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Note

Gas–liquid chromatographic analyses

III. Glass capillary gas chromatography of chloromethyl monochloro esters of aliphatic C_3–C_{12} *n*-carboxylic acids

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Recently, gas chromatographic (GC) separations of mixtures with a wide range of chain lengths of methyl monochloro[1] and methyl, methyl 2-chloro and chloromethyl esters[2] of aliphatic *n*-carboxylic acids have been reported on Carbowax 20M glass capillary columns.

This paper describes a GC study of chloromethyl monochloro esters of aliphatic C_3–C_{12} *n*-carboxylic acids. The separations of combined mixtures of even- and odd-carbon-number esters were studied, and elution times compared with those of the corresponding methyl esters by separating the mixtures with the same chain lengths under the same operating conditions.

EXPERIMENTAL

GLC analysis

A Varian Model 2400 gas chromatograph, equipped with a flame-ionization detector and 3% Carbowax 20M glass capillary column (50 m × 0.3 mm I.D.), was used for GC analyses. The column temperature was programmed from 50 to 190°C at 4°C/min and held at 190°C until the elution of peaks ceased. Nitrogen was used as the carrier gas at a flow-rate of 1 ml/min. The splitting ratio was 1:20, and the temperatures of injector and detector were 220 and 240°C, respectively.

Samples

Chloromethyl monochloro esters of aliphatic C_3–C_{12} *n*-carboxylic acids were prepared by chlorination[3] of the corresponding chloromethyl esters in the presence of benzene. Methyl monochloro esters were synthesized as described earlier[4-6]. The crude chlorination mixtures were used for GC analyses. To avoid the overlapping of peaks on GC of crude mixtures with a wide range of chain lengths, it is necessary to prevent the formation of higher chlorinated products by using a diluent and much less than an equimolar amount of chlorine.

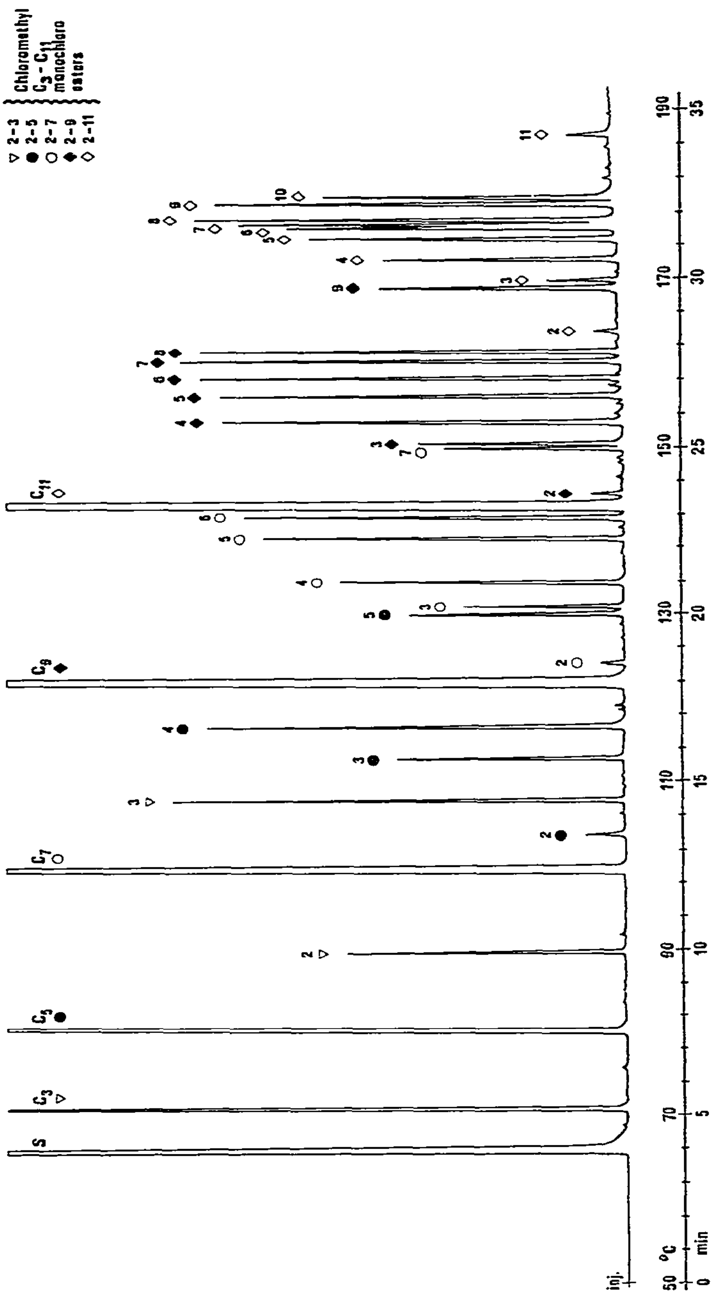

Fig. 1. Chromatogram of the mixture of chloromethyl monochloro esters of aliphatic odd-carbon-number C_3–C_{11} *n*-carboxylic acids. S = Solvent; peak number = position of Cl-substituent.

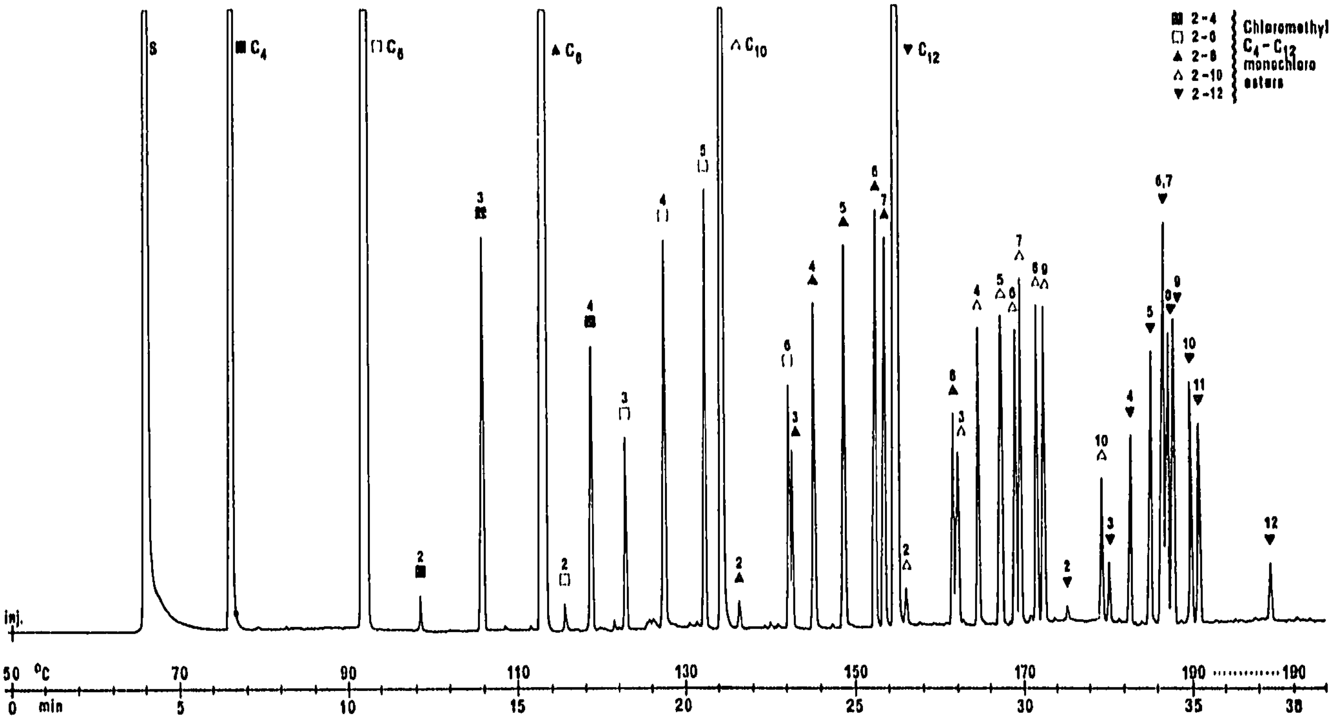

Fig. 2. Chromatogram of the mixture of chloromethyl monochloro esters of aliphatic even-carbon-number C_4–C_{12} *n*-carboxylic acids. S = Solvent; peak number = position of Cl-substituent.

TABLE I

ABSOLUTE AND RELATIVE RETENTION TIMES FOR CHLOROMETHYL ESTERS OF ALIPHATIC C_3–C_{12} *n*-CARBOXYLIC ACIDS

Chain length	*Absolute* and relative** retention times*											
	Chloromethyl ester	*Isomeric chloromethyl monochloro esters*										
		2-Cl	*3-Cl*	*4-Cl*	*5-Cl*	*6-Cl*	*7-Cl*	*8-Cl*	*9-Cl*	*10-Cl*	*11-Cl*	*12-Cl*
C_3	5.19	9.88	14.40									
	1.00	1.90	2.77									
C_4	6.50	12.14	13.91	17.15								
	1.00	1.87	2.14	2.64								
C_5	7.50	13.40	15.67	16.59	19.95							
	1.00	1.79	2.09	2.21	2.66							
C_6	10.45	16.41	18.19	19.35	20.55	23.07						
	1.00	1.57	1.74	1.85	1.97	2.21						
C_7	12.35	18.52	20.22	20.95	22.24	22.90	24.98					
	1.00	1.50	1.64	1.70	1.80	1.85	2.02					
C_8	15.77	21.60	23.18	23.80	24.70	25.57	25.81	27.88				
	1.00	1.37	1.47	1.51	1.57	1.62	1.64	1.77				
C_9	17.97	23.65	25.11	25.71	26.48	26.95	27.48	27.78	29.66			
	1.00	1.32	1.40	1.43	1.47	1.50	1.53	1.55	1.65			
C_{10}	21.12	26.53	28.00	28.62	29.29	29.69	29.85	30.34	30.57	32.33		
	1.00	1.26	1.33	1.36	1.39	1.40	1.41	1.44	1.45	1.53		
C_{11}	23.25	28.44	29.90	30.53	31.13	31.46	31.58	31.70	32.17	32.39	34.22	
	1.00	1.22	1.29	1.31	1.34	1.35	1.36	1.36	1.38	1.39	1.47	
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
	1.00	1.19	1.24	1.27	1.29	1.30	1.30	1.31	1.31	1.33	1.34	1.42

* Absolute retention times (min) measured from Figs. 1 and 2.

** Relative retention times for unchlorinated chloromethyl esters taken as 1.00.

TABLE II

RELATIVE RETENTION TIMES FOR CHLOROMETHYL ESTERS OF ALIPHATIC C_3–C_{12} *n*-CARBOXYLIC ACIDS

Chain length	*Relative retention time**											
	Chloromethyl ester	*Isomeric chloromethyl monochloro esters*										
		2-Cl	*3-Cl*	*4-Cl*	*5-Cl*	*6-Cl*	*(ω-5)-Cl*	*(ω-4)-Cl*	*(ω-3)-Cl*	*(ω-2)-Cl*	*(ω-1)-Cl*	*ω-Cl*
C_3	0.25	0.37	0.51								0.32	0.45
C_4	0.31	0.46	0.50	0.60						0.40	0.46	0.53
C_5	0.36	0.51	0.56	0.58	0.68				0.45	0.52	0.54	0.62
C_6	0.49	0.62	0.65	0.68	0.70	0.78		0.55	0.61	0.64	0.67	0.71
C_7	0.58	0.70	0.72	0.73	0.76	0.77	0.63	0.68	0.70	0.73	0.75	0.77
C_8	0.75	0.81	0.83	0.83	0.84	0.86	0.79	0.80	0.83	0.84	0.84	0.86
C_9	0.85	0.89	0.90	0.90	0.90	0.91	0.88	0.89	0.90	0.91	0.91	0.92
C_{10}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
C_{11}	1.10	1.07	1.07	1.07	1.06	1.06	1.07	1.06	1.06	1.06	1.06	1.06
C_{12}	1.24	1.18	1.16	1.16	1.15	1.15	1.17	1.16	1.15	1.15	1.15	1.15

* Relative retention times for C_{10} derivatives taken as 1.00.

RESULTS AND DISCUSSION

As expected, the isomeric monochloro chloromethyl esters are eluted in direct order from 2-chloro to ω-chloro compound, as are the corresponding methyl derivatives[1]. The gas chromatograms of the combined mixtures of odd-carbon-number C_3–C_{11} and even-carbon-number C_4–C_{12} chloromethyl monochloro esters are illustrated in Figs. 1 and 2. The absolute and relative retention times are presented in Tables I and II. All retention times were measured from sample injection and are tabulated relative to unchlorinated chloromethyl esters = 1.00 (Table I) and C_{10} derivatives = 1.00 (Table II).

The results show that all compounds are resolved except for chloromethyl 6-chloro- and 7-chlorododecanoates (Fig. 2). Bearing in mind the GC separations of methyl monochloro esters[1,5–7], it is evident that the chloromethoxy group makes the polarities of the mid-chain isomers similar, leading to overlapping peaks. On the other hand, owing to their higher boiling points, the elution times of the chloromethyl isomers increase as compared with methyl esters (Fig. 3 and Table III), causing poorer separation of the long-chain isomers.

To compare the elution times of chloromethyl and methyl esters, GC separations of the mixtures with the same chain lengths were performed under the same operating conditions; the results are presented in Table III. It can be seen that the relative retention times of chloromethyl 2-chloro isomers are smaller than those of the 3-chloro derivatives. The values of the latter, on the other hand, are always the greatest ones. This can clearly be seen from Fig. 3; the time between the elution of chloromethyl 2-chloro- and 3-chlorodecanoates is twice as long as that between the

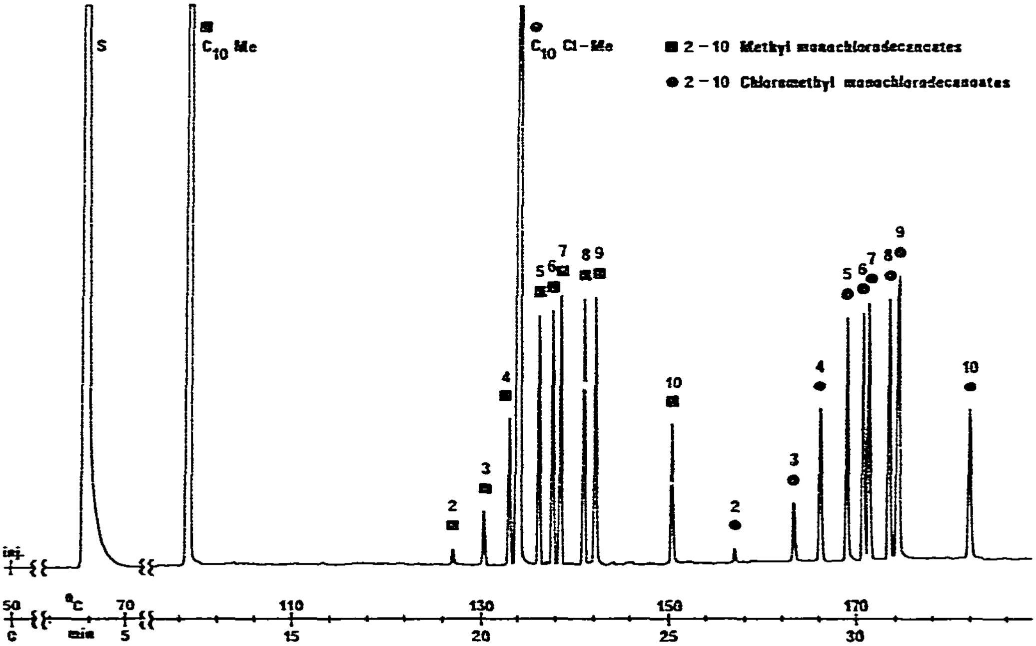

Fig. 3. Chromatogram of the mixture of methyl and chloromethyl decanoates. S = Solvent; peak number = position of Cl-substituent.

TABLE III

RELATIVE RETENTION TIMES FOR CHLOROMETHYL ESTERS OF ALIPHATIC C_3–C_{12} *n*-CARBOXYLIC ACIDS

Chain length	*Relative retention time**											
	Chloromethyl ester	*Isomeric chloromethyl monochloro esters*										
		2-Cl	*3-Cl*	*4-Cl*	*5-Cl*	*6-Cl*	*7-Cl*	*8-Cl*	*9-Cl*	*10-Cl*	*11-Cl*	*12-Cl*
C_3	1.31	1.87	2.10									
C_4	1.41	1.92	2.04	2.00								
C_5	1.49	1.92	2.06	2.05	1.89							
C_6	1.74	1.87	1.93	1.88	1.81	1.68						
C_7	1.93	1.66	1.68	1.64	1.59	1.57	1.49					
C_8	1.87	1.53	1.54	1.52	1.50	1.48	1.47	1.41				
C_9	1.83	1.47	1.48	1.46	1.44	1.43	1.41	1.40	1.36			
C_{10}	1.66	1.37	1.39	1.37	1.36	1.36	1.35	1.34	1.34	1.31		
C_{11}	1.52	1.31	1.33	1.32	1.31	1.31	1.31	1.31	1.30	1.30	1.29	
C_{12}	1.40	1.26	1.30	1.29	1.29	1.30	1.29	1.29	1.29	1.29	1.30	1.31

* Relative retention times for the corresponding methyl esters taken as 1.00, determined from the mixtures of methyl and chloromethyl esters with the same chain lengths.

elution of the corresponding methyl isomers. The chloromethoxy group has the greater effect on the 2-position making 2-chloro isomers less polar and leading to the relatively short elution times on a polar Carbowax 20M column. On a non-polar SE-52 column, however, owing to the better solubilities of less polar 2-chloro isomers, shorter times between the elution of isomers are observed.

The relative retention times of ω-chloro compounds are in general noticeably short, but with increasing chain length the differences from the other isomers decrease. Owing to the isothermal running conditions after reaching the final temperature, however, the greatest value is obtained for ω-chlorododecanoate (Table III).

ACKNOWLEDGEMENT

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