Journal of Chromatography, 325 (1985) 61–73
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 614

GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XXXI*. BUTANOYL AND MONOCHLOROBUTANOYL ESTERS OF LOWER SATURATED BRANCHED CHAIN AND UNSATURATED ALCOHOLS ON SE-30 AND OV-351 CAPILLARY COLUMNS

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(Received February 5th, 1985)

SUMMARY

The gas chromatographic retention behaviour of the butanoyl and 2-, 3- and 4-chlorobutanoyl esters of C_3–C_5 saturated aliphatic branched-chain and unsaturated C_3–C_6 alcohols on SE-30 and OV-351 glass capillary columns operated isothermally at several temperatures is reported. Retention index increments at 80, 120 and 160°C show the effects of chain branching and the olefinic and acetylenic unsaturation in the alkyl chain and the effect of the position of the chlorine substituent in the acyl chain. The results are compared with the behaviour of the corresponding *n*-alkyl esters and the chlorinated propanoyl esters.

INTRODUCTION

The gas chromatographic (GC) retention behaviour of aliphatic branched-chain and unsaturated esters has been the subject of several studies, as previously described[2], mainly using packed columns. Recently, capillary column GC has been applied to the isothermal separation of straight-chain[3], branched-chain and unsaturated[2] propanoyl esters and their monochlorinated derivatives and also of straight-chain butanoyl esters and their monochlorinated derivatives[4] on both SE-30 and OV-351, and retention index increments for the various structural features were determined.

This paper reports isothermal capillary GC of lower saturated branched-chain and unsaturated aliphatic alcohols and of their butanoyl and monochlorobutanoyl derivatives on SE-30 and OV-351 stationary phases at a variety of temperatures.

* For Part XXX, see ref. 1.

0021-9673/85/$03.30

Retention increments at 80, 120 and 160°C show the effect of variation of the various structural parameters, *i.e.*, branching and unsaturation in the alkyl chain and chlorination in the acyl chain, and the interrelationship of the variation of structural parameters in the alkyl and acyl chains.

EXPERIMENTAL

Materials

All branched-chain alcohols, 3-buten-1-ol, 4-penten-2-ol, 4-penten-1-ol and 2-propyn-1-ol were obtained from Fluka (Buchs, Switzerland) and 2-propen-1-ol and a mixture of *cis*- and *trans*-3-hexen-1-ol from Merck-Schuchardt (Darmstadt, F.R.G.). Alkenyl and alkynyl butanoates were prepared from the appropriate alcohols and butanoyl chloride or its chlorinated derivatives as described previously[5].

Gas chromatography

The GC analyses were carried out with a Perkin-Elmer Sigma 3 gas chromatograph under the following operating conditions: injector and flame ionization detector temperatures, 275°C; nitrogen carrier gas flow-rate, 1 ml min^{-1}; splitting ratio, 1:50; and chart speed, 10 mm min^{-1}. The columns used were a vitreous silica SE-30 wall-coated open-tubular (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 data were determined isothermally at the temperatures shown in the tables.

The chromatographic data were recorded with 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 M2 microprocessor system, the dead volume first being determined by regression analysis from a series of *n*-alkanes using the procedure of Grobler and Balizs[6].

RESULTS AND DISCUSSION

Retention indices of saturated branched-chain and unsaturated alcohols and the corresponding alkyl butanoates and their monochlorinated derivatives, obtained on SE-30 and OV-351 glass capillary columns, are shown in Tables I and II, respectively. As with the propanoyl esters considered previously[2], few compounds are members of homologous series and retention plots are not significant, although on SE-30 the alcohols have the lowest retention with the alkyl esters and the 2-, 3- and 4-monochloro esters having increasing retentions.

Table III shows the incremental effect of a chlorine atom substituted along the butanoic acid chain on SE-30 at 80 and 120°C for branched, saturated alcohol chains and at 120 and 160°C for olefinic and acetylenic alcohol chains. The data at 120°C are comparable to earlier results[4] for straight-chain butanoic and monochlorobutanoic esters and the increase in retention is approximately 141 retention index units (i.u.) at the adjacent 2-chloro position, 158 i.u. at the 3-chloro position, 158 i.u. at the 3-chloro position and 223 i.u. at the 4-chloro, *i.e.*, terminal, position for the saturated esters. These values are in good agreement with the results of studies of straight-chain esters, where the corresponding values were approximately 150, 160 and 230 i.u.[4].

TABLE I

RETENTION INDICES OF SATURATED C_3–C_5 BRANCHED-CHAIN AND UNSATURATED C_3–C_6 ALCOHOLS AND THEIR BUTANOYL AND MONOCHLOROBUTANOYL ESTERS ON SE-30.

	Temperature (°C)						
	60	*80*	*100*	*120*	*140*	*160*	*180*
Alcohol:							
2-Propanol	491	453	508				
2-Methyl-2-propanol	531	500	548				
2-Butanol	605	577	615	622			
2-Methyl-2-butanol	644	628	652	662	642		
2-Methyl-1-propanol	629	609	629	641	620		
3-Methyl-2-butanol	683	668	683	690	699		
2-Pentanol	697	683	692	701	704		
3-Methyl-1-butanol	733	721	723	727	738		
2-Propen-1-ol		546	576	558			
4-Penten-2-ol		679	673	675	687	734	
3-Buten-1-ol		640	640	641	620	663	
4-Penten-1-ol		757	739	730	764	794	
2-Propyn-1-ol		552	576	559	569	602	
trans-3-Hexen-1-ol		853	831	824	853	873	
cis-3-Hexen-1-ol		859	836	829	855	873	
Alkyl butanoate:							
Methylethyl	836	826	821	814	831		
Dimethylethyl	873	866	858	851	873		
1-Methylpropyl	930	923	915	906	943		
1,1-Dimethylpropyl	977	972	963	955	977		
2-Methylpropyl	946	940	930	933	956		
1,2-Dimethylpropyl	1000	993	985	978	1000		
1-Methylbutyl	1016	1010	999	992	1012		
3-Methylbutyl	1045	1039	1029	1021	1043		
2-Propenyl			884	851	868	894	918
1-Methyl-3-butenyl			1007	978	997	1006	1027
3-Butenyl			971	941	961	972	996
4-Pentenyl			1070	1045	1064	1070	1088
2-Propynyl			895	857	873	894	918
trans-3-Hexenyl			1169	1148	1166	1171	1179
cis-3-Hexenyl			1170	1150	1170	1174	1182
Alkyl 2-chlorobutanoate:							
Methylethyl	973	967	959	952	977		
Dimethylethyl	1008	1003	997	992	1012		
1-Methylpropyl	1065	1062	1054	1050	1074		
1,1-Dimethylpropyl	1110	1107	1103	1100	1126		
2-Methylpropyl	1080	1076	1069	1065	1089		
1,2-Dimethylpropyl	1133	1129	1124	1120	1143		
1-Methylbutyl	1149	1145	1138	1133	1158		
3-Methylbutyl	1177	1173	1168	1165	1189		

(*Continued on p. 64*)

TABLE I *(continued)*

	Temperature (°C)						
	60	*80*	*100*	*120*	*140*	*160*	*180*
2-Propenyl			1020	994	1016	1028	1048
1-Methyl-3-butenyl			1140	1121	1143	1150	1162
3-Butenyl			1109	1088	1109	1115	1129
4-Pentenyl			1204	1189	1211	1218	1227
2-Propynyl			1032	1007	1027	1037	1062
trans-3-Hexenyl			1305	1294	1315	1320	1326
cis-3-Hexenyl			1308	1297	1319	1323	1330
Alkyl 3-chlorobutanoate:							
Methylethyl	988	982	974	968	990		
Dimethylethyl	1027	1023	1015	1009	1034		
1-Methylpropyl	1082	1077	1070	1065	1089		
1,1-Dimethylpropyl	1130	1127	1122	1119	1143		
2-Methylpropyl	1097	1092	1085	1081	1105		
1,2-Dimethylpropyl	1150	1146	1141	1137	1161		
1-Methylbutyl	1167	1162	1156	1151	1174		
3-Methylbutyl	1193	1189	1184	1181	1204		
2-Propenyl			1032	1007	1027	1037	1962
1-Methyl-3-butenyl			1156	1138	1160	1167	1177
3-Butenyl			1121	1101	1122	1131	1144
4-Pentenyl			1220	1205	1227	1232	1243
2-Propynyl			1020	1017	1035	1045	1062
trans-3-Hexenyl			1318	1307	1328	1332	1339
cis-3-Hexenyl			1321	1311	1332	1336	1344
Alkyl 4-chlorobutanoate:							
Methylethyl	1053	1048	1039	1033	1055		
Dimethylethyl	1090	1085	1078	1074	1097		
1-Methylpropyl	1145	1140	1134	1130	1154		
1,1-Dimethylpropyl	1191	1188	1184	1180	1207		
2-Methylpropyl	1163	1158	1153	1148	1173		
1,2-Dimethylpropyl	1212	1208	1204	1201	1227		
1-Methylbutyl	1229	1224	1220	1216	1240		
3-Methylbutyl	1260	1256	1253	1251	1274		
2-Propenyl			1097	1077	1097	1105	1121
1-Methyl-3-butenyl			1220	1205	1227	1232	1243
3-Butenyl			1187	1171	1193	1200	1210
4-Pentenyl			1326	1277	1298	1303	1311
2-Propynyl			1111	1089	1109	1115	1130
trans-3-Hexenyl			1385	1377	1397	1402	1409
cis-3-Hexenyl			1389	1382	1402	1407	1415

The retention indices of the esters with olefinic unsaturation were agains essentially identical, *i.e.*, 145, 159 and 229 i.u. Similarly, acetylenic unsaturation produced minimal variation, *i.e.*, 150, 160 and 232 i.u.

The retention increments of the esters on the OV-351 column are shown in Table IV, where substantially increased retentions are evident relative to the behav-

TABLE II

RETENTION INDICES OF SATURATED C_3–C_5 BRANCHED-CHAIN AND UNSATURATED C_3–C_6 ALCOHOLS AND THEIR BUTANOYL AND MONOCHLOROBUTANOYL ESTERS ON OV-351

	Temperature (°C)						
	60	*80*	*100*	*120*	*140*	*160*	*180*
Alcohol:							
2-Propanol	949	957	981				
2-Methyl-2-propanol	930	942	981				
2-Butanol	1038	1036	1048	1114	1206		
2-Methyl-2-butanol	1028	1026	1048	1114	1206		
2-Methyl-1-propanol	1100	1094	1108	1153	1241		
3-Methyl-2-butanol	1100	1094	1108	1153	1241		
2-Pentanol	1129	1121	1130	1172	1254		
3-Methyl-1-butanol	1212	1203	1208	1238	1315		
2-Propen-1-ol		1128	1130	1167	1245		
4-Penten-2-ol		1154	1159	1184	1263		
3-Buten-1-ol		1185	1187	1209	1283		
4-Penten-1-ol		1308	1305	1305	1370		
2-Propyn-1-ol		1352	1343	1334	1395		
trans-3-Hexen-1-ol		1368	1366	1361	1423		
cis-3-Hexen-1-ol		1387	1385	1382	1442		
Alkyl butanoate:							
Methylethyl	1060	1058	1090	1145	1241		
Dimethylethyl	1060	1058	1090	1145	1241		
1-Methylpropyl	1144	1138	1159	1200	1286		
1,1-Dimethylpropyl	1163	1157	1178	1215	1304		
2-Methylpropyl	1171	1165	1185	1221	1304		
1,2-Dimethylpropyl	1200	1193	1209	1243	1318		
1-Methylbutyl	1223	1215	1230	1260	1334		
3-Methylbutyl	1270	1264	1278	1303	1373		
2-Propenyl			1198	1227	1308	1359	1397
1-Methyl-3-butenyl			1267	1290	1368	1427	1489
3-Butenyl			1272	1292	1368	1427	1489
4-Pentenyl			1370	1377	1433	1471	1528
2-Propynyl			1372	1381	1433	1471	1528
trans-3-Hexenyl			1452	1457	1517	1546	1593
cis-3-Hexenyl			1459	1466	1527	1553	1593
Alkyl 2-chlorobutanoate:							
Methylethyl	1298	1291	1304	1327	1393		
Dimethylethyl	1292	1287	1299	1327	1393		
1-Methylpropyl	1380	1375	1385	1405	1463		
1,1-Dimethylpropyl	1395	1392	1402	1424	1482		
2-Methylpropyl	1406	1403	1413	1431	1488		
1,2-Dimethylpropyl	1427	1424	1434	1454	1507		
1-Methylbutyl	1453	1450	1458	1474	1527		
3-Methylbutyl	1504	1503	1513	1529	1579		

(*Continued on p. 66*)

TABLE II *(continued)*

	Temperature (°C)						
	60	*80*	*100*	*120*	*140*	*160*	*180*
2-Propenyl			1443	1450	1514	1546	1593
1-Methyl-3-butenyl			1501	1507	1565	1590	1637
3-Butenyl			1520	1525	1582	1607	1652
4-Pentenyl			1613	1618	1671	1692	1729
2-Propynyl			1645	1651	1684	1699	1731
trans-3-Hexenyl			1696	1700	1750	1765	1797
cis-3-Hexenyl			1704	1710	1760	1776	1808
Alkyl 3-chlorobutanoate:							
Methylethyl	1353	1347	1356	1376	1435		
Dimethylethyl	1349	1344	1352	1376	1435		
1-Methylpropyl	1439	1434	1442	1460	1513		
1,1-Dimethylpropyl	1455	1451	1459	1474	1527		
2-Methylpropyl	1468	1464	1472	1488	1538		
1,2-Dimethylpropyl	1492	1490	1498	1514	1564		
1-Methylbutyl	1514	1511	1519	1533	1580		
3-Methylbutyl	1564	1565	1572	1586	1632		
2-Propenyl			1496	1501	1558	1586	1637
1-Methyl-3-butenyl			1560	1564	1618	1640	1677
3-Butenyl			1573	1577	1632	1654	1693
4-Pentenyl			1675	1680	1732	1748	1781
2-Propynyl			1689	1692	1749	1765	1797
trans-3-Hexenyl			1750	1755	1814	1816	1843
cis-3-Hexenyl			1759	1764	1824	1827	1855
Alkyl 4-chlorobutanoate:							
Methylethyl ester	1459	1456	1466	1482	1534		
Dimethylethyl	1453	1450	1458	1474	1527		
1-Methylpropyl	1539	1541	1550	1566	1615		
1,1-Dimethylpropyl	1552	1556	1565	1583	1632		
2-Methylpropyl	1572	1575	1584	1601	1650		
1,2-Dimethylpropyl	1600	1600	1604	1621	1668		
1-Methylbutyl	1615	1619	1628	1644	1689		
3-Methylbutyl	1673	1680	1690	1706	1749		
2-Propenyl			1613	1618	1671	1692	1729
1-Methyl-3-butenyl			1671	1678	1730	1748	1781
3-Butenyl			1695	1696	1749	1765	1797
4-Pentenyl			1792	1800	1851	1865	1892
2-Propynyl			1817	1817	1858	1867	1892
trans-3-Hexenyl			1868	1875	1924	1935	1960
cis-3-Hexenyl			1880	1888	1939	1950	1976

iour on the non-polar stationary phase. The retention increases for the 2-, 3- and 4-chloro esters at 120°C are 205, 259 and 368 i.u. for the saturated esters. These values are slightly lower than those for the corresponding normal-chain esters, *i.e.*, 230, 286 and 395 i.u.[4] and are expected, as some reduction in polar interactions occurs owing to the shapes of the molecules.

TABLE III

INCREMENTAL EFFECT OF POSITION OF CHLORINE SUBSTITUENT ON SE-30 AT 80, 120 AND 160°C

Alkyl substituent	*Temperature (°C)*								
	80			*120*			*160*		
	*2ClB−B**	*3ClB−B**	*4ClB−B**	*2ClB−B**	*3ClB−B**	*4ClB−B**	*2ClB−B**	*3ClB−B**	*4ClB−B**
Branched-chain ester:									
Methylethyl	141	156	222	138	154	219			
Dimethylethyl	137	157	219	141	158	223			
1-Methylpropyl	139	154	217	144	159	224			
1,1-Dimethyopropyl	135	155	216	145	164	225			
2-Methylpropyl	136	152	218	132	148	215			
1,2-Dimethylpropyl	136	153	215	142	159	223			
1-Methylbutyl	135	152	214	141	159	224			
3-Methylbutyl	134	150	217	144	160	230			
Average value	137	154	217	141	158	223			
Olefinic ester:									
2-Propenyl				143	156	226	134	143	211
1-Methyl-3-butenyl				143	160	227	144	161	226
3-Butenyl				147	160	230	143	159	228
4-Pentenyl				144	160	232	148	162	233
trans-3-Hexenyl				146	159	229	149	161	231
cis-3-Hexenyl				147	161	232	149	162	233
Acetylenic ester:									
2-Propynyl				150	160	232	143	151	221

* 2ClB−B = Increment for alkyl 2-chlorobutanoate; 3ClB−B = increment for alkyl 3-chlorobutanoate; 4ClB−B = increment for alkyl 4-chlorobutanoate; B = retention for alkyl butanoate. Retentions of butanoyl esters (B), 2-chlorobutanoyl esters (2ClB), 3-chlorobutanoyl esters (3ClB) and 4-chlorobutanoyl esters (4ClB).

TABLE IV

INCREMENTAL EFFECT OF POSITION OF CHLORINE SUBSTITUENT ON OV-351 AT 80, 120 AND 160°C

Alkyl substituent	*Temperature (°C)*								
	80			*120*			*160*		
	*2ClB – B**	*3ClB – B**	*4ClB – B**	*2ClB – B**	*3ClB – B**	*4ClB – B**	*2ClB – B**	*3ClB – B**	*4ClB – B**
Branched-chain ester:									
Methylethyl	233	289	398	182	231	337			
Dimethylethyl	229	286	392	182	231	329			
1-Methylpropyl	237	296	403	205	260	366			
1,1-Dimethylpropyl	235	294	399	209	259	368			
2-Methylpropyl	238	299	410	210	267	380			
1,2-Dimethylpropyl	231	297	407	211	271	378			
1-Methylbutyl	235	296	404	214	273	384			
3-Methylbutyl	239	301	416	226	283	403			
Average value	235	295	404	205	259	368			
Olefinic ester:									
2-Propenyl				223	274	391	187	227	333
1-Methyl-3-butenyl				217	274	388	163	213	321
3-Butenyl				233	285	404	180	227	338
4-Pentenyl				241	303	423	221	277	394
trans-3-Hexenyl				243	298	418	219	270	389
cis-3-Hexenyl				244	298	422	223	274	397
Average value				234	289	408	199	248	362
Acetylenic ester:									
2-Propynyl				270	311	436	228	294	396

* As in Table III.

TABLE V

SEPARATION BETWEEN GROUPS OF CHLORINATED ESTERS AT 80, 120 AND 160°C ON SE-30 AND OV-351

Temperature (°C)	*Stationary phase*									
	SE-30					*OV-351*				
	4-Chloro esters	*3-Chloro esters*	*2-Chloro esters*	*4-Chloro – 3-chloro esters*	*3-Chloro – 2-chloro esters*	*4-Chloro esters*	*3-Chloro esters*	*2-Chloro esters*	*4-Chloro – 3-chloro esters*	*3-Chloro – 2-chloro esters*
Branched-chain ester										
80	217	154	137	63	17	404	295	235	109	60
120	223	158	141	65	17	368	259	205	109	54
Olefinic ester										
120	229	159	145	70	14	408	289	234	119	55
160	227	158	145	69	13	362	248	199	114	49
Acetylenic ester										
120	232	160	150	72	10	436	311	270	125	41
160	221	151	143	70	8	396	294	228	102	66

TABLE VI

AVERAGE RETENTION INCREMENT RATIOS (ΔOV-351/ΔSE-30) OF SATURATED AND UNSATURATED CHLOROBUTANOATES AT 80, 120 AND 160°C

Temperature (°C)	*Acyl group*	*Alkyl group*		
		Saturated	*Olefinic*	*Acetylenic*
80	4-Chloro esters	1.86		
	3-Chloro esters	1.92		
	2-Chloro esters	1.72		
120	4-Chloro esters	1.65	1.78	1.88
	3-Chloro esters	1.64	1.82	1.94
	2-Chloro esters	1.45	1.61	1.80
160	4-Chloro esters		1.59	1.79
	3-Chloro esters		1.57	1.95
	2-Chloro esters		1.37	1.59

The data in Tables III and IV are summarized in Table V, which also shows the differences between the retention indices of the 4- and 3-chloro and the 3- and 2-chloro isomers. With the saturated esters a minimal difference is observed between the esters with straight or branched alcohol chains. A slightly increased retention is evident with the olefinic esters and a greater increase with a single acetylenic ester. The effect is generally slightly more apparent on the polar stationary phase.

Ratios of the retention increments on the two stationary phases are shown for the three series of esters in Table VI, and it is evident that the ratios of the saturated, olefinic and acetylenic 3-chloro esters are higher than those of the corresponding 2-chloro homologues. The lower values are consistent with increased steric effects due to the proximity of the chlorine atom and carbonyl group. With the branched-chain esters the values are slightly lower than those of the straight-chain esters in most instances owing to the proximity of the methyl groups and the carbonyl group. The 4-chloro esters always show higher ratios than the 2-chloro esters, being very similar

TABLE VII

RETENTION INDEX RATIOS FOR BRANCHED-CHAIN, OLEFINIC AND ACETYLENIC CHLOROBUTANOATES AT 120°C

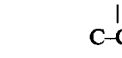
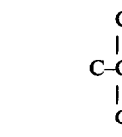
Alkyl group	*4-Chloro esters*	*3-Chloro esters*	*2-Chloro esters*
	1.43	1.42	1.39
	1.37	1.36	1.34

TABLE VII (*continued*)

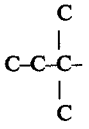
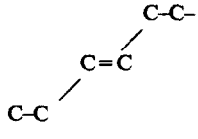
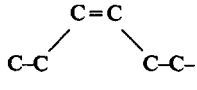
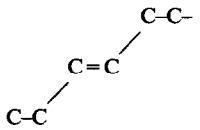
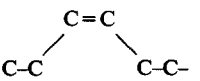
Alkyl group	*4-Chloro esters*	*3-Chloro esters*	*2-Chloro esters*
	1.39	1.37	1.34
	1.34	1.32	1.29
	1.39	1.38	1.34
	1.35	1.33	1.30
	1.35	1.33	1.30
	1.36	1.34	1.31
C=C–C–	1.50	1.49	1.46
	1.39	1.37	1.34
C=C–C–C–	1.45	1.43	1.40
C=C–C–C–C–	1.41	1.39	1.36
C–C–C=C–C–C–	1.36	1.34	1.31
	1.36	1.34	1.31
	1.37	1.35	1.32
C≡C–C–	1.67	1.66	1.64

TABLE VIII

RETENTION INCREMENT RATIOS FOR BRANCHED-CHAIN, OLEFINIC AND ACETYLENIC CHLOROBUTANOATES AT 120°C

Alkyl group	*4-Chloro esters*	*3-Chloro esters*	*2-Chloro esters*
	1.54	1.50	1.32
	1.48	1.46	1.29
	1.63	1.64	1.42
	1.64	1.58	1.44
	1.77	1.80	1.59
	1.70	1.70	1.49
	1.71	1.72	1.52
	1.75	1.77	1.57
	1.73	1.76	1.56
	1.71	1.71	1.52
	1.76	1.78	1.59
	1.82	1.89	1.67
	1.83	1.87	1.66
	1.82	1.85	1.66
	1.88	1.94	1.80

to those of the 3-chloro esters. For the straight-chain esters this has been suggested to be due possibly to the longer acyl group allowing the substituent at the terminal position to move closer to the carbonyl group[4]. With the branched-chain esters such a possibility is reduced.

The effect on retention of the individual configuration of the alkyl group of the esters is shown in Table VII. The retention index ratios given (calculated from Tables I and II) show that the polar effects are maximized by the ω-chlorine substituent, whereas a general decrease in values from the 4- to the 3- to the 2-chloro esters occurs. With the branched-chain esters it is evident that although the values are similar, the most congested esters generally show lower values. With the olefinic esters the compounds with a pendant methyl substituent adjacent to the carbonyl group has lower values. With the acetylenic esters the ratios are higher owing both to the type of unsaturation present and to its presence ot the ω- or terminal position.

The effect of the shape of the alkyl group of the esters is shown in Table VIII. Retention increment ratios (calculated from Tables III and IV) are shown and it is apparent with the branched-chain esters that the compounds with a single pendant methyl group all show a maximized polar effect with the 3-chloro, rather than the 4-chloro, esters. This effect might be considered to be due to a reduction in the polar effect due to some hindrance of those esters with multiple pendant groups. With the olefinic esters the effect of the 3-chloro esters is more evident. The enhancement occurs with the straight-chain 3-chloro esters and is reduced but equivalent to the 4-chloro ester with the compound with a methyl group adjacent to the carbonyl group. With the isomeric hexenyl esters the alkyl configuration has little effect; the 3-chloro isomer shows the greatest polar effect in both instances but the *trans* isomer, owing to its configuration, shows very slightly greater polar effects than the *cis* isomer. The alkyl ester similarly shows the maximum polar effect for the 3-chloro ester. The actual ratios shown for the esters are very similar to those found previously[2] for the 3-chloro and 2-chloro derivatives of the same alkanols, the increased chain length of the acyl compound having very little effect.

ACKNOWLEDGEMENTS

I. O. O. Korhonen gratefully acknowledges the Kalle and Dagmar Välimaa Foundation (Cultural Foundation of Finland), the Medica Corporation Research Foundation, the Alfred Kordelin Foundation and the Academy of Finland for financial support.

REFERENCES

1 J. R. Chretien, K. Szymoniak, C. Lion and J. K. Haken, *J. Chromatogr.*, 324 (1985) 355.
2 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 320 (1985) 325; and references cited therein.
3 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 319 (1985) 131.
4 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 324 (1985) 343.
5 I. O. O. Korhonen, *J. Chromatogr.*, 268 (1983) 437.
6 A. Grobler and G. Balizs, *J. Chromatogr. Sci.*, 12 (1974) 57.