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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XXVII*. RETENTION INCREMENTS OF C₁-C₁₈ PRIMARY ALKA-NOLS AND THEIR 2-CHLOROPROPANOYL AND 3-CHLOROPROPANOYL DERIVATIVES ON SE-30 AND OV-351 CAPILLARY COLUMNS

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SUMMARY

The retention behaviour of primary C_1-C_{18} *n*-alkanols and their propanoyl, 2-chloropropanoyl and 3-chloropropanoyl derivatives was examined isothermally on SE-30 and OV-351 capillary columns. Retention increments showing the effect of methylene substitution in the alkyl chains and of monochloro substitution in the acyl chains are presented. The considerable enhancement of terminal chlorine substitution is discussed.

INTRODUCTION

Korhonen¹ recently reported the separation of C_1-C_{18} primary alkanols and their propanoyl, 2-chloropropanoyl and 3-chloropropanoyl derivatives using temperature-programmed gas chromatography (GC) on SE-30 and OV-351 capillary columns. Complete separation of the 60 compounds studied was achieved on the low-polarity column whereas increased retention and some overlapping occurred on OV-351. The order of elution of the four series tended to vary with the two columns, being on SE-30 C_{n+2} -alkanol < C_n -alkyl propanoate < C_{n-2} -alkyl 3-chloropropanoate < C_{n-1} -alkyl 2-chloropropanoate and on OV-351 C_n -alkyl propanoate < C_n -alkanol < C_{n-4} alkyl 3-chloropropanoate < C_{n-2} -alkyl 2-chloropropanoate ($n \ge 6$). The lower alkanols (C_1 - C_4) were eluted before the corresponding *n*-alkyl propanoates on OV-351.

Earlier studies using temperature programming maximized the separation of various chlorinated esters with the substituent in either the acid or alcohol chain²⁻⁸.

^{*} Part XXVI: J. K. Haken, I. O. O. Korhonen and B. G. Madden, J. Chromatogr., 298 (1984) 150.

RETENTION INDICES OF	OF C ₁ -C ₁₈ <i>n</i> -ALKANOLS, ALKYL PROPANOATES AND ALKYL CHLOROPROPANOATES ON SE-30	NOLS, ALI	KYL PROI	PANOATE	S AND A	LKYL CH	LOROPRO	PPANOAT	ES ON SE	:-30	
Compounds	Carbon No.	Tempero	Temperature (°C)								
		80	001	120	140	160	180	200	220	240	260
n-Alkanols	c,	254	462	471	340						
	c2	381	496	513	369						
	ٽ	546	565	575	518						
	C4	660	649	649	628						
	ٽ	768	754	748	682						
	ပီ	863	851	845	813	823	814				
	C,	960	951	950	920	938	996				
	ڻ	1057	1050	1049	1033	1037	1042				
	ථ	1154	1149	1147	1143	1140	1140	1167			
	C10	1252	1249	1247	1247	1244	1247	1241	1256	1246	
	C11		1349	1347	1348	1349	1350	1348	1339	1348	
	C ₁₂			1448	1451	1451	1450	1449	1442	1458	
	C14			1646	1652	1655	1657	1659	1653	1661	1670
	C_{16}				1852	1858	1862	1862	1861	1865	1866
	C ₁₈					2058	2065	2063	2064	2069	2067
n-Alkyl propanoates	ں ت	607	627	622	554						
1	C2	688	692	684	656						
	చ	807	795	785	729	753	721				
	C4	901	168	884	845	854	866				
	ပိ	995	987	983	959	696	996				
	C C	1090	1084	1081	1069	1068	1068	1082			
	C,	1186	1181	1178	1174	1170	1169	1176	1162	1202	
	ບຶ	1282	1280	1276	1277	1272	1270	1267	1246	1263	
	රී		1380	1376	1377	1376	1373	1369	1356	1366	
	C_{10}			1476	1478	1478	1474	1473	1462	1459	
	C_{11}			1575	1578	1578	1577	1576	1564	1572	1580
	C12			1672	1677	1679	1680	1679	1672	1676	1677
	C14					1880	1883	1881	1877	1878	1876
	C_{16}					2079	2085	2081	2079	2081	2075
	C_{18}						2285	2278	2278	2281	2276

TABLE I

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1552 1552 1644 1738 1840 2036 2237 240	1614 1712 1810 1910 2110 2311 2516
1234 1339 1427 1427 1535 1635 1635 1635 1736 1736 1736 2039 2239	1201 1300 1402 1502 1503 1503 1503 1503 1503 2312 2312 2312 2312
1200 1309 1418 1418 1418 1418 1418 1625 1728 1625 1728 1728 1728 1728 2033 2233	1162 1162 1279 1385 1487 1593 1700 1803 1904 2208 2208 2208
1160 1216 1318 1318 1423 1527 1629 1729 1729 1832 2032 2032 2231	1083 1185 1185 1293 1399 1494 1701 1701 1803 1904 2302 2302 2499
721 807 950 1119 1119 1124 1323 1423 1525 1525 1627 1627 1627 1627 1627 1627 1627 1627	792 904 986 1192 1192 1192 1293 1394 1495 1597 1597 1590 1903 1903 2305 2305
741 814 923 1016 1115 1219 1321 1422 1524 1623 1725 1825 1825	799 880 985 985 1085 1188 1188 11393 11393 11393 11595 11597 11897 2096
790 800 903 1011 1118 1221 1421 1421 1521 1620 1719 1817	783 865 978 1086 1188 1188 1188 1292 1391 1491 1591 1591 1790
756 832 930 1122 1122 1316 1415 1515 1612	819 897 996 1092 1189 1189 1386 1486 1584 1681
774 841 932 1122 1122 1318 1415	829 902 1193 1190 1288 1387
783 851 941 1032 1126 1316 1316	838 910 1003 1192 1287
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Alkyl 2-chloropropanoates	Alkyl 3-chloropropanoates

Compounds	Carbon No.	Tempera	Temperature (°C)							
İ		80	001	120	140	160	180	200	220	
<i>n</i> -Alkanols	C1	891	917	978			-			
	C2	924	952	1015						
	ٽ	1024	1037	1031						
	C [*]	1131	1148	1124	1153					
	ڒ	1241	1256	1238	1263	1288	1210			
	ڻ ۲	1348	1357	1332	1362	1378	1358	1412		
	Ċ,	1452	1453	1427	1459	1467	1444	1461		
	പ	1556	1551	1528	1557	1555	1550	1556		
	రి	1663	1649	1627	1658	1659	1652	1664	1680	
	C_{10}		1746	1726	1760	1759	1753	1764	1783	
	C11		1845	1826	1861	1856	1853	1861	1886	
	C ₁₂		1942	1924	1962	1957	1960	1960	6261	
	C14				2164	2161	2165	2165	2177	
	C ₁₆				2365	2362	2367	2370	2375	
	C ₁₈					2563	2570	2574	2573	
n-Alkyl propanoates	C C	606	937	1003						
4 1	C2	957	776	1031						
	చి	1039	1065	1064						
	C4	1139	1159	1145	1178					
	ڻ	1238	1255	1234	1258	1288	1210			
	ပိ	1339	1353	1330	1362	1378	1358	1412		
	ن ن	1438	1445	1427	1460	1467	1444	1461		
	రి	1539	1539	1522	1557	1555	1550	1556		
	రో	1637	1634	1618	1657	1659	1652	1664	1680	
	C10		1732	1716	1755	1757	1753	1764	1783	
	C11		1831	1813	1853	1854	1853	1861	1886	
	C12		1930	1911	1953	1953	1959	1960	1979	
	C14				2153	2154	2165	2165	2177	
	C16				2350	2352	2367	2370	2375	
	C18					2550	2570	2574	2577	

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TABLE II

	1672 1759 1858 1967 2037 2145 2145 2450 2450 2852	1638 1739 1739 1912 2012 2014 2012 2381 2381 2381 2381 2381 2381 2381 23
1432 1527	1649 1742 1337 1934 2030 2133 2436 240 2842	1412 1470 1605 1794 1793 1993 2093 2093 2093 2093 2004 2297 2297 2202 2304
1260 1290 1361 1440 1529	1623 1715 1715 1922 2022 2126 2427 2627 2824	1358 1397 1489 1586 1680 1777 1982 2084 2084 2387 2387 2387 2387 2387 2387 2387 2387
1261 1288 1359 1437 1526	1625 1718 1817 1914 2014 2115 2214 2414 2412	1378 1407 1497 1582 1582 1679 1973 2073 2073 2073 2374 2374 2374
1236 1254 1340 1428 1521	1618 1717 1814 1913 2013 2112 2211 2409	1362 1400 1488 1580 1576 1773 1871 1970 2070 2170 2269 2368
1202 1229 1305 1396 1487	1580 1675 1772 1869 1966 2064	1330 – 1450 1542 1636 1732 1926 2023
1221 1250 1327 1412 1502	1594 1689 1787 1885 1981	1353 1388 1469 1558 1749 1848 1949
1202 1232 1312 1404 1500	1596 1692	1339 1378 1464 1558 1654
	•	
౮౮౮౮౮	้ ขํ บํ ฃํ ฃํ บํ บ๋ บ๋ บ๋ บํ บํ	<u></u> ပေပီပီပီပီပီပီပီပီပီပီပီပီပီပီ
Alkyl 2-chloropropanoates		Alkyl 3-chloropropanoates

Isothermal studies of simple alkyl esters have been reported by Haken and co-workers^{9,10} and also some studies of various chlorinated esters^{11,12}, including the methyl esters of interest examined at 80°C on a non-polar stationary phase¹² to elucidate the effect of structure on incremental retention index variations.

Komárek and co-workers^{13–15} also studied homologous series of esters with fluorine, chlorine, bromine and iodine substitution in both the alkyl and acyl chains, while VandenHeuvel *et al.*¹⁶ reported the GC of long-chain alcohols and some ester derivatives.

This paper describes the isothermal capillary GC at 100–260°C of the C_1 – C_{18} *n*-alkanols and of the corresponding propanoyl, 2-chloropropanoyl and 3-chloropropanoyl derivatives. Retention index increments at 120 and 220°C show more clearly the effect of substitution or retention of the homologous esters than the earlier study¹.

EXPERIMENTAL

Materials

The C₁–C₁₂, C₁₄, C₁₆ and C₁₈ *n*-alkanols were commercial products (Fluka, Buchs, Switzerland). *n*-Alkyl propanoates, 2-chloropropanoates and 3-chloropropanoates were prepared from the corresponding alkanols and acid chlorides as described earlier¹⁷; propanoyl chloride was obtained by the reaction of benzoyl chloride (Fluka) with propanoic acid (Fluka) according to Brown¹⁸, 2-chloropropanoyl chloride by chlorination¹⁹ of propanoyl chloride with N-chlorosuccinimide (E. Merck, Darmstadt, F.R.G.) and 3-chloropropanoyl chloride from 3-chloropropanoic acid²⁰ by treatment with thionyl chloride. The purity of the compounds was checked by GC.

Gas chromatography

For the GC analyses a Perkin-Elmer Sigma 3 gas chromatograph was used with 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 \times 0.33 mm I.D.), supplied by SGE (North Melbourne, Australia), and a fused-silica OV-351 WCOT column (25 m \times 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The data were determined isothermally at the temperatures shown in Tables I and II.

The chromatographic data were recorded with a Hewlett-Packard Model 3390A reporting integrator using standard programs. 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 Balizs²¹.

RESULTS AND DISCUSSION

Retention indices of the *n*-alkanols, the alkyl propanoates and the chlorinated propanoates on SE-30 and OV-351 stationary phases are shown in Tables I and II,

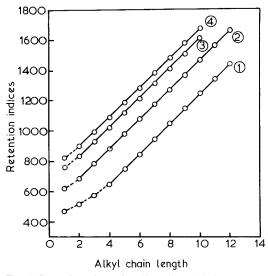


Fig. 1. Retention plots of *n*-alkanols and their propanoyl and chloropropanoyl derivatives on SE-30 at 120° C. (1) *n*-Alkanols; (2) *n*-propanoates; (3) 2-chloropropanoates; (4) 3-chloropropanoates.

respectively, and plots of the four homologous series at 120°C on both phases are shown in Figs. 1 and 2.

On the non-polar column it is evident that the alcohols have the lowest retentions and the 3-chloro esters have higher retentions than the 2-chloro esters (Fig. 1).

Table III shows retention index increments for methylene groups for the four series at 120 and 220°C on both stationary phases. It is apparent that in all instances increments close to 100 index units occur, the values at 120°C generally being slightly lower than those at 220°C; however, it is obvious that substitution in the acyl chain has little incremental effect on the alkyl chain.

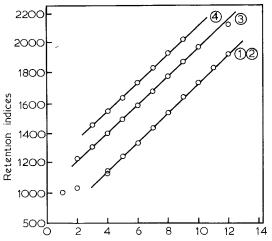


Fig. 2. Retention plots of *n*-alkanols and their propanoyl and chloropropanoyl derivatives on OV-351 at 120°C. (1) *n*-Alkanols; (2) *n*-propanoates; (3) 2-chloropropanoates; (4) 3-chloropropanoates.

Alkyl	n-Alkanols	nols			Alkyl pi	Alkyl propanoates			2-Chlor	2-Chloropropanoates	ates		3-Chlor	3-Chloropropanoates	ates	
cnum length	SE-30		0V-351		SE-30		0V-351		SE-30		0V-351		SE-30		0V-351	
	120°C	220°C	120°C	220°C	120°C	220°C	120°C	220°C	120°C	220°C	120°C	220°C	120°C	220°C	120°C	220°C
7	42*		37*		62*		28*		¥9L		27*		78*			
ŝ	62*		16^{*}		101		33*		98		¥91		66			
4	74*		93		66		81*		97		16		96		92	
S	66		114		66		89		95		16		97		94	
9	67		4		98		96		97		93		98		96	73*
7	105		95		76		76		97	109	95	87*	66	106	96	100
×	66		101		98	84*	95		66	109	76	66	100	102	98	100
6	98		66		100	110	96		100	102	76	109	98	106		92
10	100		66	103	100	106	<u>98</u>	103	76	105	76		97	107		100
11	100	83*	100	103	66	102	26	103		103	98	108		103		104
12	101	103	98	93	76	108	98	93		103		103		101		
14	66	106		66		103		66		101		101		101		116
16		104		66		101		66		100		100		96		101
18		102		66		66		101		66		101		103		101
Ω	100	104	66	66	66	104	96	100	98	103	95	103	98	103	96	102

TABLE III

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Alkyl	120°C			220°C		
chain length	$\Delta P - \Delta A^*$	$\Delta 2\text{-}CIP - \Delta P^{\star}$	43-CIP - AP*	$\Delta P - \Delta A^{\star}$	$\Delta 2$ -CIP - ΔP^{\star}	$A3-CIP - \Delta P^{\star}$
4	235	143	208			
Ś	235	139	206			
9	236	138	206			
7	228	138	208		147	223
×	227	139	210		172	241
6	229	139	208		164	237
10	229	136	205	206	163	238
11	228			225	164	239
12	224			230	159	232
14				224	156	229
16				218	154	219
18				214	153	226
Σ	230	139	207	220	159	232

INCREMENTAL EFFECT OF CONVERSION OF *n*-ALKANOLS TO PROPANOYL ESTERS AND CHLORINATION TO THE 2-CHLOROPROPA-NOVI AND 3 CHI ODOBPODANOVI DEDIVATIVES ON SE 20 AT 120 AND 30%C

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TABLE IV

 \star dP = Retention of propanoyl ester; dA = retention of *n*-alkanol. d2-C1P = Retention of 2-chloropropanoyl ester; d3-C1P = retention of 3-chloropropanoyl ester.

GC OF HOMOLOGOUS ESTERS. XXVII.

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Alkyl	120°C			220°C		
cnum length	$\Delta P - \Delta A^{\star}$	$\Delta 2$ -CIP – ΔP^{\star}	43-CIP - 4P*	$\Delta P - \Delta A^{\star}$	42-CIP - AP*	$\Delta 3-CIP - \Delta P^{\star}$
-	25	199	327			
2	16	198	I			
3	33	241	386			
4	21	251	397			
5	4	253	402			
9	-2	250	402			
7		248	401			
80	-6	250	404			
6	6-	251	405	0	287	424
10	-10	250		0	254	421
1	-13	251		0	259	422
12	-13			0	269	402
4				0	273	436
16				0	275	439
18				4	275	438
Σ		240	391		270	426

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TABLE V

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GC OF HOMOLOGOUS ESTERS. XXVII.

The incremental effect of conversion of the alcohol to the propanoate ester and of chlorination of the acyl chain of the esters on SE-30 at 120 and 220°C is shown in Table IV. The retention increase of the propanoate ester is approximately 230 index units at 120°C, a not unexpected increase as the OH group with little influence on the low-polarity phase is replaced with the much larger CH_3CH_2COO group. The methylene groups each have a value of approximately 100 index units. The values at 220°C are very slightly lower, however, not being strictly comparable as at 220°C only the higher esters were considered.

At 120°C the 2-chloropropanonyl and 3-chloropropanoyl esters show retention enhancements of approximately 139 and 207 index units and at 220°C of 159 and 232 index units, respectively, these values being in reasonable agreement with those for methyl 2- and 3-chloropropanoates, viz., 150 and 206 index units on non-polar OV-101 at 80°C¹².

On the OV-351 stationary phase polar effects might be expected to be significant, Fig. 2 showing that the alcohols have greater retentions than the propanoyl esters, the chlorinated esters having increased retention. The overall retention value increased on the polar column, while the separation of the chlorinated esters was also much increased. Table V shows incremental increases on OV-351 corresponding to the values on SE-30 given in Table IV. At 120°C the 2-chloropropanoyl and 3chloropropanoyl esters show retention enhancements of 240 and 391 index units, while at 220°C the average values are increased to 270 and 426 index units, respectively. The values at 120°C with the lower homologues are significantly lower and are not included, as comparable data for the lower esters at 220°C are not available. The considerable enhancement of the retention of the terminal or ω position of substitution is apparent and is in agreement with other studies of chlorinated esters⁷ and of compounds with other substituents⁷.

Table VI shows that the separation between two series of chloro esters at both 120 and 220°C is slightly more than doubled with the 3-chloro esters and is greater than the retention increase between the propanoyl and 2-chloropropanoyl esters. The retention increment ratio of the 3-chloro esters is higher than that of the 2-chloro homologues, as is evident in Table VI. Higher values of the ratio indicate maximization of the polar effects, while lower ratios show the increasing influence of the steric effects, as previously reported with the hindered esters²². As would be expected, a greater steric effect is due to the adjacent positions of the carbonyl and chlorine groups in the 2-chloro esters owing to the -C(O)-C(CI)-C structure compared with the -C(O)-C-C(Cl)- structure in the 3-chloro esters.

Temperature	SE-30)		OV-3	51		ΔOV	-351
(°C)	3-Cl	2-Cl	$\Delta(3-Cl-2-Cl)$	3-Cl	2-Cl	$\Delta(3-Cl-2-Cl)$	∆SE	-30
							2-Cl	3-Cl
120	207	139	68	391	240	151	1.73	1.89
220	232	159	73	426	270	156	1.70	1.84

SEPARATION BETWEEN PLOTS OF 2-CHLORO AND 3-CHLORO ESTERS AT 120 AND 220°C

TABLE VI

AND RETENTION INCREMENT RATIOS

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