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## GLASS CAPILLARY GAS CHROMATOGRAPHY-MASS SPECTROMETRY OF MIXTURES OF ISOMERIC HALOGENATED ESTERS OF CARBOXYLIC ACIDS

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### SUMMARY

The possibilities of glass capillary column gas chromatography-mass spectrometry for separation and identification of isomeric halogenated esters (halogen substituent either in the alcohol or acid chain) were investigated. Three stationary phases, OV-101, SE-54 and SP-1000, were tested. The influence of the stationary phase and the structure of the isomers on retention is discussed.

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### INTRODUCTION

Recently, the gas chromatography (GC) of homologous series of aliphatic alkyl halogenoacetates<sup>1-3</sup> and 2-halogenoethyl esters of aliphatic carboxylic acids<sup>4</sup> has been reported. It has been shown that monohalogenoacetates<sup>1</sup> and 2-halogenoethyl esters<sup>4</sup> of the same molecular weight have very similar retention characteristics on OV-101; the differences in retention indices between C<sub>6</sub>-C<sub>10</sub> *n*-alkyl monochloroacetates and 2-chloroethyl esters of C<sub>6</sub>-C<sub>10</sub> carboxylic acids vary from 5.1 to 8.2 units of retention index and in the case of C<sub>6</sub>-C<sub>10</sub> *n*-alkyl monobromoacetates and 2-bromoethyl esters of C<sub>6</sub>-C<sub>10</sub> carboxylic acids from 1.9 to 2.5 units of retention index.

As a continuation of these studies<sup>1,4</sup> the present paper deals with the GC separation of mixtures of esters of the same empirical formula on non-polar OV-101, SE-54 and polar SP-1000 glass capillary columns. The retention data at three programmed column temperatures are given for the following compounds: C<sub>6</sub>-C<sub>12</sub> *n*-alkyl acetates (Ac); ethyl esters of C<sub>6</sub>-C<sub>12</sub> *n*-carboxylic acids (EE); C<sub>6</sub>-C<sub>12</sub> *n*-alkyl monochloroacetates (MClAc); 2-chloroethyl esters of C<sub>6</sub>-C<sub>12</sub> *n*-carboxylic acids (ClEE); C<sub>6</sub>-C<sub>10</sub> *n*-alkyl monobromoacetates (MBrAc) and 2-bromoethyl esters of C<sub>6</sub>-C<sub>10</sub> carboxylic acids (BrEE). The aim of this work was to obtain GC-mass spectrometric (MS) data for halogenated esters and to determine the utility of capillary column GC combined with computer-controlled low-resolution MS in the analysis of poorly separated or unseparated peaks of isomeric halogenated esters.

## EXPERIMENTAL

*Samples*

The analysed mixtures of isomeric esters were prepared from individual compounds the preparation of which was described earlier<sup>5</sup>.

*Gas chromatography*

GC analyses were carried out on a Varian Model 3700 instrument equipped with a flame ionization detector, under the following operating conditions: injector and detector temperatures, 200°C for unhalogenated esters, 250°C for halogenated ones; carrier gas (nitrogen) linear flow-rate, 25 cm/sec; splitting ratio, 1:120; chart speed, 10 mm/min. All samples were measured by the Autolab System IV.

The glass capillary columns used were a laboratory-made OV-101 (27 m ×

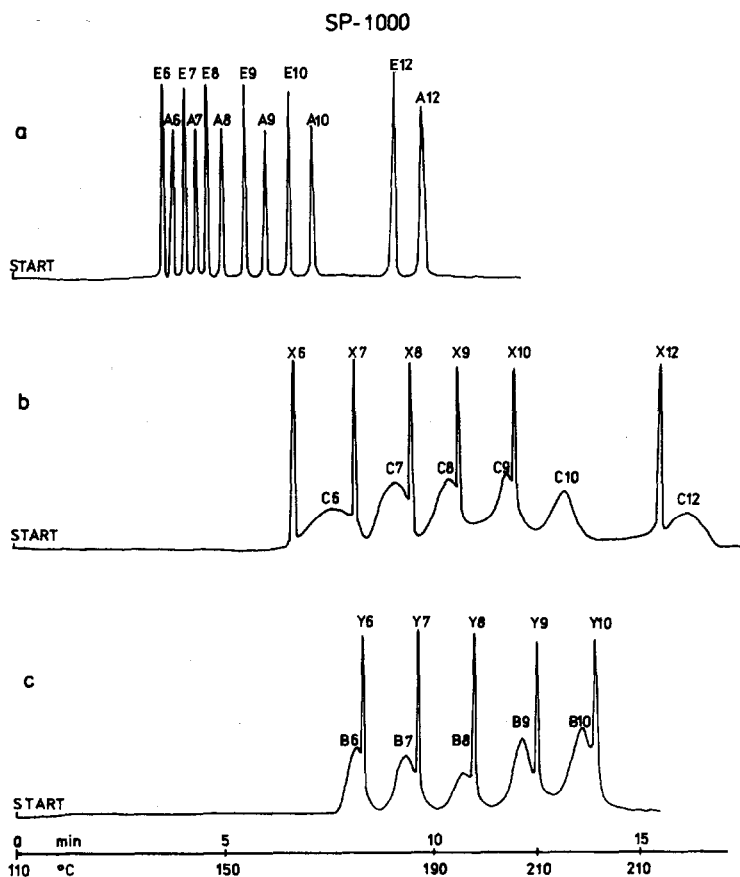


Fig. 1. Chromatograms of mixtures of isomeric esters on an SP-1000 glass capillary column. Temperature programme: 110°C rising at 8°C/min to 210°C. a, Aliphatic  $C_6$ - $C_{12}$  *n*-alkyl acetates (A6-A12) and ethyl esters of  $C_6$ - $C_{12}$  *n*-carboxylic acids (E6-E12); b, aliphatic  $C_6$ - $C_{12}$  *n*-alkyl monochloroacetates (C6-C12) and 2-chloroethyl esters of  $C_6$ - $C_{12}$  *n*-carboxylic acids (X6-X12); c, aliphatic  $C_6$ - $C_{10}$  *n*-alkyl monobromoacetates (B6-B10) and 2-bromoethyl esters of  $C_6$ - $C_{10}$  *n*-carboxylic acids (Y6-Y10).

TABLE I

RETENTION TIMES,  $t_R$ , AND RELATIVE RETENTION TIMES, RRT, FOR ALIPHATIC ACETATES, ETHYL ESTERS, MONOCHLOROACETATES, 2-CHLOROETHYL ESTERS, MONOBROMOACETATES AND 2-BROMOETHYL ESTERS ON OV-101

Peak	Compound	Temperature rising from					
		150°C at 5°C/min		110°C at 8°C/min		60°C at 7°C/min	
		$t_R$ (sec)	RRT	$t_R$ (sec)	RRT	$t_R$ (sec)	RRT
E6	EEC <sub>6</sub>	167	1.00	231	1.00	484	1.00
A6	AcC <sub>6</sub>	170	1.02	239	1.03	503	1.04
E7	EEC <sub>7</sub>	198	1.19	297	1.29	619	1.28
A7	AcC <sub>7</sub>	204	1.22	308	1.33	640	1.32
E8	EEC <sub>8</sub>	243	1.46	378	1.64	754	1.56
A8	AcC <sub>8</sub>	251	1.50	391	1.69	773	1.60
E9	EEC <sub>9</sub>	305	1.83	469	2.03	885	1.83
A9	AcC <sub>9</sub>	315	1.89	483	2.09	903	1.87
E10	EEC <sub>10</sub>	384	2.30	564	2.44	1010	2.09
A10	AcC <sub>10</sub>	397	2.38	578	2.50	1027	2.12
E12	EEC <sub>12</sub>	589	3.53	756	3.27	1241	2.56
A12	AcC <sub>12</sub>	604	3.62	768	3.32	1256	2.60
X6	ClEEC <sub>6</sub>	252	1.00	389	1.00	772	1.00
C6	MClAcC <sub>6</sub>	258	1.02	397	1.02	785	1.02
X7	ClEEC <sub>7</sub>	318	1.26	482	1.24	904	1.17
C7	MClAcC <sub>7</sub>	325	1.29	492	1.26	918	1.19
X8	ClEEC <sub>8</sub>	401	1.59	579	1.49	1030	1.33
C8	MClAcC <sub>8</sub>	409	1.62	589	1.51	1042	1.35
X9	ClEEC <sub>9</sub>	500	1.98	677	1.74	1149	1.49
C9	MClAcC <sub>9</sub>	510	2.02	686	1.76	1161	1.50
X10	ClEEC <sub>10</sub>	612	2.43	773	1.99	1263	1.64
C10	MClAcC <sub>10</sub>	622	2.47	782	2.01	1274	1.65
X12	ClEEC <sub>12</sub>	855	3.39	957	2.46	1477	1.91
C12	MClAcC <sub>12</sub>	866	3.44	963	2.48	1484	1.92
Y6	BrEEC <sub>6</sub>	310	1.00	469	1.00	880	1.00
B6	MBrAcC <sub>6</sub>	310	1.00	469	1.00	880	1.00
Y7	BrEEC <sub>7</sub>	390	1.26	566	1.21	1008	1.15
B7	MBrAcC <sub>7</sub>	390	1.26	566	1.21	1008	1.15
Y8	BrEEC <sub>8</sub>	487	1.57	664	1.42	1130	1.28
B8	MBrAcC <sub>8</sub>	487	1.57	664	1.42	1130	1.28
Y9	BrEEC <sub>9</sub>	598	1.93	762	1.62	1246	1.42
B9	MBrAcC <sub>9</sub>	598	1.93	762	1.62	1246	1.42
Y10	BrEEC <sub>10</sub>	718	2.32	857	1.83	1358	1.54
B10	MBrAcC <sub>10</sub>	718	2.32	857	1.83	1358	1.54

0.28 mm I.D., drawn from soft soda-lime glass and etched with HCl gas;  $N = 91,000$  theoretical plates for  $k = 3.83$ ), SE-54 (17 m  $\times$  0.24 mm I.D.,  $N = 78,000$  theoretical plates for  $k = 5.9$ ) supplied by Supelco (Bellefonte, PA, U.S.A.) and SP-1000 (46 m  $\times$  0.23 mm I.D.,  $N = 177,000$  theoretical plates for  $k = 4.4$ ) supplied by SGE (Australia). The column temperatures used are given in Tables I-III.

#### Gas chromatography-mass spectrometry

GC-MS data were recorded on a Varian MAT-44 S mass spectrometer con-

TABLE II

RETENTION TIMES AND RELATIVE RETENTION TIMES FOR ALIPHATIC ACETATES, ETHYL ESTERS, MONOCHLOROACETATES, 2-CHLOROETHYL ESTERS, MONOBROMOACETATES AND 2-BROMOETHYL ESTERS ON SE-54

Peak	Compound	Temperature rising from					
		150°C at 5°C/min		110°C at 8°C/min		60°C at 7°C/min	
		$t_R$ (sec)	RRT	$t_R$ (sec)	RRT	$t_R$ (sec)	RRT
E6	EEC <sub>6</sub>	83	1.00	111	1.00	276	1.00
A6	AcC <sub>6</sub>	83	1.00	115	1.04	290	1.05
E7	EEC <sub>7</sub>	95	1.14	146	1.32	385	1.39
A7	AcC <sub>7</sub>	97	1.17	152	1.37	401	1.45
E8	EEC <sub>8</sub>	114	1.37	196	1.77	503	1.82
A8	AcC <sub>8</sub>	117	1.41	204	1.84	520	1.88
E9	EEC <sub>9</sub>	142	1.71	261	2.35	623	2.26
A9	AcC <sub>9</sub>	147	1.77	271	2.44	641	2.32
E10	EEC <sub>10</sub>	182	2.19	336	3.03	740	2.68
A10	AcC <sub>10</sub>	189	2.28	348	3.14	757	2.74
E12	EEC <sub>12</sub>	310	3.73	505	4.55	962	3.49
A12	AcC <sub>12</sub>	320	3.86	518	4.67	975	3.53
X6	ClEEC <sub>6</sub>	121	1.00	212	1.00	533	1.00
C6	MClAcC <sub>6</sub>	122	1.01	217	1.02	544	1.02
X7	ClEEC <sub>7</sub>	152	1.26	280	1.32	654	1.23
C7	MClAcC <sub>7</sub>	155	1.28	286	1.35	666	1.25
X8	ClEEC <sub>8</sub>	196	1.62	359	1.69	770	1.44
C8	MClAcC <sub>8</sub>	200	1.65	365	1.72	780	1.46
X9	ClEEC <sub>9</sub>	256	2.12	443	2.09	882	1.65
C9	MClAcC <sub>9</sub>	262	2.17	450	2.12	892	1.67
X10	ClEEC <sub>10</sub>	332	2.74	530	2.50	990	1.86
C10	MClAcC <sub>10</sub>	338	2.79	537	2.53	1000	1.88
X12	ClEEC <sub>12</sub>	523	4.32	701	3.31	1194	2.24
C12	MClAcC <sub>12</sub>	531	4.39	707	3.33	1199	2.25
Y6	BrEEC <sub>6</sub>	148	1.00	272	1.00	640	1.00
B6	MBrAcC <sub>6</sub>	148	1.00	272	1.00	640	1.00
Y7	BrEEC <sub>7</sub>	192	1.30	351	1.29	759	1.19
B7	MBrAcC <sub>7</sub>	192	1.30	351	1.29	759	1.19
Y8	BrEEC <sub>8</sub>	251	1.70	436	1.60	874	1.37
B8	MBrAcC <sub>8</sub>	251	1.70	436	1.60	874	1.37
Y9	BrEEC <sub>9</sub>	326	2.20	525	1.93	986	1.54
B9	MBrAcC <sub>9</sub>	326	2.20	525	1.93	986	1.54
Y10	BrEEC <sub>10</sub>	417	2.82	614	2.26	1095	1.71
B10	MBrAcC <sub>10</sub>	417	2.82	614	2.26	1095	1.71

nected to a Varian Model 3700 gas chromatograph, equipped with a glass capillary (20 m × 0.9 mm I.D.) containing SE-54. The helium flow-rate was 0.6 ml/min and the splitting ratio 1:50. The column temperature was programmed from 150°C (chlorinated compounds) and/or 170°C (brominated ones) at 5°C/min until the elution of peaks ceased. The electron ionizing energy was 70 eV and the ion source temperature was 160–170°C. Mass numbers from  $m/z$  15 to 290 were recorded. The fragment ions of electron impact (EI) mass spectra of chlorinated and brominated esters are listed in Tables IV and V. In the chemical ionization (CI) mode, isobutane was employed

TABLE III

RETENTION TIMES AND RELATIVE RETENTION TIMES FOR ALIPHATIC ACETATES, ETHYL ESTERS, MONOCHLOROACETATES, 2-CHLOROETHYL ESTERS, MONOBROMOACETATES AND 2-BROMOETHYL ESTERS ON SP-1000

Peak	Compound	Temperature rising from					
		150°C at 5°C/min		110°C at 8°C/min		60°C at 7°C/min	
		$t_R$ (sec)	RRT	$t_R$ (sec)	RRT	$t_R$ (sec)	RRT
E6	EEC <sub>6</sub>	189	1.00	210	1.00	357	1.00
A6	AcC <sub>6</sub>	193	1.02	220	1.05	390	1.09
E7	EEC <sub>7</sub>	200	1.06	239	1.14	451	1.26
A7	AcC <sub>7</sub>	206	1.09	253	1.20	491	1.38
E8	EEC <sub>8</sub>	217	1.15	280	1.33	559	1.57
A8	AcC <sub>8</sub>	226	1.20	300	1.43	601	1.68
E9	EEC <sub>9</sub>	241	1.28	333	1.59	667	1.87
A9	AcC <sub>9</sub>	254	1.34	362	1.72	719	2.01
E10	EEC <sub>10</sub>	275	1.46	400	1.90	781	2.19
A10	AcC <sub>10</sub>	292	1.54	431	2.05	829	2.32
E12	EEC <sub>12</sub>	382	2.02	561	2.67	1005	2.82
A12	AcC <sub>12</sub>	405	2.14	587	2.80	1037	2.90
X6	ClEEC <sub>6</sub>	285	1.00	418	1.00	803	1.00
C6	MClAcC <sub>6</sub>	315	1.11	466	1.11	887	1.10
X7	ClEEC <sub>7</sub>	332	1.16	492	1.18	910	1.13
C7	MClAcC <sub>7</sub>	374	1.31	558	1.33	994	1.24
X8	ClEEC <sub>8</sub>	393	1.38	571	1.37	1016	1.27
C8	MClAcC <sub>8</sub>	447	1.57	631	1.51	1094	1.36
X9	ClEEC <sub>9</sub>	467	1.64	654	1.56	1114	1.39
C9	MClAcC <sub>9</sub>	533	1.87	720	1.72	1192	1.48
X10	ClEEC <sub>10</sub>	553	1.94	733	1.75	1212	1.51
C10	MClAcC <sub>10</sub>	625	2.19	805	1.93	1284	1.60
X12	ClEEC <sub>12</sub>	751	2.64	910	2.18	1410	1.76
C12	MClAcC <sub>12</sub>	837	2.94	990	2.37	1492	1.86
B6	MBrAcC <sub>6</sub>	329	1.00	488	1.00	910	1.00
Y6	BrEEC <sub>6</sub>	344	1.05	503	1.03	922	1.01
B7	MBrAcC <sub>7</sub>	379	1.15	554	1.14	991	1.09
Y7	BrEEC <sub>7</sub>	406	1.23	582	1.19	1026	1.13
B8	MBrAcC <sub>8</sub>	456	1.39	641	1.31	1114	1.22
Y8	BrEEC <sub>8</sub>	482	1.47	663	1.36	1127	1.24
B9	MBrAcC <sub>9</sub>	549	1.67	729	1.49	1202	1.32
Y9	BrEEC <sub>9</sub>	570	1.73	747	1.53	1228	1.35
B10	MBrAcC <sub>10</sub>	635	1.93	807	1.65	1294	1.42
Y10	BrEEC <sub>10</sub>	668	2.03	828	1.70	1324	1.45

as the reagent gas and helium as the carrier gas, under the following conditions: electron ionizing energy, 190 eV; ion source pressure, *ca.* 40 Pa; source temperature, 160–170°C. The CI mass spectra were recorded over the range  $m/z$  60 to 299. The most characteristic ions of halogenated esters are given in Table VI. In both EI and CI modes, spectra were acquired at the rate of *ca.* 40 per minute.

## RESULTS AND DISCUSSION

Gas chromatograms of mixtures of acetates and ethyl esters (a), monochlo-

TABLE IV  
EI MASS SPECTRA OF ISOMERIC CHLORINATED ESTERS

Relative intensities  $\geq 5\%$ .

<i>m/z</i>	<i>MClAcC<sub>6</sub></i> ( <i>mol.wt.</i> 178)	<i>MClAcC<sub>7</sub></i> (192)	<i>MClAcC<sub>8</sub></i> (206)	<i>MClAcC<sub>9</sub></i> (220)	<i>MClAcC<sub>10</sub></i> (234)	<i>MClAcC<sub>12</sub></i> (262)	<i>ClEEC<sub>6</sub></i> (178)	<i>ClEEC<sub>7</sub></i> (192)	<i>ClEEC<sub>8</sub></i> (206)	<i>ClEEC<sub>9</sub></i> (220)	<i>ClEEC<sub>10</sub></i> (234)	<i>ClEEC<sub>12</sub></i> (262)
27	—	32	26	23	22	—	65	71	100	83	71	49
28	—	—	—	11	11	—	8	—	—	26	16	11
29	18	59	58	50	48	47	34	39	70	67	60	55
39	5	15	14	12	11	6	13	14	20	18	15	11
41	33	85	94	80	79	82	38	48	82	89	83	79
42	36	59	69	49	45	32	33	23	38	35	30	25
43	72	64	100	100	100	100	100	100	82	100	100	100
44	—	—	—	6	6	—	5	8	5	5	—	—
49	12	16	17	13	11	8	—	—	—	—	—	—
51	—	5	5	—	—	—	—	—	—	—	—	—
54	—	8	8	8	9	11	—	—	—	—	6	—
55	35	58	76	72	74	96	21	31	54	62	57	58
56	100	100	99	87	73	79	6	11	14	16	14	12
57	9	55	41	31	37	59	—	11	61	47	29	39
60	—	—	—	—	—	—	16	14	15	11	9	8
61	—	—	—	—	—	—	6	7	8	8	6	7
62	—	—	—	—	—	—	56	59	84	96	85	70
63	—	—	—	—	—	—	29	31	44	53	44	20
64	—	—	—	—	—	—	15	16	23	26	24	40
65	—	—	—	—	—	—	10	10	16	16	15	13
67	—	—	5	5	7	10	—	—	5	5	6	5
68	—	12	17	17	21	22	—	—	—	—	5	5
69	23	30	42	40	48	60	11	7	9	—	25	16
70	—	63	61	51	47	47	7	—	—	16	—	5



TABLE V  
EI MASS SPECTRA OF ISOMERIC BROMINATED ESTERS

Relative intensities  $\geq 5\%$ .

<i>m/z</i>	<i>MBrAcC</i> <sub>6</sub> ( <i>mol.wt.</i> 222)	<i>MBrAcC</i> <sub>7</sub> (236)	<i>MBrAcC</i> <sub>8</sub> (250)	<i>MBrAcC</i> <sub>9</sub> (264)	<i>MBrAcC</i> <sub>10</sub> (278)	<i>BrEEC</i> <sub>6</sub> (222)	<i>BrEEC</i> <sub>7</sub> (236)	<i>BrEEC</i> <sub>8</sub> (250)	<i>BrEEC</i> <sub>9</sub> (264)	<i>BrEEC</i> <sub>10</sub> (278)
27	16	26	28	23	22	83	66	100	78	72
28	—	10	12	—	—	40	—	—	—	76
29	23	48	56	50	51	36	33	63	58	56
39	11	18	16	13	13	15	13	20	16	17
40	—	6	7	6	5	5	—	7	6	6
41	40	73	91	78	77	40	45	80	75	70
42	45	64	79	57	55	33	22	39	30	28
43	73	62	98	100	100	100	100	96	100	100
54	—	9	9	11	11	—	—	5	5	—
55	39	62	80	77	83	22	32	65	56	48
56	100	100	100	95	77	6	10	17	15	12
57	13	54	41	35	44	—	11	72	41	32
60	—	—	—	—	—	12	12	14	10	8
67	—	—	6	7	9	—	—	6	6	5
68	—	13	20	21	21	—	—	—	—	—
69	30	42	48	49	45	10	10	10	18	24
70	—	76	62	48	50	7	—	—	5	6
71	—	6	16	14	14	22	—	—	20	15
73	—	—	—	—	—	7	5	8	8	7
81	—	—	—	—	—	—	—	—	7	6
82	—	—	17	17	22	—	—	—	—	—
83	7	7	45	33	44	—	9	14	7	10
84	48	—	53	28	25	—	7	11	8	8
85	6	—	5	6	8	—	12	—	—	7
87	—	—	—	—	—	22	29	44	43	43
96	—	—	—	6	7	—	—	—	—	—
97	—	7	—	27	25	—	—	9	9	8





TABLE VI  
CI ISOBUTANE MASS SPECTRA OF HALOGENATED ESTERS

Ions containing higher isotopes of halogen X are not shown.

Compound	Mol.wt.	% relative intensity		Additional peaks m/z (% relative intensity)
		(M+1) <sup>+</sup>	(M+1-CH <sub>2</sub> XCOOH) <sup>+</sup>	
MClAcC <sub>6</sub>	178	34	100	—
MClAcC <sub>7</sub>	192	21	100	—
MClAcC <sub>8</sub>	206	21	100	71(9)
MClAcC <sub>9</sub>	220	19	100	71(13)
MClAcC <sub>10</sub>	234	21	100	71(13)
MClAcC <sub>12</sub>	262	21	100	71(11)
ClEEC <sub>6</sub>	178	100	—	—
ClEEC <sub>7</sub>	192	100	—	—
ClEEC <sub>8</sub>	206	100	—	—
ClEEC <sub>9</sub>	220	100	—	—
ClEEC <sub>10</sub>	234	100	—	—
ClEEC <sub>12</sub>	262	100	—	—
MBrAcC <sub>6</sub>	222	38	100	145(9), 139(5), 73(6)
MBrAcC <sub>7</sub>	236	31	100	159(19), 139(4), 73(32), 71(6), 113(6), 201(6)
MBrAcC <sub>8</sub>	250	29	100	173(5), 139(2), 73(4), 71(6)
MBrAcC <sub>9</sub>	264	21	100	187(5), 139(2), 73(6), 71(6), 85(6), 187(6)
MBrAcC <sub>10</sub>	278	13	100	201(3), 139(2), 73(4), 71(4), 85(4), 201(3)
BrEEC <sub>6</sub>	222	100	—	143(5), 145(2)
BrEEC <sub>7</sub>	236	100	—	157(4), 159(4)
BrEEC <sub>8</sub>	250	100	—	171(6), 173(3)
BrEEC <sub>9</sub>	264	100	—	185(5), 187(3)
BrEEC <sub>10</sub>	278	100	—	199(3), 201(3)

roacetates and 2-chloroethyl esters (b) and monobromoacetates and 2-bromoethyl esters (c) are illustrated in Fig. 1, analyzed on SP-1000 with a temperature programme from 110°C at 8°C/min. Tables I-III give the retention times ( $t_R$ ) and the relative retention times, RRT, at various column temperatures. The best separation occurred with a programmed temperature rising from 110°C at 8°C/min. Chlorinated isomers can be completely separated on non-polar OV-101 and/or SE-54 as well as unhalogenated esters. However, 2-bromoethyl esters and monobromoacetate isomers were not separated on non-polar columns. The separation of monochloroacetates and 2-chloroethyl esters as well as monobromoacetates and 2-bromoethyl esters on SP-1000 (Fig. 1) was limited due to unexpected small and broad peaks of monochloroacetates and/or monobromoacetates. On SP-1000 monochloroacetates were eluted before 2-chloroethyl esters, while in the case of brominated isomers this order of elution was reversed. The complete separation of the isomeric monobromoacetates and 2-bromoethyl esters could not be achieved on any of the columns in spite of the varied conditions used.

The MS data given in Tables IV and V are useful for the identification of the studied chlorinated and brominated esters. There are sufficient differences in the electron impact MS fragmentations of halogenoisomers to facilitate analysis of poorly

separated or unseparated peaks of isomeric halogenated esters. Most useful are the  $m/z$  values characteristic either of 2-halogenoethyl esters or monohalogenoacetates. Thus, significant for 2-chloroethyl esters and absent for monochloroacetates are peaks at  $m/z$  60, 61, 62/64, 63/65, 73, 86, 87, 122/124 and 135/137. Monochloroacetates are characterized by  $m/z$  49/51, 77/79 and 95/97. The characteristic peaks of the mass spectra of 2-bromoethyl esters of  $C_6$ - $C_{10}$  carboxylic acids are  $m/z$  60, 73, 87, 106/108, 107/109, 166/168, and  $m/z$  121/123, 139/141 are characteristic of monobromoacetates. Chemical ionization isobutane mass spectra (Table VI) give not only information about the molecular weight and number of chlorine and/or bromine atoms in a molecule, but also the position of substitution of halogens in acid or alcohol chain of ester. The most interesting feature of the CI isobutane mass spectra fragmentation of monochloro- and monobromoacetates is the abundant  $(M + 1 - XCH_2COOH)^+$  ion and significant temperature dependence.

Further details of the prominent peaks in EI and CI mass spectra and correlations of halogenated esters will be presented in a subsequent paper<sup>6</sup>.

## CONCLUSIONS

The separation of mixtures of monochloroacetates and 2-chloroethyl esters was achieved on non-polar OV-101 and/or SE-54 with a temperature programme from 110°C at 8°C/min, but monobromoacetates and 2-bromoethyl esters could not be separated under the same conditions.

On a polar SP-1000 column, monobromoacetates and 2-bromoethyl esters, monochloroacetates and 2-chloroethyl esters, respectively, were poorly separated. The peaks of monochloroacetates and/or monobromoacetates were broad.

There were significantly different fragments in MS fragmentations of alkyl halogenoacetates and 2-halogenoethyl esters of carboxylic acids, which can be used for identification purposes in GC-MS analysis.

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