30 AND OV-351

Chloro-acetate	*SE-30*							*OV-351*					
	80°C	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*
Methyl	705	708	691	679				1270	1264	1314	1345	1318	1368
Chloro	914	903	873	869				1619	1614	1637	1637	1637	1664
Ethyl	802	791	776	774				1302	1292	1337	1355	1336	1380
1-Chloro	926	911	895	910				1548	1539	1570	1570	1571	1600
2-Chloro	1016	1002	990	1007				1759	1755	1789	1787	1792	1803
Propyl	918	907	878	872	870			1381	1370	1410	1419	1420	1423
1-Chloro	1032	1027	1001	1011	1006			1606	1599	1634	1630	1631	1649
2-Chloro	1069	1066	1044	1954	1053			1716	1714	1749	1752	1755	1759
3-Chloro	1134	1138	1118	1130	1128			1848	1851	1890	1896	1902	1909
Butyl		1007	996	986	986			1472	1466	1500	1508	1510	1534
1-Chloro		1113	1103	1102	1106			1674	1669	1701	1701	1701	1709
2-Chloro		1162	1152	1156	1163			1793	1792	1829	1830	1840	1844
3-Chloro		1182	1174	1178	1181			1840	1844	1884	1890	1898	1907
4-Chloro		1247	1241	1247	1251			1960	1968	2010	2017	2028	2036
Pentyl			1086	1086	1089	1096				1609	1598	1583	1617
1-Chloro			1194	1198	1202	1203				1793	1789	1781	1790
2-Chloro			1234	1241	1246	1250				1901	1903	1899	1916
3-Chloro			1267	1274	1281	1283				1967	1970	1974	1983
4-Chloro			1282	1289	1295	1297				2013	2015	2022	2030
5-Chloro			1346	1353	1358	1362				2115	2120	2131	2138

Hexyl	1176	1188	1192	1184	1178				1690	1686	1687
1-Chloro	1281	1297	1302	1300	1298				1884	1887	1886
2-Chloro	1319	1337	1344	1344	1344				1982	1987	1982
3-Chloro	1341	1361	1369	1368	1370				2033	2042	2042
4-Chloro	1366	1386	1394	1395	1398				2091	2102	2106
5-Chloro	1379	1399	1407	1406	1411				2120	2132	2134
6-Chloro	1436	1455	1464	1465	1470				2211	2226	2232
Heptyl		1297	1293	1276	1275				1785	1788	1797
1-Chloro		1400	1399	1393	1395				1967	1974	1976
2-Chloro		1438	1440	1433	1435				2074	2082	2086
3-Chloro		1460	1462	1458	1460				2122	2134	2140
4-Chloro		1476	1479	1476	1479				2162	2176	2181
5-Chloro		1500	1503	1499	1503				2203	2218	2225
6-Chloro		1506	1509	1505	1508				2220	2237	2244
7-Chloro		1559	1563	1563	1564				2308	2325	2333
Octyl		1395	1391	1386	1365				1895	1888	1895
1-Chloro		1499	1497	1494	1491				2074	2075	2088
2-Chloro		1536	1537	1537	1526				2179	2184	2187
3-Chloro		1554	1558	1559	1551				2221	2231	2239
4-Chloro		1570	1572	1575	1569				2258	2270	2278
5-Chloro		1586	1588	1591	1586				2282	2295	2305
6-Chloro		1603	1606	1610	1604				2312	2326	2337
7-Chloro		1606	1609	1611	1607				2324	2339	2349
8-Chloro		1659	1663	1668	1663				2408	2425	2438

TABLE III

RETENTION INDICES OF MONOCHLORINATED C_1–C_8 *n*-ALKYL DICHLOROACETATES ON SE-30 AND OV-351

Dichloro-acetate	*SE-30*							*OV-351*				
	80°C	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*
Methyl	821	808	791	785				1361	1387	1365	1362	1391
Chloro	976	960	926	962				1687	1705	1695	1706	1700
Ethyl	887	871	872	869				1384	1404	1396	1400	1423
1-Chloro	994	980	979	985				1594	1614	1602	1601	1611
2-Chloro	1094	1083	1083	1094				1846	1870	1866	1873	1876
Propyl	979	964	934	969	969			1454	1478	1471	1469	1488
1-Chloro	1081	1071	1040	1084	1084			1647	1667	1660	1661	1673
2-Chloro	1127	1117	1089	1133	1132			1786	1812	1810	1819	1821
3-Chloro	1197	1190	1163	1209	1212			1923	1954	1959	1971	1978
Butyl		1061	1061	1072	1070			1542	1562	1554	1559	1575
1-Chloro		1156	1159	1172	1173			1709	1729	1723	1734	1733
2-Chloro		1211	1214	1229	1235			1858	1885	1885	1896	1898
3-Chloro		1231	1236	1252	1257			1906	1939	1942	1955	1961
4-Chloro		1302	1308	1325	1332			2044	2076	2083	2097	2106
Pentyl			1129	1167	1173	1172			1658	1651	1658	1664
1-Chloro			1222	1263	1272	1271			1815	1810	1813	1815
2-Chloro			1268	1313	1322	1324			1952	1950	1958	1961
3-Chloro			1300	1347	1356	1360			2014	2017	2031	2036
4-Chloro			1318	1367	1374	1378			2070	2074	2088	2097
5-Chloro			1385	1432	1440	1446			2182	2189	2205	2215

Hexyl	1260	1270	1270	1270	1273			1749	1751	1759
1-Chloro	1360	1362	1364	1367	1372			1900	1901	1900
2-Chloro	1396	1409	1412	1418	1425			2037	2044	2047
3-Chloro	1416	1433	1438	1445	1451			2085	2098	2105
4-Chloro	1442	1468	1468	1475	1485			2153	2169	2175
5-Chloro	1457	1482	1483	1490	1502			2189	2205	2214
6-Chloro	1509	1535	1541	1550	1557			2281	2300	2312
Heptyl		1372	1376	1374	1372			1848	1856	1860
1-Chloro		1462	1468	1469	1471			1999	2004	2021
2-Chloro		1505	1513	1517	1521			2130	2139	2144
3-Chloro		1527	1537	1541	1548			2175	2188	2196
4-Chloro		1548	1558	1563	1569			2224	2239	2249
5-Chloro		1576	1586	1591	1599			2273	2290	2300
6-Chloro		1582	1592	1597	1604			2289	2306	2317
7-Chloro		1636	1646	1654	1661			2377	2395	2409
Octyl		1476	1473	1476	1482			1950	1956	1961
1-Chloro		1560	1571	1567	1573			2101	2115	2124
2-Chloro		1602	1608	1614	1621			2224	2235	2239
3-Chloro		1623	1629	1637	1645			2266	2281	2291
4-Chloro		1641	1648	1657	1665			2311	2328	2338
5-Chloro		1661	1667	1677	1685			2343	2361	2371
6-Chloro		1678	1685	1695	1704			2372	2391	2403
7-Chloro		1682	1689	1699	1706			2384	2404	2416
8-Chloro		1736	1774	1754	1761			2470	2491	2506

TABLE IV

RETENTION INDICES OF MONOCHLORINATED C_1–C_8 *n*-ALKYL TRICHLOROACETATES ON SE-30 AND OV-351

Trichloro-acetate	*SE-30*							*OV-351*				
	80°C	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*
Methyl	884	875	867	876				1387	1378	1387	1392	1443
Chloro	1031	1021	1012	1038				1654	1653	1657	1661	1678
Ethyl	955	944	930	949				1400	1390	1396	1392	1443
1-Chloro	1048	1036	1023	1050				1547	1545	1550	1554	1587
2-Chloro	1152	1148	1139	1172				1836	1849	1852	1859	1873
Propyl	1044	1034	1026	1057	1066			1466	1459	1471	1463	1512
1-Chloro	1129	1123	1117	1154	1163			1590	1591	1598	1611	1628
2-Chloro	1180	1176	1172	1210	1217			1765	1778	1784	1794	1809
3-Chloro	1252	1251	1249	1288	1294			1895	1921	1931	1944	1961
Butyl		1127	1117	1148	1156			1542	1543	1550	1554	1587
1-Chloro		1208	1201	1237	1244			1647	1650	1657	1661	1678
2-Chloro		1268	1264	1301	1311			1828	1846	1851	1859	1873
3-Chloro		1291	1289	1326	1337			1875	1900	1911	1923	1941
4-Chloro		1364	1365	1403	1413			2023	2050	2061	2079	2093
Pentyl			1216	1252	1256	1256			1634	1630	1631	1668
1-Chloro			1296	1333	1338	1338			1733	1729	1736	1756
2-Chloro			1348	1387	1393	1398			1905	1908	1920	1935
3-Chloro			1382	1423	1430	1437			1969	1978	1993	2013
4-Chloro			1404	1444	1451	1459			2034	2046	2061	2078
5-Chloro			1474	1513	1523	1530			2155	2170	2188	2205

Hexyl	1315	1350	1358	1361	1367	1726	1734	1766
1-Chloro	1393	1429	1436	1442	1447	1821	1829	1844
2-Chloro	1442	1480	1488	1498	1503	1992	2006	2026
3-Chloro	1467	1505	1516	1525	1532	2042	2061	2083
4-Chloro	1498	1537	1549	1558	1566	2119	2141	2159
5-Chloro	1518	1557	1568	1575	1585	2164	2186	2205
6-Chloro	1576	1614	1625	1638	1645	2258	2281	2300
Heptyl		1453	1455	1459	1463	1826	1831	1850
1-Chloro		1527	1533	1538	1546	1915	1923	1935
2-Chloro		1575	1583	1592	1600	2085	2095	2108
3-Chloro		1599	1609	1618	1628	2132	2148	2162
4-Chloro		1622	1632	1642	1652	2191	2209	2223
5-Chloro		1652	1664	1673	1681	2249	2267	2284
6-Chloro		1659	1669	1679	1688	2266	2285	2301
7-Chloro		1714	1726	1736	1745	2354	2375	2393
Octyl		1549	1557	1562	1564	1922	1934	1949
1-Chloro		1624	1632	1637	1645	2023	2042	2057
2-Chloro		1670	1681	1690	1698	2176	2193	2218
3-Chloro		1693	1705	1714	1724	2219	2241	2256
4-Chloro		1713	1726	1736	1746	2275	2296	2313
5-Chloro		1736	1748	1760	1770	2315	2338	2355
6-Chloro		1753	1766	1778	1789	2345	2369	2387
7-Chloro		1757	1770	1782	1793	2358	2382	2401
8-Chloro		1812	1826	1838	1845	2446	2472	2491

TABLE V

INCREMENTAL EFFECT OF MONOCHLORINATION AT EACH POSITION ALONG THE ALKYL CHAIN OF ACETATES, CHLOROACETATES, DICHLOROACETATES AND TRICHLOROACETATES ON SE-30

Temperature (°C)	*Substituent*	*Acetates*								*Chloroacetates*							
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
80	1-Chloro	175	147	136	120	114				209	124	114					
	2-Chloro		224	163	154	139					214	151					
	3-Chloro			231	171	166						216					
	4-Chloro				228	177											
	5-Chloro					231											
100	1-Chloro	169	119	130	120	121	109	116	112	195	120	120	106				
	2-Chloro		189	159	158	148	139	140	134		211	159	155				
	3-Chloro			226	175	177	158	159	151			231	175				
	4-Chloro				235	188	178	171	161				240				
	5-Chloro					244	186	189	171								
	6-Chloro						239	196	188								
	7-Chloro							247	191								
	8-Chloro								241								
120	1-Chloro			109	121	123	114	121	122	182	119	123	107	108	105		
	2-Chloro			135	156	150	149	147	147		214	166	156	148	143		
	3-Chloro			199	175	181	171	168	166			240	178	181	165		
	4-Chloro				234	191	191	181	177				245	196	190		
	5-Chloro					249	199	199	187					260	203		
	6-Chloro						255	206	205						260		
	7-Chloro							259	207								
	8-Chloro								260								
140	1-Chloro				131	132	115	125	124	190	136	139	116	112	109	103	104
	2-Chloro				170	162	150	153	150		233	182	170	155	149	141	141
	3-Chloro				191	193	173	174	170			258	192	188	173	163	159
	4-Chloro				252	205	194	187	181				261	203	198	179	175
	5-Chloro					263	201	206	191					267	211	203	191
	6-Chloro						256	212	208						267	209	208
	7-Chloro							264	211							262	211
	8-Chloro								263								264
160	1-Chloro						114	125	125			136	120	113	110	106	106
	2-Chloro						151	154	154			183	177	157	152	147	146
	3-Chloro						173	176	173			258	195	192	177	169	167
	4-Chloro						194	188	184				265	206	202	186	181
	5-Chloro						202	207	195					269	215	210	197
	6-Chloro						257	213	213						272	216	215
	7-Chloro							264	214							270	218
	8-Chloro								267								272
180	1-Chloro							119	125					107	116	117	108
	2-Chloro							149	154					154	160	157	151
	3-Chloro							169	174					187	184	182	173
	4-Chloro							173	183					201	211	200	189
	5-Chloro							202	195					266	222	223	205
	6-Chloro							206	215						281	229	224
	7-Chloro							261	215							287	225
	8-Chloro								268								282

Dichloroacetates								*Trichloroacetates*							
C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
155	107 207	102 148 218						147	93 197	85 136 208					
152	109 212	107 153 226	95 150 170 241					146	92 204	89 142 217	81 141 164 237				
135	107 211	106 155 229	98 153 175 247	93 139 171 189 256	100 136 156 182 197 249			145	93 209	91 146 223	84 147 172 248	80 132 166 188 258	78 127 152 183 203 261		
177	116 225	115 164 240	100 157 180 253	96 146 180 200 265	92 139 163 198 212 265	90 133 155 176 204 210 264	84 126 147 165 185 202 206 260	162	101 223	97 153 231	89 153 178 255	81 135 171 192 261	130	74 122 146 169 199 206 261	75 121 144 164 187 204 263
		115 163 243	103 165 187 262	99 149 183 201 267	94 142 168 198 213 271	92 137 161 182 210 216 270	98 135 156 175 194 212 216 301			97 151 228	88 155 181 257	82 137 174 195 267	78 130 158 191 210 267	78 128 154 177 209 214 271	75 124 148 169 191 209 213 269
				99 152 188 206 274	97 148 175 205 220 280	95 143 167 189 217 223 289	91 138 161 181 201 219 223 278					82 142 181 203 274	81 137 164 197 214 277	79 133 159 183 214 220 277	75 128 152 184 198 216 220 276

(Continued on p. 264)

TABLE V *(continued)*

Temperature (°C)	*Substituent*	*Acetates*								*Chloroacetates*							
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
200	1-Chloro								132						120	120	126
	2-Chloro								162						166	160	161
	3-Chloro								186						192	185	186
	4-Chloro								197						220	204	204
	5-Chloro								206						233	228	221
	6-Chloro								226						292	233	239
	7-Chloro								226							289	242
	8-Chloro								281								298

on retention of the degree of acyl chlorination and the position of the alkyl chlorine substituent is discussed.

EXPERIMENTAL

The aliphatic C_1–C_5 *n*-alkyl acetates were commercial products (Fluka, Buchs, Switzerland). The C_6–C_8 *n*-alkyl acetates were prepared from the corresponding alcohols and acetyl chloride[8], as were the chloroacetates, dichloroacetates and trichloroacetates[8]. The monochlorinated derivatives were prepared by liquid-phase chlorination of the parent esters[9].

The chromatography was carried out on a Perkin-Elmer Sigma 3 instrument. The injector and detector temperatures were 275°C, with nitrogen as the carrier gas at a flow-rate of 1 ml min^{-1} and a splitting ratio of 1:50. The two columns used were an SE-30 vitreous silica wall-coated open-tubular (WCOT) column (25 m × 0.33 mm I.D.), supplied by Scientific Glass Engineering (North Melbourne, Australia) and an OV-351 fused-silica WCOT column (25 m × 0.32 mm I.D.) supplied by Orion Analytica (Espoo, Finland). The chromatographic data were recorded with a Hewlett-Packard Model 3390A reporting integrator. Retention times were measured from the time of injection and the retention indices were determined off-line using a Vector MZ microprocessor system. The dead volume was determined by regression analysis using a series of *n*-alkanes by the procedure of Grobler and Balizs[10]. The crude chlorination mixtures were used for the determinations.

RESULTS AND DISCUSSION

Retention indices of the isomeric monochlorinated C_1–C_8 *n*-alkyl acetates are shown in Table I and corresponding data for the chloroacetates, dichloroacetates and trichloroacetates are shown in Tables II–IV, respectively, each determined at several temperatures.

The incremental effect of a chlorine substituent at each position along the chain for all of the acetates and chlorinated acetate series is shown in Tables V and VI. On SE-30, in common with other chlorinated esters studied previously[3,5,11,12], a considerable increase in retention occurs at the 1- or α-position with a further gradual increase in retention as the substituent moves towards the end of the

Dichloroacetates								*Trichloroacetates*							
C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
					99	99	91						80	83	81
					152	149	139						136	137	134
					178	176	163						165	165	160
					212	197	183						199	189	182
					229	227	203						218	218	206
					284	232	222						278	225	225
						289	224							282	229
							279								281

chain. At the terminal or ω-position, a considerable increase in retention again occurs. With the chloroacetates the effect of chlorination in the α-position is greater than with the acetates at 80–120°C, whereas at higher temperatures the position is reversed. Chlorination at the ω-position has little effect with the acetate or chloroacetate esters; the values for the former are higher up to 120, at 140°C the values are essentially identical and at higher temperatures the values for the chloroacetates continue to increase such that at 200°C the difference in values is much greater than at any other temperature. The increment $\omega - \alpha$ is influenced by the high values for the α-isomer at low temperatures, which give low $\omega - \alpha$ values; at higher temperatures the retention of the α-isomer decreases slightly but that for the ω-isomer increases more significantly, resulting in higher $\omega - \alpha$ values at higher temperatures.

At all temperatures it is evident that the incremental values for both the α- and ω-isomers decrease with substitution in the chloro-, dichloro- and trichloroacetates. In all instances the absolute values of the increments due to α-substitution decrease with all the esters as the temperature is increased, while the absolute values of the ω-increments increase and accordingly the $\omega - \alpha$ values increase with increasing temperature at a greater rate. The values for the ω- and α-isomers and the $\omega - \alpha$ values are given in Table VII.

The corresponding values showing the effect of a chlorine substituent in the alkyl chain on a polar stationary phase are shown in Table VI. With retention on the polar column, considerably increased retention is shown by all series with substitution in the α-position, with a further gradual increased retention until the ω-position, where a further considerable enhancement occurs. With the three chlorinated acetate series the greatest increase in retention with substitution in the α-position occurs with the chloroacetates, with a smaller increase for the dichloroacetates and the smallest for the trichloroacetates. The values tend to decrease progressively with increasing temperature whereas the values for the ω-isomers tend to show a slight increase.

The trend with the ω-substituted esters varies with temperature. At the lowest temperature the highest value is observed with the chloroacetates, with a progressive decrease to the dichloro- to trichloroacetates. With increasing temperature the dichloroacetates show the highest retention, the values for the trichloroacetates generally being slightly different to those for the dichloroacetates.

With all three series the highest $\omega - \alpha$ values occur with the trichloroacetates,

TABLE VI

INCREMENTAL EFFECT OF MONOCHLORINATION AT EACH POSITION ALONG THE ALKYL CHAIN OF ACETATES, CHLOROACETATES, DICHLOROACETATES AND TRICHLOROACETATES ON OV-351

Temperature (°C)	*Substituent*	*Acetates*								*Chloroacetates*							
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
100	1-Chloro	320	248	255	225					349	246	225	202				
	2-Chloro		422	340	317						457	335	321				
	3-Chloro			471	369							467	368				
	4-Chloro				480								488				
120	1-Chloro	297	222	215	215					350	247	229	203				
	2-Chloro		391	297	311						463	344	326				
	3-Chloro			427	363							481	378				
	4-Chloro				476								502				
140	1-Chloro			203	188	207				323	233	224	201	184			
	2-Chloro			273	271	280					452	339	329	292			
	3-Chloro			395	324	346						480	384	358			
	4-Chloro				431	382							510	404			
	5-Chloro					475								506			
160	1-Chloro					176	205	207	218	292	215	211	193	191	194	182	179
	2-Chloro					265	279	273	285		432	333	322	305	292	289	284
	3-Chloro					330	334	320	333			477	382	372	343	337	326
	4-Chloro					362	384	357	364				509	417	401	377	363
	5-Chloro					459	408	391	381					522	430	418	387
	6-Chloro						501	409	413						521	435	417
	7-Chloro							494	426							523	429
	8-Chloro								508								513
180	1-Chloro						208	230	226	319	235	211	191	198	201	186	187
	2-Chloro						298	290	290		456	335	330	316	301	294	296
	3-Chloro						351	340	339			482	388	391	356	346	343
	4-Chloro						409	374	371				518	439	416	388	382
	5-Chloro						434	412	389					548	446	430	407
	6-Chloro						525	433	424						540	449	438
	7-Chloro							519	437							537	451
	8-Chloro								521								537
200	1-Chloro									296	220	226	175	173	199	179	193
	2-Chloro										423	336	310	299	295	289	292
	3-Chloro											486	373	366	355	343	344
	4-Chloro												502	413	419	384	383
	5-Chloro													521	447	428	410
	6-Chloro														545	447	442
	7-Chloro															536	454
	8-Chloro																543

with progressively lower values for the dichloro- and monochloroacetates owing, as indicated previously, to the pattern of variation of the retention increments of the α- and ω-isomers.

The methylene increments on the polar column have little significance owing, as shown previously, to the lack of linearity of some comparable series of acyl chain

Dichloroacetates								*Trichloroacetates*							
C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
326	210	193	167					267	147	124	105				
	462	332	316						436	299	286				
		469	364							429	333				
			502								481				
318	210	189	167	157				275	155	132	107	99			
	466	334	323	294					459	319	303	271			
		476	377	356						462	357	335			
			514	412							507	400			
				524								521			
330	206	189	169	159	151	151	151	270	154	127	107	99	95	89	101
	470	339	331	299	288	282	274		456	313	301	278	266	259	254
		488	388	366	336	327	316			460	361	348	316	306	297
			529	423	404	376	361				511	416	393	365	353
				538	440	425	393					540	438	423	393
					532	411	422						532	440	423
						529	434							528	436
							520								524
344	201	192	175	155	150	148	159	269	162	148	107	105	95	92	108
	473	350	337	300	293	283	279		467	331	305	289	272	264	259
		502	396	373	347	332	325			481	369	362	327	317	307
			538	430	418	383	372				525	430	407	378	362
				547	454	434	405					557	452	436	404
					549	450	435						547	454	435
						539	448							544	448
							535								538
309	188	185	158	151	141	161	163	235	144	116	91	88	78	85	108
	453	333	323	297	288	284	278		430	297	286	267	260	258	269
		490	386	372	346	336	330			449	354	345	317	312	307
			531	433	416	389	377				506	410	393	373	364
				551	455	440	410					537	439	434	406
					553	457	442						534	451	438
						549	455							543	452
							545								542

esters[2], where markedly curved plots resulted. The most that can be indicated for the various chloroacetates is that the ΔCH_2 values at a particular temperature are generally very similar for the mono-, di- and trichloroacetates.

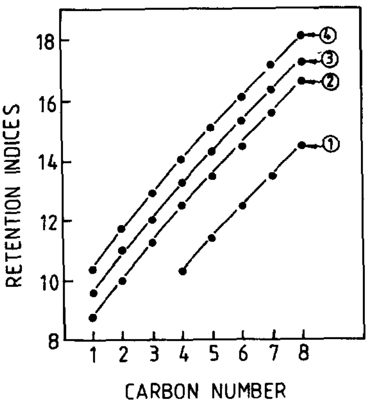
The effect of chlorine substitution in the acetate group on retention is shown in Figs. 1 and 2. Fig. 1 shows plots for the ω-substituted esters of n-alkyl acetates

TABLE VII

SUMMARY OF AVERAGE INCREMENTAL EFFECT OF POSITION OF MONOCHLORINATION IN THE ALKYL CHAIN OF ACETATES, CHLOROACETATES, DICHLOROACETATES AND TRICHLOROACETATES

Temperature (°C)	*Position of substituent**	*SE-30*				*OV-351*			
		Acetates	*Chloro-acetates*	*Dichloro-acetates*	*Trichloro-acetates*	*Acetates*	*Chloro-acetates*	*Dichloro-acetates*	*Trichloro-acetates*
80	α	138	149	121	108				
	ω	218	213	193	184				
	$\omega-\alpha$	99	96	108	114				
	ΔCH_2	116	110	111	111				
100	α	125	135	116	102	262	256		
	ω	224	219	208	201	423	440		
	$\omega-\alpha$	113	112	123	132	242	246		
	ΔCH_2	109	115	114	114	108	114		
120	α	118	124	107	95	237	257	224	161
	ω	243	234	221	224	398	449	440	403
	$\omega-\alpha$	124	131	138	155	249	256	288	323
	ΔCH_2	106	113	117	113	108	118	119	123
140	α	125	126	109	95	199	233	208	154
	ω	260	250	244	240	434	457	460	445
	$\omega-\alpha$	134	111	158	166	246	277	314	364
	ΔCH_2	105	113	111	111	106	120	119	126
160	α	121	115	100	83	202	207	188	130
	ω	263	271	269	260	491	474	492	478
	$\omega-\alpha$	141	153	169	177	289	305	347	397
	ΔCH_2	100	107	112	106	101	110	111	113
180	α	122	112	96	79	221	216	191	136
	ω	265	279	278	276	522	492	503	491
	$\omega-\alpha$	143	167	183	202	300	316	358	406
	ΔCH_2	104	102	103	103	102	113	112	116
200	α	132	122	96	81		208	182	118
	ω	281	293	284	280		482	498	472
	$\omega-\alpha$	149	171	188	199		313	361	404
	ΔCH_2		97	102	100		111	115	116

* $\Delta CH_2 = I_{\omega\text{-Cl}}(CH_2)_{x+1} - I_{\omega Cl}(CH_2)_x$.



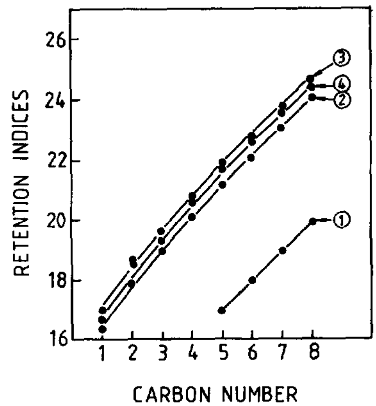


Fig. 1. Retention plots for ω-substituted esters of *n*-alkyl (1) acetates, (2) chloroacetates, (3) dichloroacetates and (4) trichloroacetates on SE-30 at 140°C.

Fig. 2. Retention plots for ω-substituted esters of *n*-alkyl (1) acetates, (2) chloroacetates, (3) dichloroacetates and (4) trichloroacetates on OV-351 at 140°C.

and chloro-, dichloro- and trichloroacetates on SE-30 at 140°C, where an increased retention occurs with increasing chlorination of the acetate group.

Fig. 2 shows a comparable plot for the same esters on OV-351 at 160°C, where it is evident that the retention is increased with the mono- and dichloroacetates but is reduced with the trichloroacetates. It is apparent with both plots that the greatest increase occurs with the monochloroacetates but that the effect is considerably greater on the polar stationary phase. The incremental changes that occur are shown in Table VIII, where it is evident that monochlorination of the acetate group leads to an enhancement of retention of 206–214 retention index units (i.u.) on the non-polar stationary phase whereas dichlorination leads to a further increase of 77–93 i.u. and trichlorination to a further increase of 76–81 i.u. With the polar stationary phase monochlorination results in an incremental increase of 414–429 i.u. with dichlorination showing a further increase of 58–79 i.u. and trichlorination a decrease of 19–38 i.u. compared with the dichloroacetates.

Table VIII also shows corresponding values for α-substitution of the same ester series and the same effects are evident, although the values are more variable. On SE-30 monochlorination results in a retention increase of 187–190 i.u., increasing by 61–93 and 64–76 i.u. with di- and trichloroacetates. On the polar stationary phase the variations are 360–384 i.u. for monochlorination, with an increase of 16–58 i.u. on dichlorination and a reduction of 38–84 i.u. on trichlorination.

Ratios of the retentions on the two stationary phases are shown in Table VIII. With ω-chlorination the values decrease both with increasing chain length and with increasing degree of chlorination, showing the increasing effect of steric considerations[13,14]. With the α-substituted esters the same trend in the results occurs but with the added consideration that the values are all reduced as compared with the values for the ω-substituted esters. This result is to be expected, as greater steric effects would be expected with the series with the alkyl chlorine substituent adjacent to the chlorinated acetate group.

TABLE VIII

INFLUENCE OF CHLORINATION OF ACETATE GROUP ON SE-30 AND OV-351 WITH α- AND ω-CHLORINATION OF THE ALKYL CHAIN

*Monochloro n-alkyl**	*OV-351 (160°C)*							
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
ω-Chlorination								
Acetate					1691	1796	1894	1994
Chloroacetate	1637	1787	1896	2017	2120	2211	2308	2408
Dichloroacetate	1695	1866	1959	2083	2189	2281	2377	2470
Trichloroacetate	1657	1852	1931	2061	2170	2258	2354	2446
ClA−A					429	415	414	414
2ClA−A						485	483	476
3ClA−A						462	460	452
ΔCl					429	415	414	414
Δ2Cl−ΔCl	58	79	63	66	69	70	69	62
Δ3Cl−Δ2Cl	−38	−14	−28	−22	−19	−23	−23	−24
α-Chlorination								
Acetate					1408	1500	1607	1704
Chloroacetate	1637	1570	1630	1701	1789	1884	1967	2074
Dichloroacetate	1695	1602	1660	1723	1810	1900	1999	2101
Trichloroacetate	1657	1550	1598	1657	1729	1821	1915	2023
ClA−A					381	384	360	370
2ClA−A					402	400	392	397
3ClA−A					321	321	308	319
ΔCl					381	384	360	370
Δ2Cl−ΔCl	58	32	30	22	21	16	32	27
Δ3Cl−Δ2Cl	−38	−52	−62	−66	−81	−79	−84	−78

* ClA−A = chloroacetate−acetate; 2ClA−A = dichloroacetate−acetate; 3ClA−A = trichloroacetate−acetate; Δ2Cl−ΔCl = dichloroacetate−chloroacetate; Δ3Cl−Δ2Cl = trichloroacetate−dichloroacetate.

SE-30 (140°C)								*Ratio OV-351/SE-30*							
C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
			1033	1142	1249	1350	1451					1.48	1.44	1.40	1.37
869	1007	1130	1247	1353	1455	1559	1659	1.88	1.77	1.68	1.62	1.57	1.52	1.48	1.45
962	1094	1209	1325	1432	1535	1636	1736	1.76	1.71	1.62	1.57	1.53	1.49	1.45	1.42
1038	1172	1288	1403	1513	1614	1714	1812	1.60	1.58	1.50	1.47	1.43	1.40	1.37	1.35
			214	211	206	209	208								
			292	290	286	286	285								
			370	371	365	364	361								
			214	211	206	209	208								
93	87	79	78	79	80	77	77								
76	78	79	78	81	79	78	76								
			912	1011	1108	1211	1312					1.39	1.35	1.33	1.30
869	910	1011	1102	1198	1297	1400	1499	1.88	1.73	1.61	1.54	1.49	1.45	1.41	1.38
962	985	1084	1172	1263	1362	1462	1560	1.76	1.63	1.53	1.47	1.43	1.40	1.37	1.35
1038	1050	1154	1237	1333	1429	1527	1624	1.60	1.48	1.38	1.34	1.30	1.27	1.25	1.25
			190	187	189	189	187								
			260	252	254	251	248								
			325	322	321	316	312								
			190	187	189	189	187								
93	75	73	70	65	65	62	61								
76	65	70	65	70	67	65	64								

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