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TEMPERATURE-PROGRAMMED GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC RESOLUTION OF C_2–C_5 ALKYL HALOGENOACETATES AND HALOGENOETHYL ESTERS OF C_2–C_5 CARBOXYLIC ACIDS WITH THE SAME MOLECULAR WEIGHT ON SE-54 AND SP-1000 GLASS CAPILLARY COLUMNS

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SUMMARY

The possibilities for reliable identification based on the electron impact and methane chemical ionization mass spectra of C_2–C_5 alkyl monochloro-, monobromo- and trichloroacetates and isomeric 2-chloro-, 2-bromo- and 2,2,2-trichloroethyl esters of C_2–C_5 carboxylic acids in poorly resolved chromatographic peaks of these chemical isomers were investigated. Temperature-programmed gas chromatography–mass spectrometry on non-polar SE-54 and polar SP-1000 glass capillary columns has been used to study the chromatographic separation and the retention order of pairs of halogenoacetates and halogenoethyl esters.

INTRODUCTION

The gas chromatography (GC) of homologous series of halogenated esters substituted in either the acid or the alcohol moiety on several low-polarity and polar packed and capillary columns has been studied mainly by Haken and Korhonen[1], Korhonen and Lind[2] and Komárek *et al.*[3].

Systematic GC studies of following halogenoacetates have been reported: C_1–C_{16} *n*-alkyl and C_3–C_5 isoalkyl monochloroacetates[3–7,9,10,12], dichloro-[3–7,9,10] and trichloroacetates[3–7,9,10], monobromoacetates[3,4,8–10,12], dibromo- and tribromoacetates[8–10], monoiodoacetates and trifluoroacetates[3,4]. The retention behaviour of 2-chloroethyl[2,3,11,12], 2,2-di-chloroethyl[2], 2,2,2-trichloroethyl[2,3,11], 2-bromoethyl[3,11,12] and 2-iodoethyl[3,11] esters of aliphatic C_2–C_{20} *n*-alkanoic and C_4–C_6 isoalkanoic acids has also been systematically studied.

In the GC determination of free carboxylic acids, the 2-chloroethyl[13] and 2,2,2-trichloroethyl[14] esters have been used. The utility of *n*-alkyl trichloroacetates for retention indexing in environmental analyses with electron-capture detection (ECD) was demonstrated[15].

The retentions of pairs of halogenated esters with the same molecular weight

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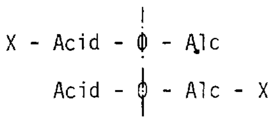
but differing molecular "mirror image", *i.e.*, halogenoacetates (1) having the same carbon number and positions of the halogen atoms (X) in the acid chains (Acid) as in the alcohol chains (Alc) of 2-halogenoethyl esters (2), have been studied by Komárek *et al.*[3] on OV-101 and SP-400 glass capillary columns. The principle of the study can be seen more clearly from the following structural formulae:



1

2

It was shown that "mirror" pairs of halogenated esters have very similar retention indices on both the non-polar OV-101 and SP-400 phases[3,4,11]. Because of the imperfect separation of isomeric halogenated esters, capillary GC with temperature programming, coupled with MS, was used for separation and identification of mixtures of aliphatic C_6–C_{12} *n*-alkyl monochloro- or monobromoacetates and 2-chloro- or 2-bromoethyl esters of C_6–C_{12} *n*-carboxylic acids[12].

Also the retention indices of isomeric aliphatic C_2–C_5 *n*-alkyl and C_4–C_5 isoalkyl esters of monochloro-, monobromo- and trichloroacetic acids[4] and 2-chloro-, 2-bromo- and 2,2,2-trichloroethyl esters of *n*-C_2–C_5 and *iso*-C_4–C_5 monocarboxylic acids[11] differ only by a few retention index units on non-polar OV-101. Moreover, different signs of the retention index differences between isomeric halogenoacetates (1) and 2-halogenoethyl esters (2) were found (Table I). This might mean that the retention order within the "mirror" pairs of halogenated esters changes in the two homologous series on OV-101. In particular, ethyl monochloroacetates would be eluted before 2-chloroethyl acetate, whereas for other monochloro "mirror" pair esters the retention order would be 2-chloroethyl ester < monochloroacetate. As regards brominated esters, the ethyl and propyl monobromoacetates would be eluted before the corresponding isomeric 2-bromoethyl acetate and propionate, respectively,

TABLE I

RETENTION INDICES OF C_2–C_5 *n*-ALKYL AND C_4–C_5 ISOALKYL ESTERS OF MONOCHLORO-, MONOBROMO- AND TRICHLOROACETATES[4] AND 2-CHLORO-, 2-BROMO- AND 2,2,2-TRICHLOROETHYL ESTERS OF *n*-C_2–C_5 AND *iso*-C_4–C_5 MONOCARBOXYLIC ACIDS[11] ON AN OV-101 GLASS CAPILLARY COLUMN AT 80°C

Number of carbon atoms in acyl or alcohol chain of ester	*Retention index differences between isomeric halogenoacetate (1) and halogenoethyl ester (2)*		
	Monochloroesters	*Monobromoesters*	*Trichloroesters*
n-Alkyl chain			
2	−19.0	−8.4	−3.4
3	0.7	−5.8	−5.8
4	11.2	3.6	0.5
5	11.3	4.1	0.8
Isoalkyl chain			
4	10.5	2.9	1.5
5	19.0	10.8	8.1

whereas C_4 and C_5 alkyl chain esters would appear in the sequence 2-bromoethyl ester < monobromoacetate. In the case of trichloro derivatives, the elution sequence of the "mirror" pairs of esters would be the same, as evidenced by the brominated esters.

In this work, significant features useful for identification of both the electron impact (EI) and methane chemical ionization (CI) mass spectra of C_1–C_5 *n*-alkyl and C_3–C_5 isoalkyl monochloroacetates (MClAc), monobromoacetates (MBrAc) and trichloroacetates (TClAc) and 2-chloroethyl (2-ClEE), 2-bromoethyl (2-BrEE) and 2,2,2-trichloroethyl (TClEE) esters of *n*-C_2–C_5 and *iso*-C_4–C_5 aliphatic monocarboxylic acids are discussed. The aim of this work was to verify the change in the elution order within the studied series of isomeric halogenated esters by employing temperature-programmed gas chromatography–mass spectrometry (GC–MS) on non-polar SE-54 and polar SP-1000 glass capillary columns.

EXPERIMENTAL

GC–MS analyses were performed on a Varian MAT 44 S mass spectrometer connected with a Varian Model 3700 gas chromatograph. Glass capillary columns coated with non-polar SE-54 (20 m × 0.30 mm I.D.) supplied by Finnigan (Bremen, F.R.G.) and polar SP-1000 (46 m × 0.23 mm I.D.) supplied by SGE (North Melbourne, Australia) were employed. The injector temperature was 250°C. Helium (0.99996 pure, Messer Griesheim, Düsseldorf, F.R.G.) was used as the carrier gas at a flow-rate of *ca.* 1 ml/min. The splitting ratio was of *ca.* 1:50. The column temperature was programmed from 70 to 220°C at 10, 20, 30°C/min (SE-54) and from 70 to 210°C at 5, 10, 20°C/min (SP-1000) and held at the final value until elution of peaks had ceased.

In the EI mode the electron energy was 70 eV and the ion-source temperature was 160–170°C. Mass numbers from *m/z* 15 to 249 were recorded. In the CI mode, methane (0.99995 pure, Messer Griesheim) was employed as reagent gas under the following conditions: electron ionizing energy, 200 eV; ion-source pressure, *ca.* 40 Pa; source temperature, 160–170°C. The CI mass spectra were recorded over the range *m/z* 60–299. In both EI and CI modes, spectra were acquired at the rate of *ca.* 40 per minute. Mass spectra listed in Tables II–VII were taken at the maxima of the overloaded chromatographic peaks to ensure an approximately constant sample pressure in the ion source during the scanning period.

Model mixtures of halogenated esters were obtained from the individual esters which were first prepared by the usual sulphuric acid-catalysed azeotropic esterification.

RESULTS AND DISCUSSION

The EI mass spectra of C_1–C_5 *n*-alkyl and C_3–C_5 isoalkyl monochloro-, monobromo- and trichloroacetates and of isomeric 2-halogenoethyl esters of *n*-C_2–C_5 and *iso*-C_4–C_5 aliphatic monocarboxylic acids are listed in Tables II–IV, all peaks greater or equal to 5% of the base peak (100%) being tabulated.

Although the most intense fragment peaks in the EI mass spectra of the studied halogenated esters are due to aliphatic ions formed by fragmentation of the alkyl chains, there are some significant peaks which distinguish the position of halogen substitution in the alcohol and the acid chain, respectively. For poorly separated or even unseparated chromatographic peaks of isomeric halogenated esters, most useful for identification purposes are the *m/z* values characteristic either of 2-halogenoethyl

TABLE II

EI MASS SPECTRA OF C_1–C_5 *n*-ALKYL AND C_3–C_5 ISOALKYL MONOCHLOROACETATES (MClAc) AND 2-CHLOROETHYL ESTERS (2-ClEE) OF *n*-C_2–C_5 AND *iso*-C_4–C_5 CARBOXYLIC ACIDS

m/z ≥15; relative intensities ≥5%.

m/z	*MClAc*								*2-ClEE*					
	C_1	C_2	C_3	C_4	C_5	iC_3	iC_4	iC_5	C_2	C_3	C_4	C_5	iC_4	iC_5
15	100	8	9	9	7	16	10	9	25	6	11	10	7	18
26		5	6	7	7					12	10	14	7	12
27		23	43	34	34	25	29	34	16	53	73	91	48	100
28	9	25		16	7		6	15		13	8	28	7	10
29	43	100	17	88	50		52	48		77	8	74		50
30										5				
31	6		6				6			5				
39			9	15	16	10	20	20			13	17	9	31
40				5			6	5						8
41			41	81	49	31	68	58			33	57	28	78
42	18	13	51	21	85	21	33	54	8		22	18	12	34
43			100	14	100	100	49	100	100		100	17	100	64
45						5								7
49	42	12	21	22	19	16	23	23						6
51	14		6	7	6	5	7	7						
55				14	47		10	83				20		9
56				100			100	12		5		16		14
57			6	65			55	14		100		65		71
59	66													20
60											7	20		20
61												6		7
62									14	19	31	57	11	65
63										14	21	37	16	47
64	12									6	10	18		20
65											6	11	5	14
69					7			9						
70					66			85						
71					18			28			99		64	
73									25			7		
77	18	13	34	30	26	31	37	27						
79	6		11	10	9	11	12	9						
85												100		98
86												22		26
87										20		8		12
95			14		9			6						
101											11		6	5
108							7							
115												8		6
121						8								
122											6	13		18
124														5

esters or halogenoacetates. Thus, significant for all the C_1–C_5 alkyl monochloroacetates (Table II) but absent for the isomeric 2-chloroethyl esters are peaks at *m/z* 49/51 and 77/79. 2-Chloroethyl esters of C_2–C_5 carboxylic acids are characterized by peaks at *m/z* 62/64 and 63/65. In the case of brominated esters (Table III), all the monobromoacetates can be characterized by the presence of ions at *m/z* 93/95 and

TABLE III

EI MASS SPECTRA OF C_1–C_5 *n*-ALKYL AND C_4–C_5 ISOALKYL MONOBROMOACETATES (MBrAc) AND 2-BROMOETHYL ESTERS (2-BrEE) OF *n*-C_2–C_5 AND *iso*-C_4–C_5 CARBOXYLIC ACIDS

m/z ≥ 15; relative intensities ≥5%.

m/z	*MBrAc*							*2-BrEE*					
	C_1	C_2	C_3	C_4	C_5	iC_4	iC_5	C_2	C_3	C_4	C_5	iC_4	iC_5
15	100	12	13	6	7	6	7	29	8	13	12	9	19
26		7	9					5	13	12	16	9	13
27		30	53	20	29	17	25	21	55	80	100	56	100
28		30	5	10	6		8		16	12	31	10	13
29	67	100	22	49	43	28	33		76	7	66		45
30	6												
31			8										
39			13	9	15	12	15			12	16	9	28
41		5	56	49	44	39	42			30	51	28	70
42	27	19	100	21	90	26	49	7		22	16	11	30
43		20	97	11	81	30	65	100		100	19	100	60
55				12	45	7	59				20		8
56				100		100	8				15		14
57			6	28		27	11		100		64		69
59	42		5										20
60											12		11
69					11		9						
70					100		100						
71					8		10			88		60	
72	29					5				5			
85											76		71
87								7		5	17		20
93	16	6	9	5	6								
95	15	6	8	5	5								
101									15				5
106								7	12	13	16	7	15
107									8	13	24	10	30
108	5							7	12	13	17	7	15
109									7	12	23	10	29
115										13		13	
121	8	10	21	8	11	11	10						
123	7	10	20	8	10	11	8						
129											11		10
139			21		5								
141			19		5								
152	5												
154	5												
166										5	11		13
168										5	11		13

121/123. On the other hand, for the 2-bromoethyl esters, typical fragment ions are those at *m/z* 106/108 and 107/109.

In the EI mass fragmentation pattern of the trichloroesters (Table IV) there are no sufficiently intense common peaks characteristic either of all the C_2–C_5 alkyl trichloroacetates or of the 2,2,2-trichloroethyl esters of C_2–C_5 carboxylic acids. However, trichloroacetate and trichloroethyl ester isomeric pairs can be reliably distin-

TABLE IV

EI MASS SPECTRA OF C_2–C_5 *n*-ALKYL AND C_3–C_5 ISOALKYL TRICHLOROACETATES (TClAc) AND 2,2,2-TRICHLOROETHYL ESTERS (TClEE) OF *n*-C_2–C_5 AND *iso*-C_4–C_5 CARBOXYLIC ACIDS

m/z ≥ 15; relative intensities ≥ 5%.

m/z	*TClAc*							*TClEE*					
	C_2	C_3	C_4	C_5	iC_3	iC_4	iC_5	C_2	C_3	C_4	C_5	iC_4	iC_5
15					11	9		20		7	6		13
26									10	10	15	7	12
27	17	33	27	20	23	38	23		19	36	45	22	39
28			12			7	6		7		21		
29	100	8	100	34		95	32		63	8	90		49
39		6	12	9	8	24	12			11	20	8	33
40						7							9
41		33	79	30	24	100	36			35	64	29	87
42		11	6	32	9	16	20	5		22	19	11	37
43		100	5	100	100	74	100	100		88	19	100	80
45										6			17
47						7							
55			13	21		15	35				26		9
56			25			45	5				24		16
57			75			98	13		100		58		57
59											6		27
60										35	85		100
61										8	13		15
69				6			8						5
70				15			22						
71				18			23			100		75	
72										6			
73								19		6	17		
82			5			7							
85											100		97
86											7		8
87									12				11
95										6	9		11
96											6		6
97											6		7
110					5								
117					7	7							
119					7	7							
131											6		8
133											6		8
190										6	12		22
192										6	12		21
194													7

TABLE V

METHANE CI MASS SPECTRA OF C_1–C_5 *n*-ALKYL AND C_3–C_5 ISOALKYL MONOCHLOROACETATES (MClAc) AND 2-CHLOROETHYL ESTERS (2-ClEE) OF *n*-C_2–C_5 AND *iso*-C_4–C_5 CARBOXYLIC ACIDS

m/z ⩾60; relative intensities ⩾2%.

m/z	*MClAc*								*2-ClEE*					
	C_1	C_2	C_3	C_4	C_5	iC_3	iC_4	iC_5	C_2	C_3	C_4	C_5	iC_4	iC_5
61									23					
63									30	35	12	10	15	15
65									11	12	4	3	5	5
69					5			3						
70					3			2						
71		5			100			100			100		100	
72					5			6			4		4	
75										31				
77	20	7	2	3			4							
79	6	2												
83														3
85												100		100
86												5		5
87									65					
88									3					
89											8			
95		100	100	100	11	100	100							
97		25	28	28	3	28	27							
101										93				
102										6				
103												6		11
109	100													
110	3													
111	34													
115											54			
116											4			
122														2
123		80	7	10	3	7	14		100					
124		4							5					
125		28	3	3		3	4		33					
129												39		41
130												3		3
135			5	6		4	7							
137			28	2		34	3			100				
138										5				
139			8			8				26				
151				17			17				51		46	
152											4			
153				5			6				17		14	
163												4		
165					4			3		3		54		54
166												4		4
167												18		18
179											3			
193												4		3

guished from each other due to differences in the fragmentation of the acyl and alcohol chains of the esters.

The methane CI mass spectra of the isomeric halogenated esters are compiled in Tables V–VII to make clear the differences between pairs of esters; all peaks greater or equal to 2% of the base peak (100%) are tabulated.

TABLE VI

METHANE CI MASS SPECTRA OF C_1–C_5 *n*-ALKYL AND C_4–C_5 ISOALKYL MONOBROMOACETATES (MBrAc) AND 2-BROMOETHYL ESTERS (2-BrEE) OF *n*-C_2–C_5 AND *iso*-C_4–C_5 CARBOXYLIC ACIDS

m/z ≥ 60, relative intensities ≥ 2%.

m/z	*MBrAc*							*2-BrEE*					
	C_1	C_2	C_3	C_4	C_5	iC_4	iC_5	C_2	C_3	C_4	C_5	iC_4	iC_5
61	3	3	6	6		7							
69					6		3						
70					6		4						
71					100		100			100		100	
72					6		5			4		4	
73	3					3							
75	5	3											
85											100		100
86											5		5
87		3						100					
88								4					
89		4											
101									100				
102									5				
107								27	21	22	24	22	23
109								26	17	19	20	18	20
115										86		79	
116										6		6	
121	20	9	3	3		5							
123	21	9	3	3		5							
129											81		65
130											6		5
139		61	100	98	5	95							
141		64	94	100	6	100							
153	93												
154	6												
155	100												
156	3												
166		3											
167		100	11	14		17		12					
168		7											
169		77	9	11		14		12					
170		3											
179			7	9		11							
181			40	7		10			10				
183				32					10				
195					31	44				12		20	
197					31	40				12		19	
207		3											
209		3									18		17
211											18		15

TABLE VII

METHANE CI MASS SPECTRA OF C_2–C_5 *n*-ALKYL AND C_3–C_5 ISOALKYL TRICHLOROACETATES (TClAc) AND 2,2,2-TRICHLOROETHYL ESTERS (TClEE) OF *n*-C_2–C_5 AND *iso*-C_4–C_5 CARBOXYLIC ACIDS

m/z ≥60; relative intensities ≥2%.

m/z	*TClAc*							*TClEE*					
	C_2	C_3	C_4	C_5	iC_3	iC_4	iC_5	C_2	C_3	C_4	C_5	iC_4	iC_5
60					30								
61					9			100					
62								3					
63	7	4	10		9	3							
65	3		4										
69				59			49						
70				4	4		4						
71				100	3		100			100		100	
72				5			4			4		3	
73			72			100							
74						4							
75									100				
76									3				
77		25			13								
79		7			2								
83	6		13		10	4							5
85	3		8		5	3					100		100
86											5		6
87											4		
89								22		65		69	
90										3		2	
91			26			4							
93			8										
101											10		
103								3	14		69		39
104											4		
109	5												
111	5	3	3		2								
113	3	2											
117		3	3		3					9		9	
119		3	3		3								
127	7												
129	6	3			3								
131								2	2	2	8	2	7
141		7			16								
143		4			9								
145		4			3								
155	100							70					
156	4							4					
157	56							34					
158	3												
159	10							7					
163	24	31	12		43	2							
165	23	30	13		42	3							
167	8	10	4		13								

(*Continued on p. 100*)

TABLE VII (*continued*)

m/z	*TClAc*							*TClEE*					
	C_2	C_3	C_4	C_5	iC_3	iC_4	iC_5	C_2	C_3	C_4	C_5	iC_4	iC_5
169		100			44				58				
170		5							4				
171		69			30				38				
172		3							2				
173		13			5				6				
183			100			11				42		57	
184			5							3		4	
185			68			7				28		37	
186			3										
187			7							4		5	
191	54	7	13		14	4		25					
192	3												
193	44	7	11		10	3		22					
195	14				3			7					
197											60		50
198											4		3
199											32		26
201											3		4
203		3	12		12	3							
205		62	8		100	3			21				
206		2			6								
207		52			99				20				
208					4								
209		15			28				7				
217						3							
219			49			11				21		22	
220			3									2	
221			51			7				19		23	
223			13							5		6	
233											28		19
234											2		2
235											23		17
237											7		5
261											3		2
263											3		2

The methane CI mass spectra also show characteristic ions useful in distinguishing between halogenoacetates and halogenoethyl esters. In particular, monochloroacetates show characteristic peaks at *m/z* 95/97, 2-chloroethyl esters at *m/z* 63/65 (Table V). Similarly, peaks distinguishing monobromoacetates and 2-bromoethyl esters (Table VI) are at *m/z* 139/141 and at *m/z* 107/109 respectively. The CI mass spectra of trichloroacetates (Table VII) show characteristic peaks at *m/z* 163/165/167 with relative intensities indicating the presence of three chlorine atoms. On the contrary, the common significant peaks at *m/z* 131/133/135 of 2,2,2-trichloroethyl esters of C_2–C_5 monocarboxylic acids are very weak, but the methane CI as well as EI spectra can be used to distinguish between these chemical isomers.

It may be concluded that both the EI and methane CI modes of ionization are useful to distinguish between the isomeric halogenated esters. In particular, the softer methane CI yields simpler, more easily understood spectra with significant information about the isomeric differences between pairs of esters. Thus this mode was preferred over the more conventional EI, especially for simultaneous identification of the isomeric pairs of esters in unseparable chromatographic peaks.

The separation and the retention sequence of isomeric halogenated esters could be determined using GC–MS because it permits resolution of normally unresolved GC peaks. Tables VIII–IX give the relative retention times for the studied esters at various temperatures on non-polar SE-54 and polar SP-1000 glass capillary columns. The retention times, expressed by the scan numbers, were measured from the sample injection.

The retention data on SE-54 (Table VIII) show that halogenoacetates and halogenoethyl esters are eluted in the general order, halogenoethyl ester < halogenoacetate. However, ethyl and propyl monobromoacetates and trichloroacetates are exceptions to this order, *i.e.*, they were eluted before the isomeric 2-bromoethyl and 2,2,2-trichloroethyl ester, respectively. Simultaneously, there are five complete overlappings on SE-54, *i.e.*, 2-chloroethyl acetate and ethyl monochloroacetate, 2-chloroethyl propionate and propyl monochloroacetate, 2-bromoethyl butanoate and butyl monobromoacetate, 2-bromoethyl pentanoate and pentyl monobromoacetate, 2,2,2-trichloroethyl pentanoate and pentyl trichloroacetate. Moreover, it became apparent that with increasing temperature gradient the differences in retention of the "mirror" pairs of halogenated esters were reduced. Hence, the retention behaviour of the studied esters on SE-54 under temperature programming conditions may be considered to be very similar to that found on OV-101 under isothermal conditions[4,11].

The data recorded on the polar SP-1000 phase (Table IX) show that the same general retention order of isomeric monochlorinated and monobrominated esters is valid as on the non-polar SE-54 phase. Consequently, the halogenoethyl esters were eluted before the corresponding halogenoacetates, but with the following exceptions: 2-chloroethyl acetate after ethyl monochloroacetate, 2-bromoethyl acetate after ethyl monobromoacetate and 2-bromoethyl propionate after propyl monobromoacetate, 2-chloroethyl propionate and propyl monochloroacetate overlapped.

However, the polar SP-1000 phase seems to be unsuitable for monochloro- and monobromoacetates, giving broad chromatographic peaks of unusual shape (Figs. 1 and 2). Especially, with butyl and pentyl esters of both monochloroacetic and monobromoacetic acids, the height of the chromatographic peaks is considerably reduced.

For the trichloro isomers on SP-1000 (Table IX) the retention order trichloroacetate < 2,2,2-trichloroethyl ester was found together with perfect separation.

CONCLUSIONS

According to our GC–MS results, the change in the retention order within isomeric ester pairs is confirmed. Hence the retention order observed for one pair of isomeric esters may not be generally valid for the whole homologous series.

For the MS identification of the studied halogenoacetates and halogenoethyl

TABLE VIII

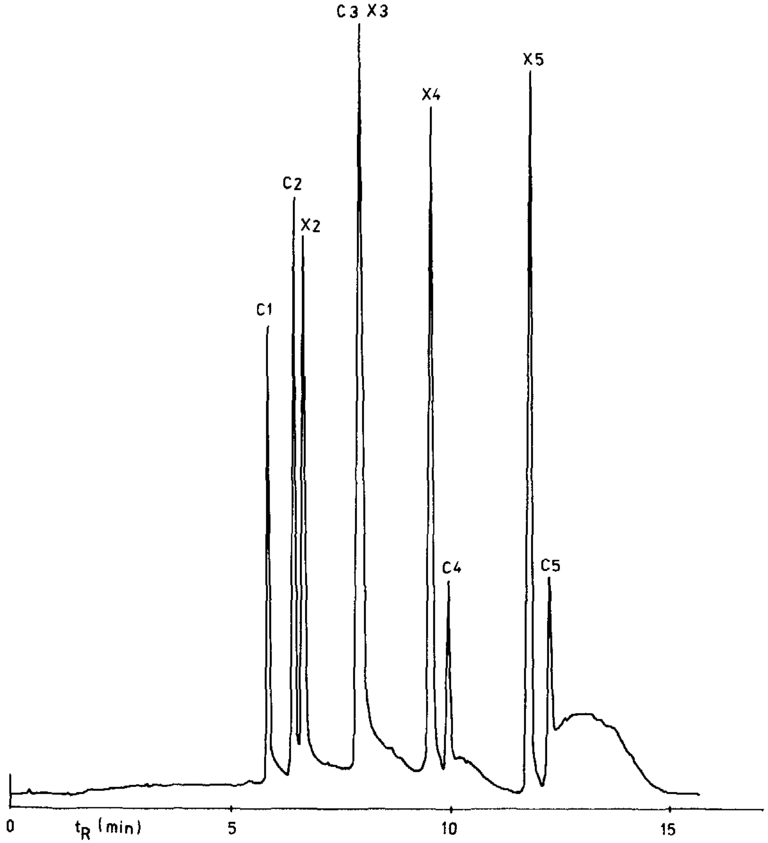
RETENTION TIMES, t_R, EXPRESSED BY THE SCAN NUMBER, SN, AND RELATIVE RETENTION TIMES, RRT, OF ISOMERIC PAIRS OF ESTERS OBTAINED ON NON-POLAR SE-54 WITH TEMPERATURE PROGRAMMING FROM 70 TO 220°C AT 10, 20, 30°C/MIN

Compound	*10°C/min*		*20°C/min*		*30°C/min*	
	SN	*RRT*	*SN*	*RRT*	*SN*	*RRT*
MClAcC$_1$	111	0.425	106	0.544	105	0.625
2-ClEEC$_2$	126	0.483	118	0.605	113	0.672
MClAcC$_2$	126	0.483	118	0.605	113	0.673
2-ClEEC$_3$	158	0.605	137	0.703	126	0.750
MClAcC$_3$	158	0.605	137	0.703	126	0.750
2-ClEEC$_4$	198	0.759	161	0.826	144	0.857
MClAcC$_4$	204	0.782	163	0.836	146	0.869
2-ClEEC$_5$	255	0.977	192	0.985	166	0.988
MClAcC$_5$	261	1.000	195	1.000	168	1.000
MClAciC$_3$	140	0.591	127	0.683	120	0.741
2-ClEEiC$_4$	178	0.751	153	0.823	138	0.852
MClAciC$_4$	182	0.768	154	0.828	140	0.864
2-ClEEiC$_5$	226	0.954	181	0.973	158	0.975
MClAciC$_5$	237	1.000	186	1.000	162	1.000
2-BrEEiC$_4$	218	0.776	174	0.833	155	0.861
MBrAciC$_4$	222	0.790	177	0.847	158	0.878
2-BrEEiC$_5$	274	0.975	204	0.976	177	0.983
MBrAciC$_5$	281	1.000	209	1.000	180	1.000
MBrAcC$_1$	126	0.419	119	0.541	113	0.604
2-BrEEC$_2$	149	0.495	135	0.614	126	0.674
MBrAcC$_2$	148	0.492	133	0.605	123	0.658
2-BrEEC$_3$	192	0.638	159	0.723	144	0.770
MBrAcC$_3$	188	0.625	157	0.714	141	0.754
2-BrEEC$_4$	241	0.801	188	0.855	164	0.877
MBrAcC$_4$	241	0.801	188	0.855	164	0.877
2-BrEEC$_5$	301	1.000	220	1.000	187	1.000
MBrAcC$_5$	301	1.000	220	1.000	187	1.000
TClEEC$_2$	184	0.538	158	0.645	142	0.693
TClAcC$_2$	181	0.529	155	0.633	141	0.688
TClEEC$_3$	231	0.675	185	0.755	162	0.790
TClAcC$_3$	229	0.670	182	0.743	160	0.780
TClEEC$_4$	281	0.822	212	0.865	182	0.888
TClAcC$_4$	283	0.827	213	0.863	182	0.888
TClEEC$_5$	342	1.000	245	1.000	205	1.000
TClAcC$_5$	342	1.000	245	1.000	205	1.000
TClAciC$_3$	200	0.621	165	0.702	148	0.755
TClEEiC$_4$	260	0.807	199	0.847	172	0.878
TClAciC$_4$	263	0.817	201	0.855	174	0.888
TClEEiC$_5$	318	0.988	233	0.991	193	0.985
TClAciC$_5$	322	1.000	235	1.000	196	1.000

TABLE IX

RETENTION TIMES, t_R, EXPRESSED BY THE SCAN NUMBER, SN, AND RELATIVE RETENTION TIMES, RRT, OF ISOMERIC PAIRS OF ESTERS OBTAINED ON POLAR SP-1000 WITH TEMPERATURE PROGRAMMING FROM 70 TO 210°C AT 5, 10, 20°C/MIN

Compound	*5°C/min*		*10°C/min*		*20°C/min*	
	SN	*RRT*	*SN*	*RRT*	*SN*	*RRT*
$MClAcC_1$	260	0.495	222	0.592	188	0.691
$2\text{-}ClEEC_2$	293	0.558	242	0.645	199	0.732
$MClAcC_2$	285	0.542	237	0.632	196	0.721
$2\text{-}ClEEC_3$	346	0.659	275	0.733	216	0.794
$MClAcC_3$	346	0.659	275	0.733	219	0.805
$2\text{-}ClEEC_4$	414	0.788	313	0.835	238	0.875
$MClAcC_4$	430	0.819	323	0.861	243	0.893
$2\text{-}ClEEC_5$	507	0.966	363	0.968	267	0.981
$MClAcC_5$	525	1.000	375	1.000	272	1.000
$MClAciC_3$	279	0.582	233	0.666	197	0.755
$2\text{-}ClEEiC_4$	350	0.731	276	0.788	221	0.847
$MClAciC_4$	373	0.779	290	0.828	228	0.873
$2\text{-}ClEEiC_5$	447	0.933	332	0.948	251	0.962
$MClaciC_5$	479	1.000	350	1.000	261	1.000
$2\text{-}BrEEiC_4$	446	0.778	333	0.826	253	0.878
$MBrAciC_4$	462	0.806	342	0.848	257	0.892
$2\text{-}BrEEiC_5$	551	0.962	391	0.970	284	0.986
$MBrAciC_5$	573	1.000	403	1.000	288	1.000
$MBrAcC_1$	332	0.530	267	0.633	217	0.723
$2\text{-}BrEEC_2$	381	0.609	295	0.699	232	0.773
$MBrAcC_2$	360	0.575	282	0.668	225	0.750
$2\text{-}BrEEC_3$	443	0.707	328	0.777	251	0.836
$MBrAcC_3$	434	0.693	323	0.765	247	0.823
$2\text{-}BrEEC_4$	521	0.832	370	0.877	273	0.910
$MBrAcC_4$	527	0.842	372	0.882	273	0.910
$2\text{-}BrEEC_5$	621	0.992	422	1.000	300	1.000
$MBrAcC_5$	626	1.000	422	1.000	300	1.000
$TClAcC_2$	326	0.555	261	0.638	214	0.723
$TClEEC_2$	374	0.637	289	0.706	230	0.777
$TClAcC_3$	386	0.657	297	0.762	234	0.791
$TClEEC_3$	426	0.726	319	0.779	247	0.834
$TClAcC_4$	466	0.794	342	0.836	260	0.878
$TClEEC_4$	497	0.846	360	0.880	269	0.909
$TClAcC_5$	557	0.948	393	0.961	287	0.969
$TClEEC_5$	587	1.000	409	1.000	296	1.000
$TClAciC_3$	304	0.578	247	0.664	205	0.740
$TClAciC_4$	401	0.762	304	0.817	238	0.859
$TClEEiC_4$	423	0.804	315	0.846	245	0.884
$TClAciC_5$	504	0.958	361	0.970	271	0.978
$TClEEiC_5$	526	1.000	372	1.000	277	1.000



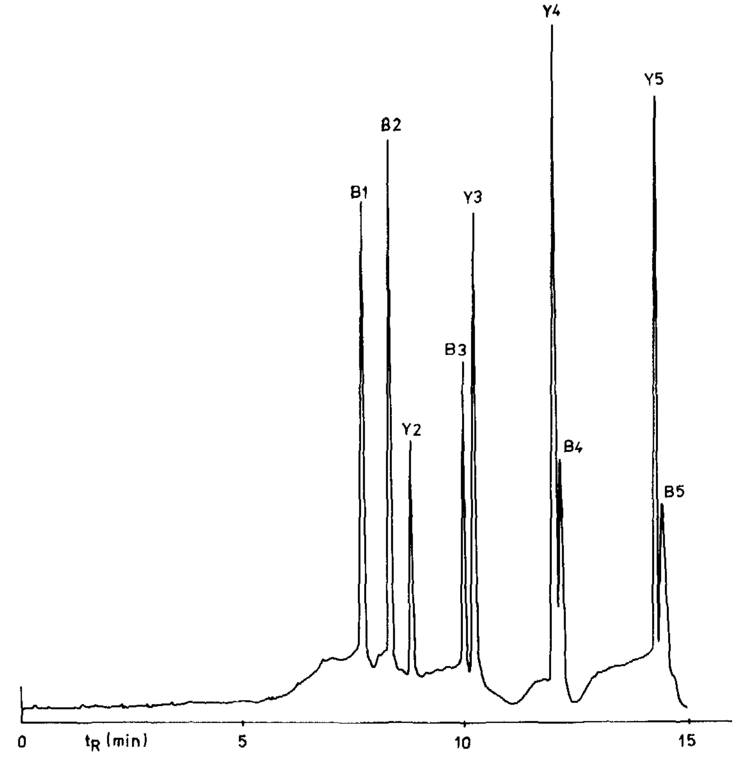


Fig. 1. GC–MS separation of a mixture (1:1) of C_1–C_5 *n*-alkyl esters of monochloroacetic acid (C1–C5) from corresponding isomeric 2-chloroethyl esters of C_2–C_5 *n*-carboxylic acids (X2–X5) on a SP-1000 glass capillary column with temperature programming from 70°C at 5°C/min.

Fig. 2. GC–MS separation of a mixture (1:1) of C_1–C_5 *n*-alkyl esters of monobromoacetic acid (B1–B5) from corresponding isomeric 2-bromoethyl esters of C_2–C_5 *n*-carboxylic acids (Y2–Y5) on a SP-1000 glass capillary column with temperature programming from 70°C at 5°C/min.

esters, methane CI is recommended because both molecular weight and structural information can be obtained.

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