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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XXXII*. CAPILLARY CHROMATOGRAPHY OF C_1–C_{18} MONOCHLORINATED *n*-ALKYL ACETATES

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SUMMARY

The effect on retention of the position of chlorine substitution in C_1–C_{18} monochlorinated *n*-alkyl acetates is reported. Incremental effects in terms of retention indices determined on a non-polar (SE-30) and a polar (OV-351) capillary column operated isothermally at increasing temperatures from 100 to 260°C are shown. A comparison is presented of the effect of substitution in the alkyl and acyl chains by a consideration of studies of monochlorinated C_5–C_{18} *n*-carboxylic esters.

INTRODUCTION

The gas chromatographic (GC) separation of the methyl esters of various monochlorinated *n*-carboxylic acids have been reported. Earlier studies have considered temperature programmed separation of the methyl esters of C_2–C_{20} *n*-carboxylic acids[1]. The retention behaviour and incremental effect on retention of the methyl esters of chlorinated propanoic and butanoic acids[2] and of the monochlorinated C_5–C_{18} monocarboxylic acids[3] have been reported. The latter work showed the effect on retention of the position of a chlorine substituent in the acyl or acid chain by an examination of the incremental effect expressed as retention indices of the isomeric C_5–C_{18} carboxylic acids using an SE-30 and a Carbowax 20M capillary column operated at a series of temperatures.

The effect of monochlorination in the alkyl or alcohol chain has not bbeen as extensively studied. Studies to maximise the separation of complex mixtures of various chlorinated esters with substitution in both the acyl and alkyl chains has been reported using temperature programming and capillary columns coated with SE-30, Carbowax 20M and OV-351[4].

* For Part XXXI, see J. K. Haken, B. G. Madden and I. O. O. Korhonen, *J. Chromatogr.*, 325 (1985) 61.

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TABLE I

RETENTION INDICES OF C_1–C_{18} MONOCHLORINATED *n*-ALKYL ACETATES ON SE-30 AND OV-351

Values of the overlapping mid-chain isomers of higher esters are approximative (*cf.* ref. 9).

Isomeric acetate	*SE-30*								
	60°C	*80°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*220°C*
Methyl	509	505	505						
Chloro	691	680	674						
Ethyl	613	577	607						
1-Chloro	744	724	726						
2-Chloro	817	801	796						
Propyl	711	685	676	696					
1-Chloro	838	821	806	805					
2-Chloro	864	848	835	831					
3-Chloro	924	916	902	895					
Butyl		810	786	774	781				
1-Chloro		930	906	895	912				
2-Chloro		964	944	930	951				
3-Chloro		981	961	949	972				
4-Chloro		1038	1021	1008	1033				
Pentyl		912	885	867	879				
1-Chloro		1026	1006	990	1011				
2-Chloro		1051	1033	1017	1041				
3-Chloro		1078	1062	1048	1072				
4-Chloro		1089	1073	1058	1084				
5-Chloro		1143	1129	1116	1142				
Hexyl			1008	972	993	1000			
1-Chloro			1117	1086	1108	1114			
2-Chloro			1147	1121	1143	1151			
3-Chloro			1166	1143	1166	1173			
4-Chloro			1186	1163	1187	1194			
5-Chloro			1194	1171	1194	1202			
6-Chloro			1247	1227	1249	1257			
Heptyl			1095	1070	1086	1090	1093		
1-Chloro			1211	1191	1211	1215	1212		
2-Chloro			1235	1217	1239	1244	1242		
3-Chloro			1254	1238	1260	1266	1262		
4-Chloro			1266	1251	1273	1278	1276		
5-Chloro			1284	1269	1292	1297	1295		
6-Chloro			1291	1276	1298	1303	1299		
7-Chloro			1342	1329	1350	1354	1354		
Octyl			1194	1165	1188	1189	1190	1178	
1-Chloro			1306	1287	1312	1314	1315	1310	
2-Chloro			1328	1312	1338	1343	1344	1340	
3-Chloro			1345	1331	1358	1362	1364	1364	
4-Chloro			1355	1342	1369	1373	1373	1375	
5-Chloro			1365	1352	1379	1384	1385	1384	
6-Chloro			1382	1370	1396	1402	1405	1404	
7-Chloro			1385	1372	1399	1403	1405	1404	
8-Chloro			1435	1425	1451	1456	1458	1459	
Nonyl				1292	1292	1293	1293	1285	
1-Chloro				1408	1414	1415	1416	1412	
2-Chloro				1432	1439	1442	1444	1443	
3-Chloro				1451	1458	1461	1463	1463	
4-Chloro				1460	1467	1472	1472	1473	
5-Chloro				1469	1477	1481	1483	1483	

		OV-351								
240°C	*260°C*	*60°C*	*80°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*220°C*
		823	839	844	877					
		1181	1180	1164	1174					
		881	880	875	908					
		1150	1153	1123	1130	1202				
		1315	1319	1297	1299	1354				
		981	978	943	992	1075				
		1217	1222	1198	1207	1278				
		1296	1304	1283	1289	1348				
		1418	1425	1414	1419	1470				
		1080	1079	1053	1064	1154				
		1292	1298	1278	1279	1342				
		1377	1384	1370	1375	1425				
		1424	1432	1422	1427	1478				
		1523	1539	1533	1540	1585				
				1195	1182	1212	1232			
				1401	1387	1419	1408			
				1469	1460	1492	1497			
				1528	1525	1558	1562			
				1563	1564	1594	1594			
				1652	1657	1687	1691			
				1277	1255	1286	1295	1277		
				1472	1457	1492	1500	1485		
				1540	1532	1576	1574	1575		
				1581	1578	1627	1629	1628		
				1626	1627	1679	1679	1686		
				1647	1650	1700	1703	1711		
				1747	1737	1789	1796	1802		
				1385	1372	1401	1400	1385		
				1582	1578	1602	1607	1615		
				1647	1647	1673	1673	1675		
				1686	1691	1718	1720	1725		
				1717	1723	1753	1757	1759		
				1749	1756	1787	1791	1797		
				1767	1775	1806	1809	1818		
				1846	1857	1889	1894	1904		
				1468	1454	1490	1486	1485		
				1659	1658	1702	1704	1711		
				1722	1724	1771	1771	1775		
				1758	1764	1814	1819	1824		
				1787	1794	1845	1850	1856		
				1802	1811	1862	1867	1874		
				1830	1840	1893	1899	1909		
				1842	1852	1905	1912	1922		
				1918	1932	1987	1994	2006		
					1568	1593	1602	1579	1617	
					1769	1798	1799	1802	1793	
					1838	1869	1872	1872	1886	
					1883	1912	1917	1922	1937	
					1907	1940	1945	1953	1961	
					1920	1956	1960	1967	1978	

(*Continued on p. 82*)

TABLE I (*continued*)

Isomeric acetate	*SE-30*								
	60°C	*80°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*220°C*
6-Chloro				1478	1486	1490	1492	1493	
7-Chloro				1491	1499	1505	1506	1511	
8-Chloro				1494	1501	1506	1507	1511	
9-Chloro				1545	1553	1558	1560	1564	
Decyl					1393	1393	1389	1384	
1-Chloro					1512	1515	1514	1513	
2-Chloro					1537	1542	1542	1544	
3-Chloro					1555	1561	1562	1564	
4-Chloro					1565	1570	1572	1573	
5-Chloro					1573	1578	1580	1582	
6-Chloro					1580	1585	1588	1589	
7-Chloro					1585	1591	1594	1595	
8-Chloro					1599	1606	1608	1610	
9-Chloro					1601	1606	1608	1610	
10-Chloro					1651	1658	1661	1664	
Undecyl					1493	1495	1493	1487	1491
1-Chloro					1612	1616	1618	1616	1617
2-Chloro					1637	1643	1646	1646	1649
3-Chloro					1655	1661	1665	1666	1671
4-Chloro					1664	1670	1675	1676	1679
5-Chloro					1672	1678	1682	1684	1687
6-Chloro					1678	1685	1689	1690	1693
7-Chloro					1682	1689	1692	1694	1695
8-Chloro					1686	1694	1698	1700	1702
9-Chloro					1700	1708	1712	1715	1716
10-Chloro					1700	1708	1712	1715	1718
11-Chloro					1752	1759	1764	1768	1769
Dodecyl						1596	1594	1594	1591
1-Chloro						1716	1717	1718	1716
2-Chloro						1743	1745	1747	1747
3-Chloro						1761	1764	1767	1767
4-Chloro						1770	1774	1776	1777
5-Chloro						1777	1781	1784	1784
6-Chloro						1783	1787	1790	1791
7-Chloro						1786	1789	1791	1791
8-Chloro						1789	1794	1796	1797
9-Chloro						1794	1798	1801	1802
10-Chloro						1807	1812	1815	1816
11-Chloro						1808	1812	1815	1816
12-Chloro						1859	1865	1868	1869
Tetradecyl							1797	1795	1793
1-Chloro							1918	1917	1918
2-Chloro							1947	1946	1949
3-Chloro							1966	1966	1970
4-Chloro							1974	1975	1979
5-Chloro							1982	1983	1986
6-Chloro							1988	1989	1992
7-Chloro							1988	1989	1992
8-Chloro							1991	1992	1996
9-Chloro							1992	1993	1996
10-Chloro							1996	1997	2000

		OV-351								
240°C	*260°C*	*60°C*	*80°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*220°C*
					1933	1969	1976	1984	1996	
					1957	1994	2002	2010	2022	
					1967	2004	2012	2020	2032	
					2047	2086	2095	2106	2118	
						1699	1691	1688	1713	
						1900	1897	1901	1914	
						1969	1970	1976	1985	
						2011	2014	2026	2030	
						2038	2042	2054	2060	
						2051	2055	2067	2072	
						2062	2067	2079	2086	
						2070	2076	2090	2096	
						2093	2100	2115	2122	
						2104	2111	2126	2133	
						2185	2193	2210	2215	
						1802	1804	1808	1800	1819
						2000	2000	2005	2013	2044
						2070	2072	2080	2086	2099
						2111	2117	2127	2134	2149
						2138	2144	2154	2160	2179
						2150	2157	2167	2175	2191
						2159	2166	2177	2185	2200
						2164	2172	2183	2190	2202
						2171	2180	2192	2199	2214
						2195	2204	2217	2225	2241
						2205	2214	2227	2237	2252
						2285	2294	2311	2320	2336
							1876	1896	1898	1900
							2097	2079	2099	2099
							2170	2179	2179	2183
							2213	2225	2230	2236
							2239	2252	2256	2265
							2251	2264	2269	2278
							2260	2273	2279	2287
							2262	2275	2280	2287
							2267	2281	2287	2294
							2275	2289	2296	2303
							2299	2314	2320	2332
							2309	2324	2332	2341
							2390	2407	2416	2429
1796							2094	2103	2100	2106
1924							2305	2319	2317	2325
1956							2368	2382	2385	2395
1975							2412	2427	2433	2447
1985							2439	2453	2460	2475
1993							2450	2464	2472	2486
1997							2458	2472	2480	2494
1997							2460	2474	2482	2495
2000							2463	2476	2485	2500
2000							2464	2478	2487	2501
2005							2468	2482	2491	2506

(*Continued on p. 84*)

TABLE I (*continued*)

Isomeric acetate	*SE-30*								
	60°C	*80°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*220°C*
11-Chloro							2000	2002	2005
12-Chloro							2014	2015	2019
13-Chloro							2014	2015	2019
14-Chloro							2066	2068	2072
Hexadecyl								1996	1994
1-Chloro								2117	2117
2-Chloro								2147	2148
3-Chloro								2166	2168
4-Chloro								2175	2177
5-Chloro								2182	2184
6-Chloro								2188	2191
7-Chloro								2188	2191
8-Chloro								2191	2193
9-Chloro								2192	2193
10-Chloro								2193	2195
11-Chloro								2194	2196
12-Chloro								2197	2199
13-Chloro								2201	2204
14-Chloro								2215	2219
15-Chloro								2215	2219
16-Chloro								2267	2271
Octadecyl									2193
1-Chloro									2315
2-Chloro									2347
3-Chloro									2367
4-Chloro									2376
5-Chloro									2383
6-Chloro									2389
7-Chloro									2389
8-Chloro									2391
9-Chloro									2392
10-Chloro									2393
11-Chloro									2393
12-Chloro									2394
13-Chloro									2395
14-Chloro									2397
15-Chloro									2402
16-Chloro									2415
17-Chloro									2416
18-Chloro									2468

The elution series of one series, *i.e.*, *n*-alkyl acetates with mono-, di- and trichlorination has been reported[5,6] with similar separations by Komárek *et al.*[7] on an OV-101 capillary column operated at 80°C for the C_1–C_5 and 200°C for the C_6–C_{16} esters, respectively. Data of the C_1–C_8 chlorinated *n*-alkyl acetates on non-polar and polar columns has been reported by Haken *et al.*[8], as also are of monochlorinated C_9–C_{18} *n*-alkyl acetates by Korhonen[9].

		OV-351								
240°C	*260°C*	*60°C*	*80°C*	*100°C*	*120°C*	*140°C*	*160°C*	*180°C*	*200°C*	*220°C*
2012							2475	2490	2499	2515
2026							2498	2515	2525	2541
2026							2509	2526	2536	2551
2080							2589	2608	2620	2635
1996								2309	2312	2312
2125								2509	2512	2523
2155								2583	2592	2601
2177								2630	2641	2652
2186								2656	2668	2680
2191								2667	2680	2691
2199								2675	2688	2699
2199								2676	2689	2700
2201								2677	2691	2701
2201								2678	2692	2703
2203								2679	2693	2704
2203								2680	2694	2705
2307								2684	2700	2712
2212								2691	2707	2720
2227								2716	2732	2745
2227								2727	2743	2757
2280								2809	2826	2840
2198	2192								2516	2516
2324	2322								2693	2709
2356	2355								2781	2796
2377	2378								2844	2853
2386	2386								2870	2880
2392	2394								2882	2892
2400	2400								2889	2897
2401	2400								2889	2897
2402	2401								2890	2899
2403	2402								2891	2900
2403	2402								2892	2901
2404	2403								2893	2902
2404	2403								2894	2902
2405	2404								2894	2903
2407	2408								2899	2909
2413	2414								2907	2918
2427	2430								2933	2946
2427	2430								2944	2956
2480	2484								3027	3041

The present work considers the monochlorinated *n*-alkyl acetates of chain length C_1–C_{18} with the effect of substitution being shown along the chain on non-polar (SE-30) and polar (OV-351) capillary columns operated at temperatures between 60 and 260°C. The work is comparable with that which considered the methyl esters of isomeric monochlorinated C_5–C_{18} carboxylic acids and together the works show the relative effect of monochlorination in both the acid and alcohol chains. The

TABLE II

INCREMENTAL EFFECT OF MONOCHLORO SUBSTITUTION AT EACH POSITION ALONG THE ALKYL CHAIN ON SE-30 AND OV-351

Temp. (°C)	*Substituent*	*SE-30*														
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}
60	1-Chloro	182	131	127												
	2-Chloro		204	153												
	3-Chloro			213												
	4-Chloro															
80	1-Chloro	175	147	136	120	114										
	2-Chloro		224	163	154	139										
	3-Chloro			231	171	166										
	4-Chloro				228	177										
	5-Chloro					231										
100	1-Chloro	169	119	130	120	121	109	116	112							
	2-Chloro		189	159	158	148	139	140	134							
	3-Chloro			226	175	177	158	159	151							
	4-Chloro				235	188	178	171	161							
	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	116						
	2-Chloro			135	156	150	149	147	147	140						
	3-Chloro			199	175	181	171	168	166	159						
	4-Chloro				234	191	191	181	177	168						
	5-Chloro					249	199	199	187	177						
	6-Chloro						255	206	205	186						
	7-Chloro							259	207	199						
	8-Chloro								260	202						
	9-Chloro									253						
140	1-Chloro				131	132	115	125	124	122	119	119				
	2-Chloro				170	162	150	153	150	147	144	144				
	3-Chloro				191	193	173	174	170	166	162	162				
	4-Chloro				252	205	194	187	181	175	172	171				
	5-Chloro					263	201	206	191	185	180	179				
	6-Chloro						256	212	208	194	187	185				
	7-Chloro							264	211	207	192	189				
	8-Chloro								263	209	206	193				
	9-Chloro									261	208	207				
	10-Chloro										258	207				
	11-Chloro											259				
160	1-Chloro						114	125	125	122	122	121	120			
	2-Chloro						151	154	154	149	149	148	147			
	3-Chloro						173	176	173	168	168	166	165			
	4-Chloro						194	188	184	179	177	175	174			
	5-Chloro						202	207	195	188	185	183	181			
	6-Chloro						257	213	213	197	192	190	187			
	7-Chloro							264	214	212	198	194	190			
	8-Chloro								267	213	213	199	193			
	9-Chloro									265	213	213	198			
	10-Chloro										265	213	211			
	11-Chloro											264	212			
	12-Chloro												263			

OV-351

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}
358	269	236	212											
	434	315	297											
		437	344											
			443											
341	273	244	219											
	439	326	305											
		447	353											
			460											
320	248	255	225	206	195	197	191							
	422	340	317	274	263	262	254							
		471	369	333	304	301	290							
			480	368	349	332	319							
				457	370	364	334							
					470	382	362							
						461	374							
							450							
297	222	215	215	205	202	206	204	201						
	391	297	311	278	277	275	270	270						
		427	363	343	323	319	310	315						
			476	382	372	351	340	339						
				475	395	384	357	352						
					482	403	386	365						
						485	398	389						
							478	399						
								479						
		203	188	207	206	201	212	205	201	198				
		273	271	280	290	272	281	276	270	268				
		395	324	346	341	317	324	319	312	309				
			431	382	393	352	355	347	339	336				
				475	414	386	372	363	352	348				
					503	405	403	376	363	357				
						488	415	401	371	362				
							497	411	394	369				
								493	405	393				
									486	403				
										483				
				176	205	207	218	197	206	196	221	211		
				265	279	273	285	270	279	268	294	274		
				330	334	320	333	315	323	313	337	318		
				362	384	357	364	343	351	340	363	345		
				459	408	391	381	358	364	353	375	356		
					501	409	413	374	376	362	384	364		
						494	426	400	385	368	386	366		
							508	410	409	376	391	369		
								493	420	400	399	370		
									502	410	423	374		
										490	433	381		
											514	404		

(*Continued on p. 88*)

TABLE II (*continued*)

Temp. (°C)	*Substituent*	*SE-30*														
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}
	13-Chloro															
	14-Chloro															
180	1-Chloro							119	125	123	125	125	123	121		
	2-Chloro							149	154	151	153	153	151	150		
	3-Chloro							169	174	170	173	172	170	169		
	4-Chloro							173	183	179	183	182	180	177		
	5-Chloro							202	195	190	191	189	187	185		
	6-Chloro							206	215	199	199	196	193	191		
	7-Chloro							261	215	213	205	199	195	191		
	8-Chloro								268	214	219	205	200	194		
	9-Chloro									267	219	219	204	195		
	10-Chloro										272	219	218	199		
	11-Chloro											271	218	203		
	12-Chloro											271	276	217		
	13-Chloro													217		
	14-Chloro													269		
	15-Chloro															
	16-Chloro															
200	1-Chloro								132	127	129	129	124	122	121	
	2-Chloro								162	158	160	159	153	151	151	
	3-Chloro								186	178	180	179	173	171	170	
	4-Chloro								197	188	189	189	182	180	179	
	5-Chloro								206	198	198	197	190	188	186	
	6-Chloro								226	208	205	203	196	194	192	
	7-Chloro								226	226	211	207	197	194	192	
	8-Chloro								281	226	226	213	202	197	195	
	9-Chloro									279	226	228	207	198	196	
	10-Chloro										280	228	221	202	197	
	11-Chloro											281	221	207	198	
	12-Chloro												274	220	201	
	13-Chloro													220	205	
	14-Chloro													273	219	
	15-Chloro														219	
	16-Chloro														271	
	17-Chloro															
	18-Chloro															

behaviour is compared with that of simple alkyl esters which have been extensively studied. An earlier study[10] attempted to show the same effects from a consideration of temperature programmed retention data.

EXPERIMENTAL

The aliphatic C_1–C_5 *n*-alkyl acetates were commercial products (Fluka, Buchs, Switzerland). The C_6–C_{18} *n*-alkyl acetates were prepared from the corresponding alcohols and acetyl chloride[11]. The C_2–C_{18} *n*-chloroalkyl acetates were prepared by chlorination of the parent esters with chlorine in the liquid phase[12] and chloromethyl acetate as described earlier[13].

GC was carried out on a Perkin-Elmer Sigma 3 instrument. The injector and

OV-351

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}
												415		
												495		
					208	230	226	223	213	197	183	216	200	
					298	290	290	293	288	272	283	279	274	
					351	340	339	343	338	346	329	324	321	
					409	374	371	374	366	319	356	350	347	
					434	412	389	388	379	359	368	361	358	
					525	433	424	405	391	369	377	369	366	
						519	437	431	402	375	379	371	367	
							521	441	427	384	385	373	368	
								527	438	409	393	375	369	
								522	522	419	418	379	370	
										503	428	387	371	
											511	412	375	
												423	382	
												505	407	
													418	
													500	
								176	201	213	201	217	200	177
								269	272	286	281	285	280	265
								320	317	334	232	333	329	328
								344	347	360	358	360	356	354
								361	359	375	371	372	368	366
								379	373	385	381	380	376	373
								405	383	390	382	382	377	373
								415	409	399	389	385	379	374
								501	420	425	398	387	380	375
									502	437	422	391	381	376
										520	434	399	382	377
											518	425	388	378
												436	395	378
												520	420	383
													431	391
													514	417
														428
														511

detector temperatures were 275°C, with nitrogen as carrier gas at a flow-rate of 1 ml min^{-1} and a split ratio of 1:50. The two columns used were: a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.33 mm I.D.) supplied by Scientific Glass Instruments (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 crude chlorination mixture of monochlorinated esters was used. The chromatographic data was 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 with the procedure of Grobler and Balizs[14].

RESULTS AND DISCUSSION

Table I shows retention indices of the C_1–C_{18} monochlorinated *n*-alkyl acetates on SE-30 and OV-351 stationary phases respectively obtained at temperatures between 60 and 260°C. The incremental efect of substitution of a chlorine atom at each position along the alkyl chain is shown in Table II. With chlorination at the 1- or α-position a significant increase in retention is evident on both phases while the retention of the isomers as the substituent moves along the chain gradually increases until the ω-position where a further considerable increase is observed. The individual contribution of particular position of substitution tends to decrease on both phases as the alkyl chain length is increased, this being in agreement with substitution in the acyl chain[3]. The actual increment at the ω-position is relatively constant although it may show a small but significant increase with temperature and chain length.

The incremental values on the SE-30 column are very similar to those reported with acyl substitution[3] although from comparison with Table II it is difficult to suggest that substitution in either chain had any pronounced effect. The summary of incremental values (Tables III–V) shows that a chlorine substituent in the α- and

TABLE III

SUMMARY OF INCREMENTAL EFFECTS ON SE-30

Temp. (°C)	*Position of substituent*	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}
100	1	169	119	130	120	121	109	116	112							
	ω	169	189	226	235	244	239	247	241							
	ω − 1		70	96	115	123	130	131	129							
	ΔCH_2		122	106	119	108	118	95	93							
120	1			109	121	123	114	121	122	116						
	ω			199	234	249	255	259	260	253						
	ω − 1			90	113	126	141	138	138	137						
	ΔCH_2				113	108	111	102	96	120						
140	1				131	132	115	125	124	122	119	119				
	ω				252	263	256	264	263	261	258	259				
	ω − 1				121	131	141	139	139	139	139	140				
	ΔCH_2					109	107	101	101	102	98	101				
160	1						114	125	125	122	122	121	120			
	ω						257	264	267	265	265	264	263			
	ω − 1						143	139	142	143	143	143	143			
	ΔCH_2							97	102	102	100	101	100			
180	1							119	125	123	125	125	123	121		
	ω							261	268	267	272	271	271	269		
	ω − 1							142	143	144	147	146	148	148		
	ΔCH_2								104	102	101	103	101	101		
200	1								132	127	129	129	124	122	121	
	ω								281	279	280	281	274	273	271	
	ω − 1								149	152	151	152	150	151	150	
	ΔCH_2									105	100	104	100	100	100	
220	1											126	125	125	123	122
	ω											278	278	279	277	275
	ω − 1											152	153	154	154	153
	ΔCH_2												100	102	100	99

ω-positions has less effect in the alkyl chain at lower temperatures and shorter chain lengths. However, at higher temperatures with longer alkyl chains the increments increase and become larger than the values of the corresponding acyl substituted compounds[3]. Overall, however, the effect along the methylene chain, *i.e.*, ω-α, is greater than for acyl substitution.

The effect of increasing the methylene chain length is such that the esters of lower chain length and examined at lower temperatures have slightly lower (ΔCH_2) increments in the alkyl chain and for the longer chain esters the behaviour is essentially identical.

The retention behaviour on the OV-351 column parallels that on SE-30 both with regard to the α-, ω- and $\omega - \alpha$ increments except in each case the values are approximately doubled. The relative effects are shown in Figs. 1 and 2 where each position of substitution is shown for the C_9 and C_{16} esters on both phases. The difference between α- and ω-substitution is shown as ΔI. The esters selected are comparable with examples shown previously for acyl substituted esters[3].

Methylene increments (ΔCH_2) on the polar column were obtained by subtraction of values of the isomers with ω-substitution, *i.e.*, $I_{\omega\text{-Cl}}(CH_2)_{x+1} - I_{\omega\text{-Cl}}(CH_2)_x$

TABLE IV

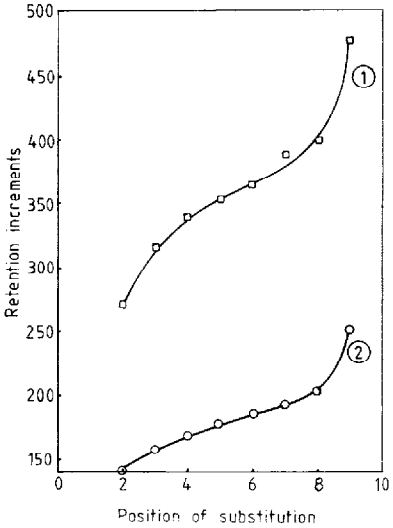
SUMMARY OF INCREMENTAL EFFECTS ON OV-351

Temp. (°C)	*Position of substituent*	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}
100	1	320	248	255	225	206	195	197	191							
	ω	320	422	471	480	457	470	461	450							
	$\omega - 1$	–	174	216	255	251	275	264	259							
	ΔCH_2	–	133	117	119	119	95	99	72							
120	1	297	222	215	215	205	202	206	204	201						
	ω	297	391	427	476	475	482	485	478	479						
	$\omega - 1$		169	212	261	270	280	279	274	278						
	ΔCH_2		125	120	121	117	80	120	75	115						
140	1			203	188	207	206	201	212	205	201	198				
	ω			395	431	475	503	488	497	493	486	483				
	$\omega - 1$			192	243	268	297	287	285	288	285	285				
	ΔCH_2				115	102	102	100	98	99	99	100				
160	1					176	205	207	218	197	206	196	221	211		
	ω					459	501	494	508	493	502	490	514	495		
	$\omega - 1$					283	296	287	290	296	296	294	293	284		
	ΔCH_2						101	98	100	101	98	101	96	100		
180	1						208	230	226	223	213	197	183	216	200	
	ω						525	519	521	527	522	503	511	505	500	
	$\omega - 1$						317	289	295	304	309	306	328	289	300	
	ΔCH_2							102	102	100	104	101	96	101	101	
200	1									176	201	213	201	217	200	177
	ω									501	502	520	518	520	514	511
	$\omega - 1$									325	301	307	317	303	314	334
	ΔCH_2										97	105	96	102	103	101
220	1											225	199	219	211	193
	ω											517	529	529	528	525
	$\omega - 1$											292	330	310	317	332
	ΔCH_2												93	103	103	101

TABLE V

SUMMARY OF INCREMENTAL EFFECTS ON OV-351/SE-30

Temp. (°C)	*Position of substituent*	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{16}	C_{18}
100	1	1.89	2.08	1.96	1.88	1.70	1.79	1.70	1.71								
	ω	1.89	2.23	2.08	2.04	1.87	1.97	1.87	1.87								
	$\omega - 1$	–	2.49	2.25	2.22	2.04	2.12	2.02	2.01								
	ΔCH_2	–	1.09	1.10	1.00	1.10	0.81	1.04	0.77								
120	1			1.97	1.78	1.67	1.77	1.70	1.67	1.73							
	ω			2.15	2.03	1.91	1.89	1.87	1.84	1.89							
	$\omega - 1$			2.36	2.30	2.14	1.99	2.02	1.99	2.03							
	ΔCH_2				1.07	1.08	0.72	1.18	0.78	0.96							
140	1				1.44	1.57	1.79	1.61	1.71	1.68	1.69	1.66					
	ω				1.71	1.81	1.96	1.85	1.89	1.89	1.88	1.86					
	$\omega - 1$				2.01	2.05	2.11	2.06	2.05	2.07	2.05	2.04					
	ΔCH_2					0.94	1.05	0.99	0.97	0.97	1.01	0.99					
160	1						1.80	1.66	1.74	1.61	1.69	1.62	1.84				
	ω						1.94	1.87	1.90	1.86	1.89	1.86	1.95				
	$\omega - 1$						2.07	2.06	2.04	2.07	2.07	2.06	2.05				
	ΔCH_2							1.01	0.98	0.99	0.98	1.00	0.96				
180	1							1.93	1.81	1.81	1.70	1.58	1.49	1.79			
	ω							1.99	1.94	1.97	1.92	1.86	1.89	1.88			
	$\omega - 1$							2.04	2.06	2.11	2.10	2.10	2.22	1.95			
	ΔCH_2								0.98	0.98	1.03	0.98	0.95	1.00			
200	1									1.39	1.56	1.65	1.62	1.78	1.65		
	ω									1.80	1.79	1.85	1.89	1.90	1.90		
	$\omega - 1$									2.14	1.99	2.02	2.11	2.01	2.09		
	ΔCH_2										0.97	1.01	0.96	1.02	1.03		
220	1											1.79	1.59	1.75	1.72	1.58	
	ω											1.86	1.90	1.90	1.91	1.91	
	$\omega - 1$											1.92	2.16	2.01	2.06	2.17	
	ΔCH_2												0.93	1.01	1.03	1.02	



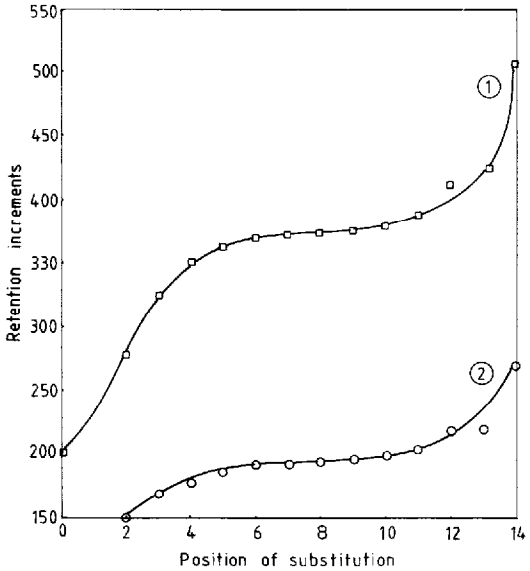


Fig. 1. Plot showing effect of the position of monochloro substitution on retention of nonanoate esters on (1) OV-351 at 120°C and (2) SE-30.

Fig. 2. Plot showing effect of the position of monochloro substitution on retention of tetradecanoate esters on (1) OV-351 at 180°C and (2) SE-30.

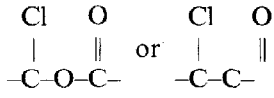
TABLE VI

COMPARISON OF AVERAGE INCREMENTAL RATIOS FOR ACYL[3] AND ALKYL SUBSTITUTION

Temperature (°C)	*Substituent*	*Acyl*	*Alkyl*
100	α	2.12	1.73
	ω	2.10	1.90
	ω − α	2.06	2.05
120	α	1.93	1.71
	ω	1.79	1.88
	ω − α	1.67	2.03
140	α	1.70	1.67
	ω	1.80	1.88
	ω − α	1.91	2.08
160	α	—	1.71
	ω	—	1.90
	ω − α	—	2.06
180	α	1.72	1.73
	ω	1.83	1.92
	ω − α	1.95	2.08
200	α	1.65	1.61
	ω	1.78	1.86
	ω − α	1.96	2.06

and the values obtained are higher by several index units at each temperature with corresponding values obtained from the work which considered acyl substitution.

The lower retention of the compounds with the chlorine substituent adjacent to an oxygen atom rather than a carbon atom, *i.e.*



might be attributed to the ease of transfer of the various polar effects through the chain.

The ratios of the incremental effects of substitution are shown with comparable values for compounds with acyl substitution (Table VI). With the substituent in the position closest to the carboxyl group it is apparent that the acyl compounds tend to show a reduction in value with increasing temperatures while the alkyl compounds have initially lower values but these increase with temperature and become slightly greater, except at 200°C, than those of the acyl compounds. Terminal substitution generally shows greater values with the alkyl substituted compounds. The difference in the ratios of $(\omega - \alpha)$ retention shows consistently higher results with substitution in the alkyl chain with the exception that at 100°C the values are essentially identical.

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