Note

Gas—liquid chromatographic analyses

II. Glass capillary gas chromatography of methyl monochloro esters of aliphatic C$_2$–C$_{18}$ *n*-carboxylic acids

ILPO O. O. KORHONEN

Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1–3, SF-40100 Jyväskylä 10 (Finland)
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Recently, gas chromatographic (GC) separations of combined mixtures of methyl monochloro esters of aliphatic C$_3$–C$_6$ (ref. 1) and C$_7$–C$_{10}$ *n*-carboxylic acids[2] and of methyl, methyl 2-chloro and chloromethyl esters of aliphatic C$_2$–C$_{20}$ *n*-carboxylic acids[3] have been reported.

This paper describes a GC study of all methyl monochloro esters of aliphatic C$_2$–C$_{18}$ *n*-carboxylic acids on a Carbowax 20M glass capillary column. The separations of combined mixtures of even- and odd-carbon-number esters were studied under the same running conditions.

EXPERIMENTAL

GLC analysis

A Varian Model 2400 gas chromatograph, equipped with a flame-ionization detector, was used for GC analyses. The chromatograph was fitted with a 90 m × 0.3 mm I.D. 3 % Carbowax 20M glass capillary column. Nitrogen was used as the carrier gas at a flow-rate of 1.8 ml/min. The column temperature was programmed from 50 to 200°C at 4°C/min and held at 200°C until elution of peaks ceased. The splitting ratio was 1:20 and the temperatures of injector and detector were 220 and 240°C, respectively.

Samples

Methyl monochloro esters of aliphatic C$_3$–C$_6$ *n*-carboxylic acids were synthesized in pure form as described earlier[4]. Methyl monochloro esters of the C$_7$–C$_{18}$ acids were prepared by chlorination[2,5] of the corresponding methyl esters. The crude chlorination mixtures were used for GC analyses.

RESULTS AND DISCUSSION

The polarity of the isomeric monochloro esters increases with increasing distance between the chloro and ester groups, which leads to the better separations of isomers on polar than on non-polar columns.

The gas chromatograms of the combined mixtures of even-carbon-number C_2–C_{18} and odd-carbon-number C_3–C_{17} methyl monochloro esters are illustrated in Figs. 1 and 2 and the relative retention times of the compounds are presented in Tables I and II. All retention times were measured from sample injection and are tabulated relative to unchlorinated methyl esters = 1.00 (Table I) and C_{10} derivatives = 1.00 (Table II). Fig. 3 illustrates the same data as Table I.
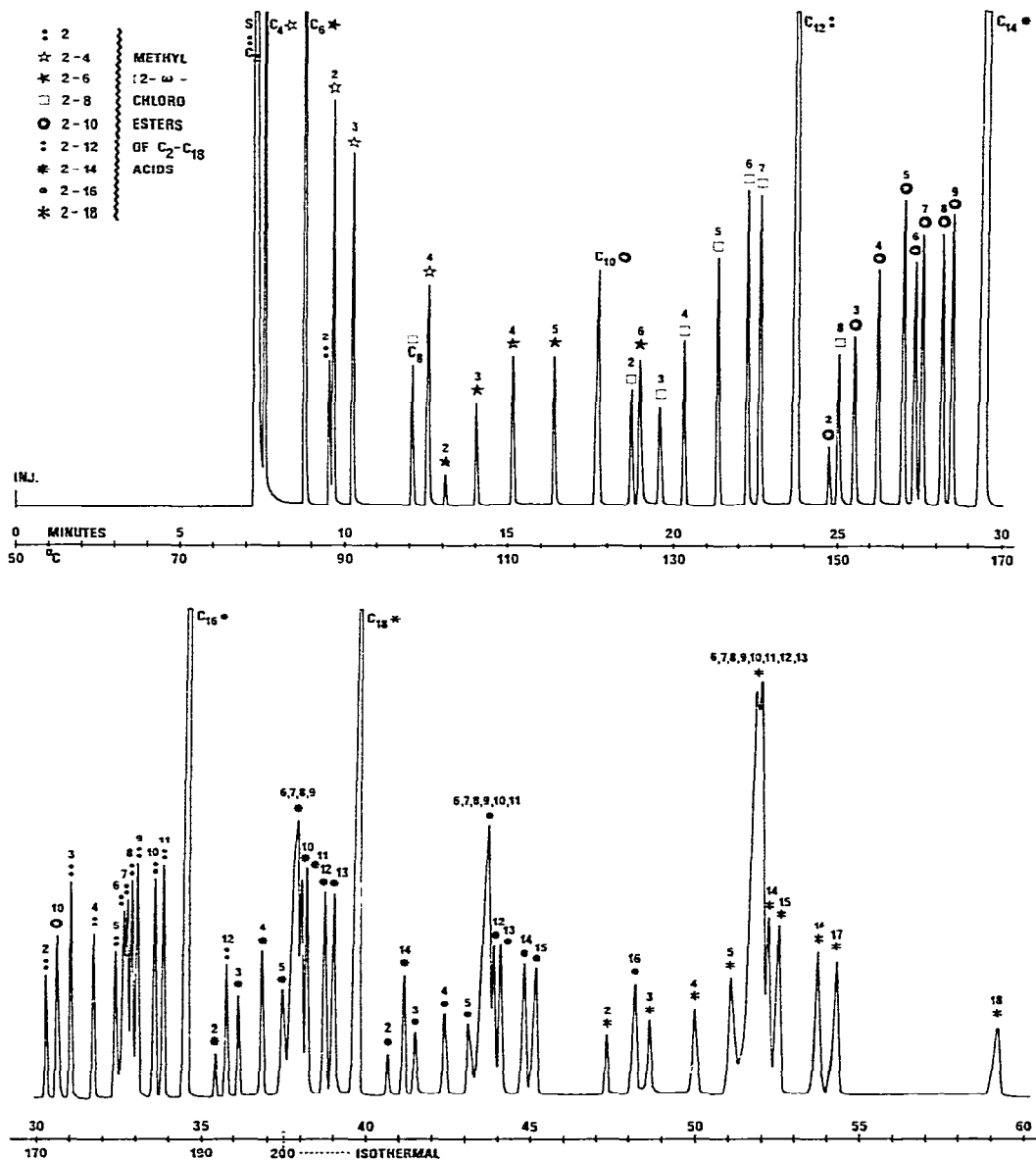

Fig. 1. Chromatogram of the mixture of methyl monochloro esters of aliphatic even-carbon-number C_2–C_{18} n-carboxylic acids.
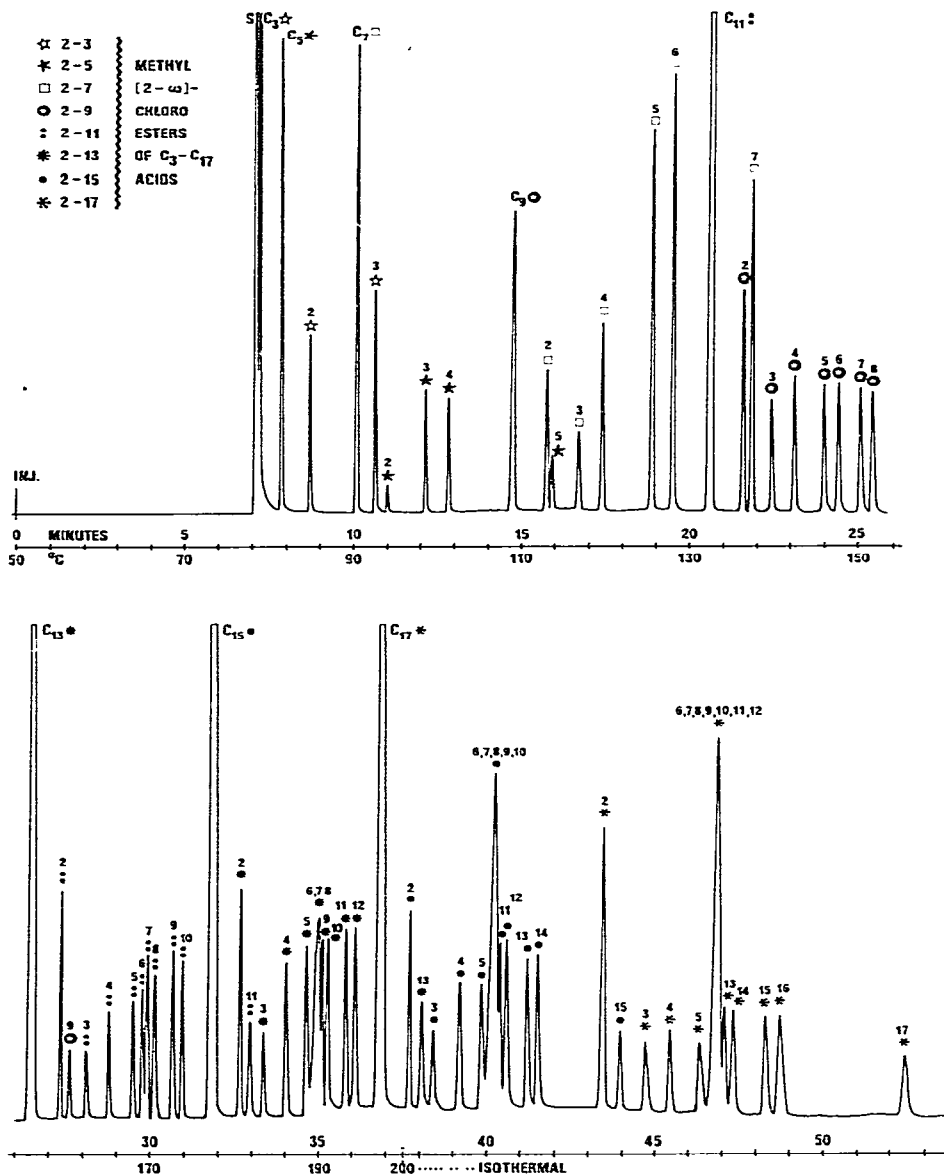
Fig. 2. Chromatogram of the mixture of methyl monochloro esters of aliphatic odd-carbon-number C_3–C_{17} n-carboxylic acids.

The chromatograms show that the mixtures of even- and odd-carbon-number esters can be separated. However, the GC analysis of combined mixture of all C_2–C_{18} methyl monochloro esters resulted in several overlapping peaks, particularly with long-chain isomers.

All of the isomeric monochloro esters are resolvable up to a chain length of C_{12}^-; for longer chain lengths up to C_{18}, the peaks of the mid-chain isomers from 6-

TABLE I

RELATIVE RETENTION TIMES FOR METHYL MONOCHLORO ESTERS OF ALIPHATIC C_2–C_{18} n-CARBOXYLIC ACIDS

Isomeric monochloro esters	Relative retention time*																
	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}
Methyl ester	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2-Cl	1.31	1.21	1.28	1.41	1.49	1.56	1.55	1.46	1.40	1.33	1.28	1.24	1.21	1.19	1.17	1.18	1.19
3-Cl		1.48	1.36	1.55	1.60	1.65	1.62	1.53	1.44	1.36	1.31	1.26	1.23	1.21	1.20	1.21	1.22
4-Cl			1.66	1.63	1.72	1.72	1.68	1.57	1.48	1.40	1.34	1.29	1.26	1.23	1.22	1.23	1.26
5-Cl				2.03	1.87	1.87	1.77	1.63	1.53	1.43	1.37	1.31	1.28	1.25	1.25	1.26	1.28
6-Cl					2.16	1.93	1.84	1.66	1.55	1.44	1.38	1.32	1.29	1.26	1.26	1.27	1.30
7-Cl						2.16	1.88	1.70	1.56	1.45	1.38	1.32	1.29	1.26	1.26	1.27	1.30
8-Cl							2.07	1.73	1.59	1.46	1.39	1.33	1.29	1.26	1.26	1.27	1.30
9-Cl								1.88	1.61	1.49	1.40	1.34	1.30	1.26	1.26	1.27	1.31
10-Cl									1.73	1.50	1.42	1.35	1.31	1.27	1.27	1.27	1.31
11-Cl										1.60	1.43	1.36	1.32	1.28	1.28	1.28	1.31
12-Cl											1.51	1.44	1.33	1.29	1.29	1.29	1.31
13-Cl													1.40	1.30	1.31	1.31	1.31
14-Cl														1.38	1.31	1.31	1.31
15-Cl															1.39	1.32	1.32
16-Cl																1.42	1.35
17-Cl																	1.37
18-Cl																	1.49
Methyl ester**	7.23***	7.28	7.60	7.87	8.81	10.12	12.12	14.75	17.75	20.66	23.80	26.52	29.42	31.90	34.70	36.90	39.85

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

** Absolute retention times (min) for unchlorinated methyl esters.

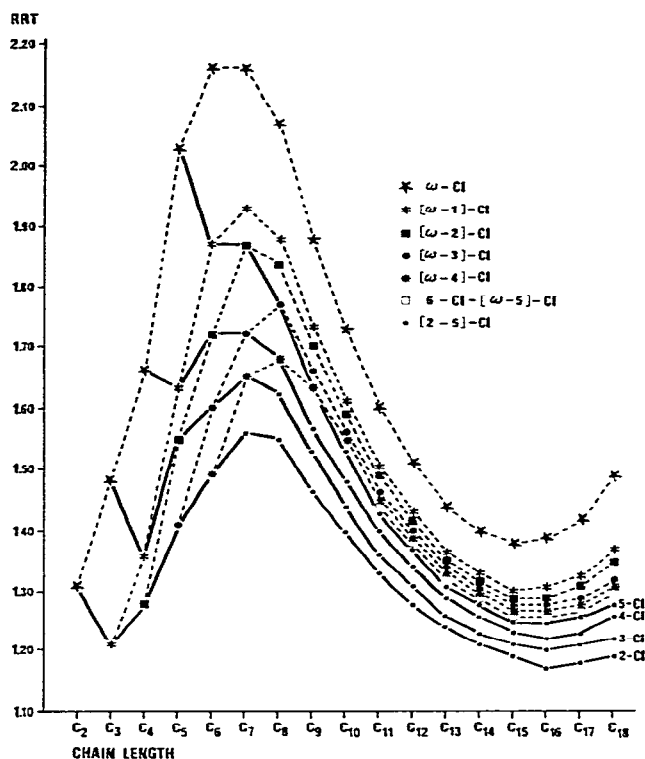*** Retention time determined using methyl hexanoate as solvent.

Fig. 3. Relative retention times (RRT) for methyl monochloro esters of aliphatic C_2–C_{18} n-carboxylic acids. Retention times were measured from Figs. 1 and 2 and are presented relative to unchlorinated methyl esters = 1.00.

chloro to (ω-5)-chloro compounds always overlap. Several columns and various running conditions were used but the mid-chain isomers of the C_{13}–C_{18} esters could not be separated. Although the methyl monochlorododecanoates are fully resolved[5] and the separations of longer chain isomers are slightly better when the column temperature is programmed slowly, long retention times and broad peaks of long-chain isomers are obtained.

From Fig. 3 it can be seen that isomeric monochloro esters leave the column in direct sequence from the 2-chloro to the ω-chloro compound. Terminally chlorinated products are the most polar, leading to relatively long retention times compared with other isomers.

Under the running conditions used the greatest relative retention times are observed for C_6–C_8 isomers (Fig. 3, Table I) and the values decrease with increasing chain length. With long-chain isomers, however, the relative retention times increase with increasing chain length owing to the isothermal running conditions after 37.5 min.

As shown in Table II, the relative retention times for isomeric monochloro esters from the 2-chloro to the ω-chloro compound are constant, particularly for long-chain esters. With short-chain compounds (C_2–C_6), however, the 2-chloro and

TABLE II

RELATIVE RETENTION TIMES FOR METHYL MONOCHLORO ESTERS OF ALIPHATIC C_2-C_{18} n-CARBOXYLIC ACIDS

Chain length	Relative retention time*	Isomeric monochloro esters									
	Methyl ester	2-Cl	3-Cl	4-Cl	5-Cl	6-**(ω-5)-Cl	(ω-4)-Cl	(ω-3)-Cl	(ω-2)-Cl	(ω-1)-Cl	ω-Cl
C_2	0.41	0.39									0.31
C_3	0.42	0.35	0.42							0.31	0.35
C_4	0.43	0.39	0.40	0.48					0.34	0.36	0.41
C_5	0.44	0.45	0.48	0.49	0.59			0.40	0.43	0.45	0.52
C_6	0.50	0.53	0.55	0.58	0.61	0.69	0.48	0.51	0.54	0.58	0.62
C_7	0.57	0.64	0.65	0.66	0.70	0.71	0.61	0.63	0.67	0.68	0.71
C_8	0.68	0.76	0.77	0.78	0.79	0.82	0.74	0.77	0.79	0.80	0.82
C_9	0.83	0.87	0.88	0.88	0.89	0.90	0.88	0.88	0.89	0.89	0.90
C_{10}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
C_{11}	1.16	1.11	1.10	1.10	1.09	1.09	1.09	1.09	1.09	1.09	1.08
C_{12}	1.34	1.22	1.22	1.21	1.20	1.20	1.20	1.20	1.19	1.19	1.17
C_{13}	1.49	1.32	1.31	1.30	1.28	1.28	1.28	1.28	1.27	1.27	1.24
C_{14}	1.66	1.43	1.41	1.40	1.39	1.39	1.39	1.38	1.37	1.37	1.34
C_{15}	1.80	1.52	1.50	1.49	1.47	1.48	1.47	1.47	1.46	1.45	1.43
C_{16}	1.95	1.64	1.63	1.61	1.59	1.60	1.60	1.60	1.59	1.58	1.57
C_{17}	2.08	1.75	1.75	1.73	1.71	1.72	1.72	1.71	1.71	1.71	1.71
C_{18}	2.25	1.91	1.90	1.90	1.89	1.90	1.90	1.90	1.90	1.90	1.93
C_{10}***	17.75	24.80	25.59	26.32	27.11		27.48	27.69	28.29	28.59	30.70

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

** Values for C_6–C_9 compounds determined from retention times of 6-chloro isomers and for C_{10}–C_{18} compounds from the average retention times of 6-(ω-5)-chloro isomers.

*** Absolute retention times (min) for C_{10} derivatives.

ω-chloro isomers give rise to the greatest disparities, which can clearly be seen from the first value in each column.

REFERENCES

1 I. O. O. Korhonen and J. N. J. Korvola, *Acta Chem. Scand.*, B 35 (1981) 139.
2 I. O. O. Korhonen and J. N. J. Korvola, *Acta Chem. Scand.*, in press.
3 I. O. O. Korhonen, *J. Chromatogr.*, 209 (1981) 96.
4 M. T. Pitkänen, I. O. O. Korhonen and J. N. J. Korvola, *Tetrahedron*, 37 (1981) 529.
5 I. O. O. Korhonen and J. N. J. Korvola, *Acta Chem. Scand.*, submitted for publication.