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Note

Glass capillary gas chromatography of methyl, methyl 2-chloro and chloromethyl esters of C_2–C_{20} *n*-carboxylic acids

ILPO O. O. KORHONEN
Department of Chemistry, University of Jyväskylä, SF-40100 Jyväskylä 10 (Finland)
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Numerous papers has been published on the gas chromatography (GC) of carboxylic acids and their derivatives[1], but studies on their chloroalkyl esters have not been reported. On the other hand, the GC of fluorinated carboxylic acids and their methyl esters has been described[2,3].

Recently, the chlorination of short-[4], medium-[5] and long-chain[6] methyl esters have been reported to produce all possible monochloro isomers and also chloromethyl esters. GC product analyses indicated that the monochloro esters are eluted in sequence from 2-chloro to ω-chloroisomers, the 2-chloro esters always being eluted first. Chloromethyl esters left the column after 3-chloro[4] and 4-chloro isomers[5].

This paper describes a study of the GC of all methyl, methyl 2-chloro and chloromethyl esters of C_2–C_{20} *n*-carboxylic acids.

EXPERIMENTAL

Apparatus

GC analyses were carried out on a Varian Model 2400 gas chromatograph equipped with a flame-ionization detector and a 90 ft. × 0.012 in. I.D. glass capillary column coated with 5% Carbowax 20M, with a flow-rate of nitrogen of 1 ml/min. The column temperature was held at 40°C for 4 min, then programmed from 40 to 235°C at 8°C/min. The splitting ratio was 1:20. The temperatures of the injector and detector were 200 and 220°C, respectively.

The samples were purified by preparative GC on a 10 ft. × 3/8 in. O.D. aluminium tube packed with 10% Carbowax 20M on Chromosorb W (60–80 mesh). Appropriate temperatures were used, with a flow-rate of nitrogen of 100 ml/min.

Samples

Methyl esters were obtained by the usual sulphuric acid-catalysed esterification of commercial acids (Fluka, Buchs, Switzerland). Methyl 2-chloro esters were prepared from the corresponding 2-chloro acid chlorides[7] and methanol, except methyl chloroacetate, which was prepared from commercial chloroacetic acid (Fluka) by esterification. Chloromethyl esters[8] were synthesized from the corresponding acid chlorides and paraformaldehyde in the presence of a trace amount of zinc chloride.

The samples were purified, if necessary, by preparative GC and their structures were verified by NMR spectroscopy before GC analysis.

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RESULTS AND DISCUSSION

The gas chromatograms of methyl, methyl 2-chloro and chloromethyl esters are presented in Fig. 1, and the separation of a mixture of these esters is shown in Fig. 2. The retention data of the esters are given in Table I.

Polar stationary phases are more efficient than non-polar ones for the separation of isomeric monochloro esters. Even all eleven methyl monochlorododecanoates were resolvable in a Carbowax 20M glass capillary column[6].

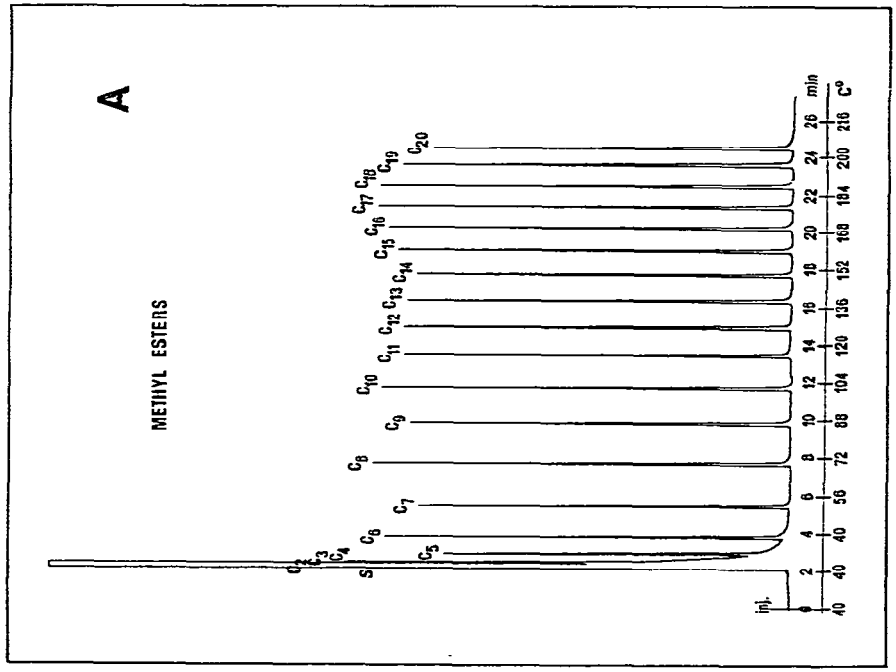
It is necessary to use temperature programming for the analysis of a mixture with a wide range of chain lengths. The initial temperature should be low enough to allow the short-chain derivatives to be separated from the solvent peak, and a sufficiently high subsequent temperature is required so that the long-chain isomers will be eluted sharply. This can be achieved by using a relatively short column, a rapid temperature programming rate and dilute samples.

All compounds were resolved, except methyl acetate, methyl propionate and partly also methyl butyrate, the peaks of which overlapped with that of the solvent. The separation of the mixture of esters was nearly complete; only methyl octanoate and chloromethyl pentanoate partly overlapped (Fig. 2).

TABLE I
RELATIVE RETENTION TIMES (RRT) FOR METHYL, METHYL 2-CHLORO AND CHLOROMETHYL ESTERS OF C_2–C_{20} *n*-CARBOXYLIC ACIDS

n-Carboxylic acid	*Retention time (min)**			*RRT***			*RRT****		
	Methyl ester	*Methyl 2-chloro ester*	*Chloro-methyl ester*	*Methyl ester*	*Methyl 2-chloro ester*	*Chloro-methyl ester*	*Methyl ester*	*Methyl 2-chloro ester*	*Chloro-methyl ester*
C_2	1.95[§]	5.92	3.93	1.00	3.04	2.02	0.16	0.37	0.24
C_3	2.10[§]	4.68	5.35	1.00	2.23	2.55	0.17	0.29	0.32
C_4	2.39	6.03	6.87	1.00	2.52	2.87	0.19	0.38	0.41
C_5	3.09	7.57	8.85	1.00	2.45	2.86	0.25	0.47	0.53
C_6	4.53	9.40	10.57	1.00	2.08	2.33	0.36	0.59	0.63
C_7	6.61	11.23	12.27	1.00	1.70	1.86	0.53	0.70	0.73
C_8	8.74	12.94	13.83	1.00	1.48	1.58	0.70	0.81	0.83
C_9	10.70	14.51	15.33	1.00	1.36	1.43	0.86	0.91	0.92
C_{10}	12.43	15.95	16.70	1.00	1.28	1.34	1.00	1.00	1.00
C_{11}	14.04	17.32	18.00	1.00	1.23	1.28	1.13	1.09	1.08
C_{12}	15.54	18.63	19.27	1.00	1.20	1.24	1.25	1.17	1.15
C_{13}	16.91	19.86	20.48	1.00	1.17	1.21	1.36	1.25	1.23
C_{14}	18.23	21.10	21.68	1.00	1.16	1.19	1.47	1.32	1.30
C_{15}	19.48	22.26	22.79	1.00	1.14	1.17	1.57	1.40	1.36
C_{16}	20.73	23.31	23.85	1.00	1.12	1.15	1.67	1.46	1.43
C_{17}	21.88	24.40	24.89	1.00	1.12	1.14	1.76	1.53	1.49
C_{18}	22.98	25.45	25.91	1.00	1.11	1.13	1.85	1.60	1.55
C_{19}	24.05	26.44	26.82	1.00	1.10	1.12	1.93	1.66	1.61
C_{20}	25.12	27.41	27.96	1.00	1.09	1.11	2.02	1.72	1.67

* From Fig. 2.
** Relative retention time for methyl esters taken as 1.00.
*** Relative retention time for C_{10} derivatives taken as 1.00.
§ Retention times determined using methyl hexanoate as solvent.


A
METHYL ESTERS
S
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
C17
C18
C19
C20
inj.
min
C°

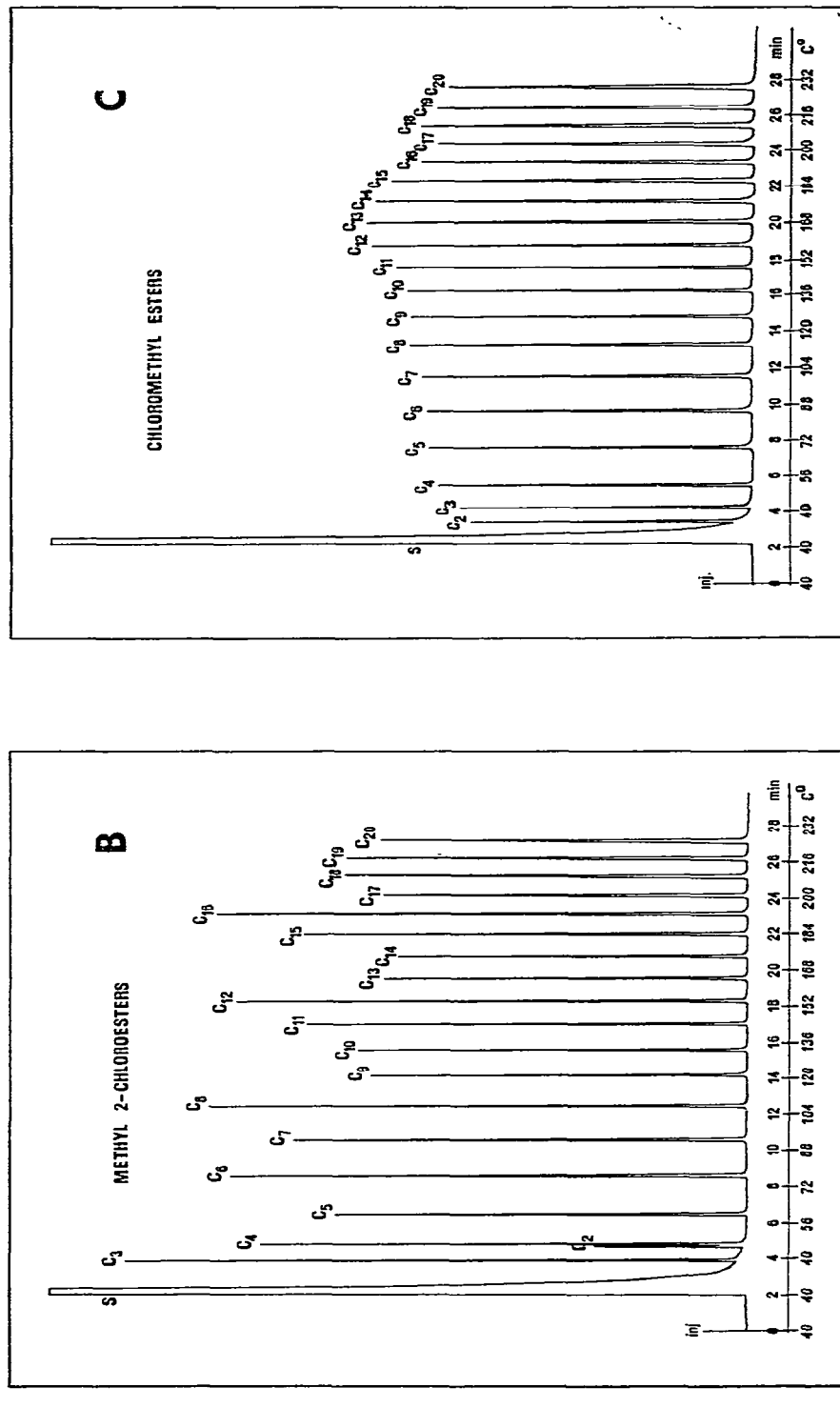


Fig. 1. Chromatograms of methyl (A), methyl 2-chloro (B) and chloromethyl esters (C) of C_2–C_{20} *n*-carboxylic acids.

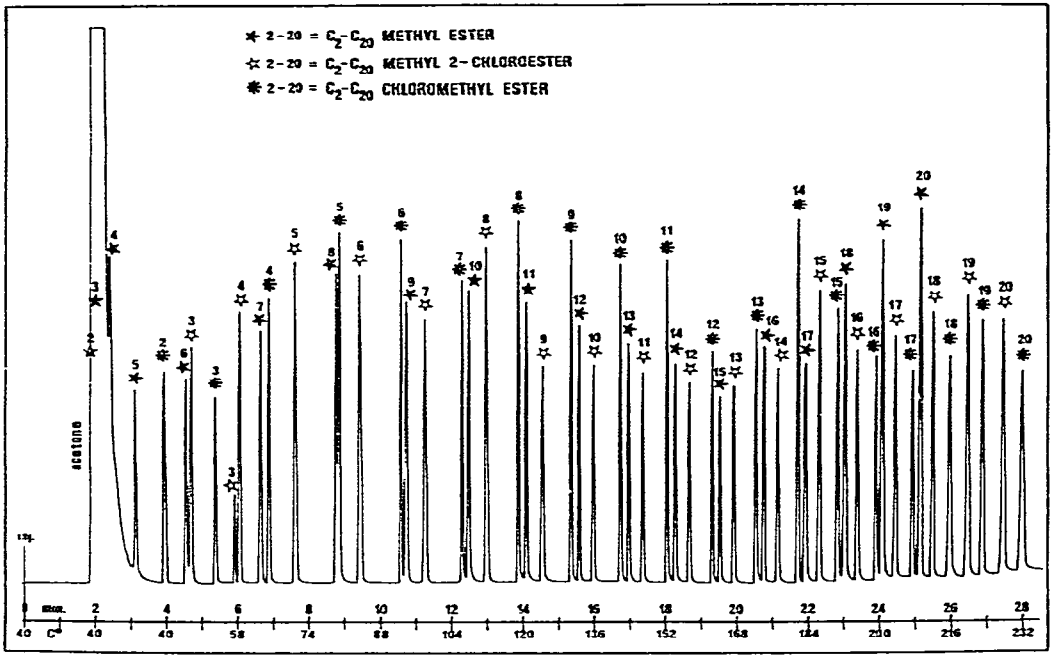


Fig. 2. Chromatogram of a mixture of methyl, methyl 2-chloro and chloromethyl esters of C_2–C_{20} *n*-carboxylic acids.

In general the samples left the column in the order methyl ester, methyl 2-chloro ester and chloromethyl ester, and in order of increasing chain length. With acetic acid derivatives, however, chloromethyl acetate, owing to its lower boiling point, was eluted before methyl chloroacetate. Also, methyl 2-chloropropionate was eluted before the latter compound.

Previous work[4–6] has indicated that all ω-chloro compounds have longer retention times than the other isomers. The terminal ω-chloro substituent seems to make methyl chloroacetate more polar than methyl 2-chloropropionate, which leads to opposite orders of elution on a polar column compared with methyl and chloromethyl esters. The retention times of methyl chloroacetate relative to methyl 2-chloropropionate on a polar Carbowax 20M and a non-polar OV-101 column were 1.26 and 0.78, respectively. The same effect has been reported with fluorinated acids and their methyl esters[2,3].

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