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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XVI*. MONOCHLORO ALIPHATIC ESTERS

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SUMMARY

The retention behaviour of methyl, chloromethyl and the isomeric methyl monochloro esters of *n*-carboxylic acids and of the branched-chain C_5 carboxylic acids on Carbowax 20M and SE-30 capillary columns has been examined. The effect on retention of the position of the chlorine substituent and of branching in the acid chain is discussed and the results are compared with those of other studies of aliphatic esters.

INTRODUCTION

Several recent papers have described the retention behaviour of the methyl, methyl 2-chloro and chloromethyl esters of C_2–C_{20} *n*-carboxylic acids[1], the isomeric methyl monochloro esters of C_2–C_{18} *n*-carboxylic acids[2], the isomeric chloromethyl monochloro esters of C_3–C_{12} *n*-carboxylic acids[3] and the methyl, chloromethyl and the corresponding monochloro esters of pivalic, 2-methylbutyric, isovaleric and valeric acids[4]. The data were obtained using Carbowax 20M glass capillary columns[1–3] or a vitreous silica SE-30 wall-coated open tubular column[4]. The studies were conducted using linear temperature programming and with modest programming rates the data for homologues showed an incremental effect with the variation of a structural parameter being readily apparent.

The retention behaviour of aliphatic ester series that have been studied[5–11] where the influence of chain branching[11] and unsaturation[6,10] have been considered. This paper considers the situation where the substituent, *i.e.*, chlorine, possesses an acknowledged acceptor character. This is in complete contrast to the earlier series studied where the secondary interactive group present, either a double bond[6,10], an alkyl group[5,7,9,11] or another carbonyl group[8], is of a donor character and complementary to the effect of the ester carbonyl group.

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EXPERIMENTAL

A Varian Model 2400 instrument with a flame-ionization detector was used. Three columns were employed: (1) a 90 ft. × 0.012 mm I.D. glass capillary column coated with 5% Carbowax 20M; (2) a 50 m × 0.3 mm I.D. glass capillary column coated with 3% Carbowax 20M; and (3) a 25 m × 0.22 mm I.D. vitreous silica SE-30 SCOT column (Scientific Glass Engineering, Melbourne, Australia).

The data in Table I were obtained using the first Carbowax 20M column with isothermal operation at 40°C for 4 min and then temperature programmed from 40 to 235°C at 8°C/min[1]. The data in Tables II and III were obtained using the second Carbowax 20M column with temperature programming from 50 to 190°C at 4°C/min[2–4]. The data were not corrected for dead volume.

RESULTS AND DISCUSSION

The retention times of the methyl, the methyl 2-chloro and the chloromethyl esters of the C_2–C_{20} *n*-aliphatic acids from the work of Korhonen[1] are shown in Table I. Fig. 1 shows plots of the data, three curvilinear plots being observed; data for several of the lower homologues have been omitted as elution was carried out under isothermal conditions rather than with temperature programming. As expected, the retention times of the chlorinated esters are higher than those of the *n*-alkyl esters,

TABLE I

RETENTION TIMES OF METHYL, METHYL 2-CHLORO AND CHLOROMETHYL ESTERS OF C_2–C_{20} *n*-CARBOXYLIC ACIDS

n-Carboxylic acid	*Retention time (min)*		
	Methyl ester	*Methyl 2-chloro ester*	*Chloromethyl ester*
C_2	1.95	5.92	3.93
C_3	2.10	4.68	5.35
C_4	2.39	6.03	6.87
C_5	3.09	7.57	8.85
C_6	4.53	9.40	10.57
C_7	6.61	11.23	12.27
C_8	8.74	12.95	13.83
C_9	10.70	14.51	15.33
C_{10}	12.43	15.95	16.70
C_{11}	14.04	17.32	18.00
C_{12}	15.54	18.63	19.27
C_{13}	16.91	19.86	20.48
C_{14}	18.23	21.10	21.68
C_{15}	19.48	22.26	22.79
C_{16}	20.73	23.31	23.85
C_{17}	21.88	24.40	24.89
C_{18}	22.98	25.45	25.91
C_{19}	24.05	26.44	26.82
C_{20}	25.12	27.41	27.96

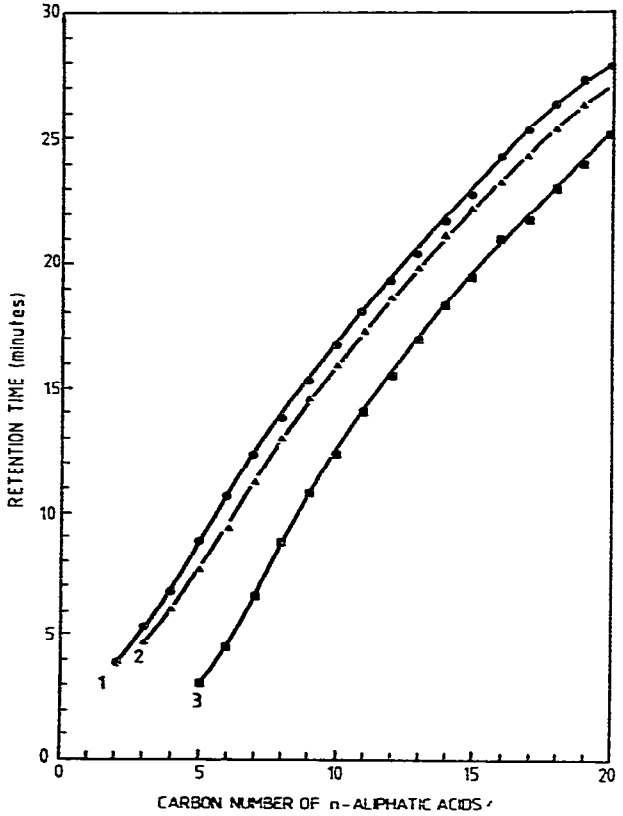


Fig. 1. Plot showing retention of methyl esters (curve 3), methyl 2-chloro esters (curve 2) and chloromethyl esters (curve 1) of C_2–C_{20} *n*-aliphatic acids.

and also the chloromethyl ester series show slight and consistently greater retention times the methyl 2-chloro esters. This effect is as previously observed with alkyl esters, where a methylene group[5,7], a methyl substituent[11] or a double bond[6,10] had a greater effect on retention when in the alcohol rather than in the acid chain. In these series donor effects due to the carbonyl group, unsaturation or methyl groups are significant and greater retention, as observed, is associated with the position of the ether link. With the chlorinated esters the substituent with an acknowledged acceptor character might be expected to reduce the overall polar effect when associated with the alcohol chain; however, this does not occur and the retentions follow the pattern previously observed.

The effect of the position of the chlorine atom in the acid chain may be observed by considering the retention of methyl and chloromethyl esters of isomeric monochloro aliphatic acids (Table II). The isomeric monochloro esters are eluted in order of increasing distance of the substituent groups from the carbonyl group although, as is evident from Fig. 2, a significant increase in retention occurs with the ω-chloro isomers. This is as observed with terminal unsaturation, which has been extensively studied with unsaturated fatty esters[12–17]. However, with the fatty acid esters a double bond adjacent to the carbonyl group, *i.e.*, equivalent here to the 2-chloro

TABLE II

RETENTION TIMES (min) OF METHYL AND CHLOROMETHYL ESTERS OF ALIPHATIC C_2–C_{12} *n*-CARBOXYLIC ACIDS

Chain length	*Methyl ester*	*Isomeric monochloro ester*										
		2-Cl	*3-Cl*	*4-Cl*	*5-Cl*	*6-Cl*	*7-Cl*	*8-Cl*	*9-Cl*	*10-Cl*	*11-Cl*	*12-Cl*
C_2	7.23	9.47										
C_3	7.28	8.81	10.77									
C_4	7.60	10.72	10.33	12.62								
C_5	7.87	11.73	12.20	12.83	15.98							
C_6	8.81	13.74	14.10	15.15	16.47	19.03						
C_7	10.12	15.79	16.70	17.41	18.92	19.53	21.86					
C_8	12.12	18.79	19.63	20.36	21.45	22.30	22.79	25.09				
C_9	14.75	21.54	22.57	23.16	24.04	24.49	25.08	25.52	27.73			
C_{10}	17.75	24.85	25.56	26.27	27.16	27.51	27.69	28.22	28.58	30.71		
C_{11}	20.66	27.47	28.10	28.92	29.54	29.75	29.96	30.16	30.78	31.00	33.06	
C_{12}	23.80	30.46	31.18	31.89	32.61	32.84	32.84	33.08	33.32	33.80	34.03	35.94
	Chloro-methyl ester											
C_3	5.19	9.88	14.40									
C_4	6.50	12.14	13.91	17.15								
C_5	7.50	13.40	15.67	16.59	19.95							
C_6	10.45	16.41	18.19	19.35	20.55	23.07						
C_7	12.35	18.52	20.22	20.95	22.24	22.90	24.98					
C_8	15.77	21.60	23.18	23.80	24.70	25.57	25.81	27.88				
C_9	17.97	23.65	25.11	25.71	26.48	26.95	27.48	27.78	29.66			
C_{10}	21.12	26.53	28.00	28.62	29.29	29.69	29.85	30.34	30.57	32.33		
C_{11}	23.25	28.44	29.90	30.53	31.13	31.46	31.58	31.70	32.17	32.39	34.22	
C_{12}	26.21	31.32	32.54	33.20	33.80	34.16	34.18	34.30	34.43	34.91	35.16	37.28

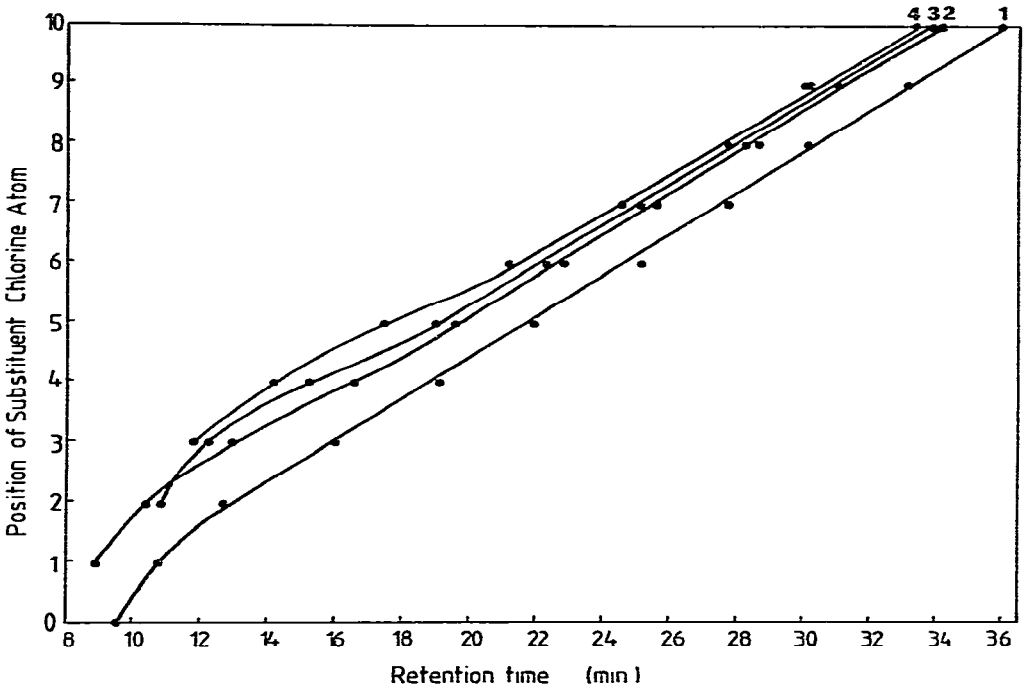


Fig. 2. Plot showing elution sequence of isomeric monochloro esters. 1, $\omega - 3$; 2, $\omega - 2$; 3, $\omega - 1$; 4, ω.

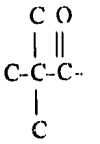
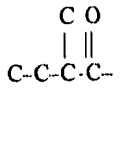
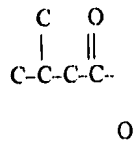
TABLE III

RETENTION TIMES OF METHYL, CHLOROMETHYL AND METHYLMONOCHLORO ESTERS OF ALIPHATIC C_5-CARBOXYLIC ACIDS

*Compound**	*Retention time (min)*	
	Carbowax 20M column	*SE-30 column*
Mi pivalate	4.18	3.55
Cl-Me pivalate	5.73	8.40
Me chloropivalate	6.74	10.45
Me 2-methylbutyrate	4.34	4.70
Me 2-chloro-2-methylbutyrate	6.03	9.69
Me 3-chloro-2-methylbutyrate (e)**	6.91	10.68
Cl-Me 2-methylbutyrate	7.20	11.07
Me 3-chloro-2-methylbutyrate (t)**	7.56	11.60
Me 2-chloromethylbutyrate	8.51	12.72
Me 4-chloro-2-methylbutyrate	9.30	13.68
Me isovalerate	4.36	4.74
Me 2-chloroisovalerate	6.83	10.55
Me 3-chloroisovalerate	6.55	9.49
Cl-Me isovalerate	7.70	11.07
Me 4-chloroisovalerate	10.20	14.22
Me valerate	4.60	5.91
Me 2-chlorovalerate	7.70	12.15
Me 3-chlorovalerate	9.15	13.05
Cl-Me valerate	9.37	13.63
Me 4-chlorovalerate	10.13	14.05
Me 5-chlorovalerate	15.60	18.04

TABLE IV

EFFECT ON RETENTION OF BRANCHING AND OF THE POSITION OF THE CHLORINE SUBSTITUENT IN THE ACID CHAIN

Structure of parent	*Methyl esters*		*Chloromethyl esters*		*2-Chloro (methyl ester)*		*2-Chloromethyl (methyl ester)*		*3-chloro (methyl ester)*		*4-Chloro (methyl ester)*		*5-Chloro (methyl ester)*	
	Polar	*Non-polar*	*Polar*	*Non-polar*	*Polar*	*Non-polar*	*Polar*	*Non-polar*	*Polar*	*Non-polar*	*Polar*	*Non-polar*	*Polar*	*Non-polar*
	4.18	3.15	5.73	1.37			6.74	1.61						
	4.34	4.70	7.20	1.66	6.03	1.39	8.51	1.96	6.91 7.56	1.59* 1.74**	9.30	2.30		
	4.36	4.74	7.70	1.70	6.83	1.57			6.55	1.50	10.20	2.34		
	4.60	5.91	9.27	1.93	7.70	1.67			9.15	1.99	10.13	2.20	15.60	18.04

* *Erythro* form.

** *Threo* form.

isomer, or in close proximity, *i.e.*, equivalent here to the 3-chloro isomer, also produces a significant enhancement of retention owing to donor–donor effects. Such an effect is not observed with the chloro esters, as is evident in Fig. 2, where little separation occurs between the $\omega - 1$ and $\omega - 2$ esters or any of the other series which are partly overlapped with the area shown in the figure. Similarly, no significant reduction in retention of these two isomers would appear to occur due to the close proximity of the acceptor group to the carbonyl group.

The same effect is observed with the chloromethyl monochloro esters where some general increase in retention of all esters with the additional chlorine atom occurs; however, it does not appear that any undue enhancement of retention is experienced because of the additional substituent.

The retention times of chloromethyl and methylmonochloro esters of branched-chain C_5 esters are shown in Table III; in common with other simple esters, little variation of the elution order occurs with variation of the polarity of the stationary phase. The esters are assembled in Table IV according to the structure of the parent acids. Elution of the simple esters followed the established trend, with the most highly branched species, *i.e.*, the pivalate ester, having the lowest retention time. The four chloromethyl esters follow the same trend as the 2-chloromethyl esters which, as previously indicated, have lower retention times than the esters with substituents in the alcohol chain. Table III suggests a variation of this trend, as chloromethyl pivalate has a lower retention time than methyl chloropivalate; however, the structures of the two compounds are not equivalent and when the latter compound is compared (Table IV) with methyl 2-chloromethylbutyrate the expected trend is observed. The 3-chloro esters have greater retention times than the 2-chloro esters, although an anomaly occurs with methyl 3-chloro-2-methylbutyrate, where both the *erythro* and *threo* forms exhibit a higher retention time than expected owing to branching of the acid chain and a lower retention than expected owing to the position of the chlorine substituent. The 4-chloro esters follow the common pattern and have higher retention times than the 3-chloro esters, although the retention of the iso- and normal acids are very similar, while the 5-chlorovalerate ester with a terminal chlorine atom has a substantially higher retention time than any of the other esters.

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