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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XXVII*. RETENTION INCREMENTS OF C_1 - C_{18} PRIMARY ALKANOLS 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 ($n \geq 6$). 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.

TABLE II
RETENTION INDICES OF C₁-C₁₈ *n*-ALKANOLS, ALKYL PROPANOATES AND ALKYL CHLOROPROPANOATES ON OV-351

Compounds	Carbon No.	Temperature (°C)													
		80	100	120	140	160	180	200	220						
<i>n</i> -Alkanols	C ₁	891	917	978											
	C ₂	924	952	1015											
	C ₃	1024	1037	1031											
	C ₄	1131	1148	1124	1153										
	C ₅	1241	1256	1238	1263	1288	1210								
	C ₆	1348	1357	1332	1362	1378	1358	1412							
	C ₇	1452	1453	1427	1459	1467	1444	1461							
	C ₈	1556	1551	1528	1557	1555	1550	1556							
	C ₉	1663	1649	1627	1658	1659	1652	1664						1680	
	C ₁₀		1746	1726	1760	1759	1753	1764						1783	
	C ₁₁		1845	1826	1861	1861	1856	1861						1886	
	C ₁₂		1942	1924	1962	1962	1957	1960						1979	
	C ₁₄					2164	2161	2165						2177	
	C ₁₆					2365	2362	2370						2375	
	C ₁₈						2563	2570						2573	
	<i>n</i> -Alkyl propanoates	C ₁	909	937	1003										
		C ₂	957	977	1031										
		C ₃	1039	1065	1064										
C ₄		1139	1159	1145	1178										
C ₅		1238	1255	1234	1258	1288	1210								
C ₆		1339	1353	1330	1362	1378	1358	1412							
C ₇		1438	1445	1427	1460	1467	1444	1461							
C ₈		1539	1539	1522	1557	1555	1550	1556							
C ₉		1637	1634	1618	1657	1659	1652	1664						1680	
C ₁₀			1732	1716	1755	1757	1753	1764						1783	
C ₁₁			1831	1813	1853	1853	1854	1861						1886	
C ₁₂			1930	1911	1953	1953	1953	1960						1979	
C ₁₄					2153	2154	2165	2165						2177	
C ₁₆					2350	2352	2367	2370						2375	
C ₁₈						2550	2570	2574						2577	

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-workers¹³⁻¹⁵ 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 C₁-C₁₈ *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 × 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 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,

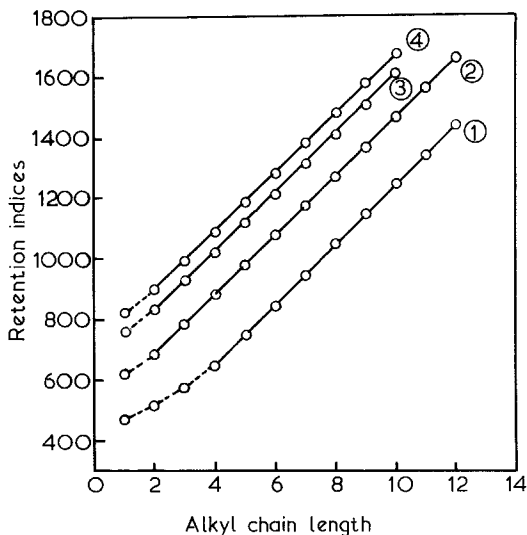


Fig. 1. Retention plots of *n*-alkanols and their propanoyl and chloropropanoyl derivatives on SE-30 at 120°C. (1) *n*-Alkanols; (2) *n*-propanoates; (3) 2-chloropropanoates; (4) 3-chloropropanoates.

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.

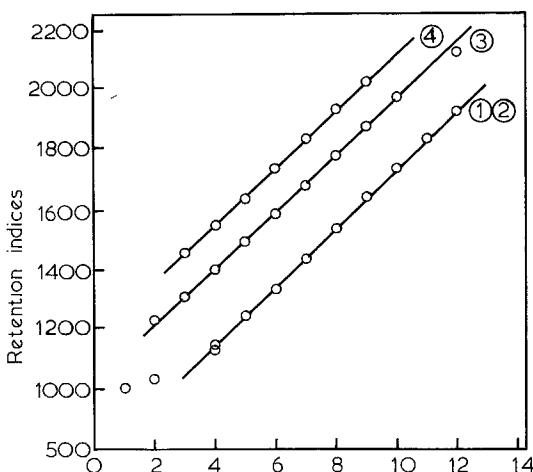


Fig. 2. Retention plots of *n*-alkanols and their propanoyl and chloropropanoyl derivatives on OV-351 at 120°C. (1) *n*-Alkanols; (2) *n*-propanoates; (3) 2-chloropropanoates; (4) 3-chloropropanoates.

TABLE III
METHYLENE INCREMENTS FOR HOMOLOGOUS *n*-ALKANOLS AND ESTERS AT 120 AND 220°C ON SE-30 AND OV-351

Alkyl chain length	<i>n</i> -Alkanols		Alkyl propanoates			2-Chloropropanoates			3-Chloropropanoates			
	SE-30		OV-351		SE-30	OV-351	SE-30	OV-351	SE-30	OV-351	SE-30	OV-351
	120°C	220°C	120°C	220°C	120°C	220°C	120°C	220°C	120°C	220°C	120°C	220°C
2	42*	37*	62*		28*		76*		27*		78*	
3	62*	16*	101		33*		98		76*		99	
4	74*	93	99		81*		97		91		96	92
5	99	114	99		89		95		91		97	94
6	97	94	98		96		97		93		98	96
7	105	95	97		97		97		95		99	73*
8	99	101	98		84*		99	109	97	87*	99	96
9	98	99	100		95		100	109	97	99	100	106
10	100	99	100	103	96		97	102	97	109	98	102
11	100	83*	99	103	98		103	103	98	108	97	106
12	101	103	97	93	98		103	103		103	101	101
14	99	106	99	99	99		101	101	100	101	101	116
16	104	104	99	99	101		100	100	100	100	101	101
18	102	102	99	99	99		101	99	99	101	103	101
Σ	100	104	99	99	104	96	100	98	95	103	98	96

* Not included in average values.

TABLE IV
 INCREMENTAL EFFECT OF CONVERSION OF *n*-ALKANOLS TO PROPANOYL ESTERS AND CHLORINATION TO THE 2-CHLOROPROPA-
 NOYL AND 3-CHLOROPROANOYL DERIVATIVES ON SE-30 AT 120 AND 220°C

Alkyl chain length	220°C						
	ΔP	ΔA^*	$\Delta 2-CIP$ - ΔP^*	$\Delta 3-CIP$ - ΔP^*	ΔP - ΔA^*	$\Delta 2-CIP$ - ΔP^*	$\Delta 3-CIP$ - ΔP^*
4	235		143	208			
5	235		139	206			
6	236		138	206		147	223
7	228		138	208		172	241
8	227		139	210		164	237
9	229		139	208	206	163	238
10	229		136	205	225	164	239
11	228				230	159	232
12	224				224	156	229
14					218	154	219
16					214	153	226
18					220	159	232
Σ	230		139	207			

* ΔP = Retention of propanoyl ester; ΔA = retention of *n*-alkanol. $\Delta 2-CIP$ = Retention of 2-chloropropanoyl ester; $\Delta 3-CIP$ = retention of 3-chloropropanoyl ester.

TABLE V
 INCREMENTAL EFFECT OF CONVERSION OF *n*-ALKANOLS TO PROPANOYL ESTERS AND CHLORINATION TO THE 2-CHLOROPROPA-
 NOYL AND 3-CHLOROPROANOYL DERIVATIVES ON OV-351 AT 120° AND 220°C

Alkyl chain length	120°C				220°C				
	$\Delta P - \Delta A^*$	$\Delta 2\text{-CIP} - \Delta P^*$	$\Delta 3\text{-CIP} - \Delta P^*$	$\Delta P - \Delta A^*$	$\Delta 2\text{-CIP} - \Delta P^*$	$\Delta 3\text{-CIP} - \Delta P^*$	$\Delta P - \Delta A^*$	$\Delta 2\text{-CIP} - \Delta P^*$	$\Delta 3\text{-CIP} - \Delta P^*$
1	25	199	327						
2	16	198	—						
3	33	241	386						
4	21	251	397						
5	-4	253	402						
6	-2	250	402						
7	-1	248	401						
8	-6	250	404						
9	-9	251	405				0	287	424
10	-10	250					0	254	421
11	-13	251					0	259	422
12	-13						0	269	402
14							0	273	436
16							0	275	439
18							4	275	438
Σ		240	391					270	426

* ΔP = Retention of propanoyl ester; ΔA = retention of *n*-alkanol. $\Delta 2\text{-CIP}$ = Retention of 2-chloropropanoyl ester; $\Delta 3\text{-CIP}$ = retention of 3-chloro-
 propanoyl ester.

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 $\text{CH}_3\text{CH}_2\text{COO}$ 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-chloropropanoyl 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 3-chloropropanoyl 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 $-\text{C}(\text{O})-\text{C}(\text{Cl})-\text{C}$ structure compared with the $-\text{C}(\text{O})-\text{C}-\text{C}(\text{Cl})-$ structure in the 3-chloro esters.

TABLE VI

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

Temperature (°C)	SE-30			OV-351			$\frac{\Delta\text{OV-351}}{\Delta\text{SE-30}}$	
	3-Cl	2-Cl	$\Delta(3\text{-Cl} - 2\text{-Cl})$	3-Cl	2-Cl	$\Delta(3\text{-Cl} - 2\text{-Cl})$	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

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