

CHROM. 16.332

GLASS CAPILLARY GAS CHROMATOGRAPHY OF HOMOLOGOUS SERIES OF ESTERS

V. SEPARATION OF HALOGENOACETATES OF C_1 - C_{16} ALIPHATIC ALCOHOLS AND 2-HALOGENOETHYL ESTERS OF C_2 - C_{16} ALIPHATIC ACIDS WITH THE SAME MOLECULAR WEIGHT ON AN SP-400 GLASS CAPILLARY COLUMN

KAREL KOMÁREK*, JAN KŘÍŽ and JAROSLAV CHURÁČEK

Department of Analytical Chemistry, Institute of Chemical Technology, 532 10 Pardubice (Czechoslovakia)
and

KAREL TESAŘÍK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 662 28 Brno (Czechoslovakia)

SUMMARY

The gas chromatographic separation of halogenoacetates of C_1 - C_{16} aliphatic alcohols and 2-halogenoethyl esters of C_2 - C_{16} aliphatic acids and comparisons of retentions of pairs of these esters having the same molecular weights has been studied on SP-400 glass capillary columns. The influence of the type of halogen atoms, their number and their positions in esters on their retention was examined. Kováts retention indices were used to interpret the results.

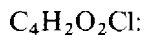
INTRODUCTION

The identification of halogenated esters that contain halogen atoms in either the alcohol chain, the acid chain or both is carried out by chemical reaction and by the identification of both parts of the esters'. This identification can be carried out with or without previous hydrolysis.

In the preparation of derivatives and the hydrolysis of halogenated esters, it must be taken into consideration that the halogen atoms in the ester molecule may be unstable and easily replaced with different functional groups, such as hydroxyl groups. Dehydrohalogenation can occur in some instances and the identification may be complicated or impossible. The methods used for the preparation of derivatives of both parts of esters are chosen so that their identification can be carried out by classical methods¹ or more modern methods involving separations^{2,3} or their combination with spectral techniques⁴. This paper describes the gas chromatographic (GC) separation and identification of halogenated esters and the comparison of retentions of pairs of halogenated esters with the same molecular weights but differing as molecular "mirror image", *i.e.* having the same carbon atom number and positions

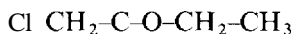
of the halogen atoms in the acid chains of halogenoacetates as in the alcohol chains of 2-halogenoethyl esters. The retentions of "mirror" pairs of esters of two homologous series have been studied, such as monochloroacetates of n-alkanols and 2-chloroethyl esters of n-alkanoic acids, monochloroacetates of isoalkanols and 2-chloroethyl esters of isoalkanoic acids, trichloroacetates of n-alkanols and 2,2,2-trichloroethyl esters of n-alkanoic acids, trichloroacetates of isoalkanols and 2,2,2-trichloroethyl esters of isoalkanoic acids, etc.

The principle of the study can be seen more clearly from the following structural formulae:



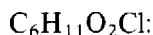
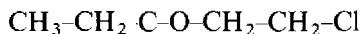
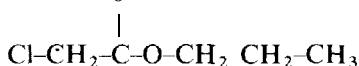
0

0



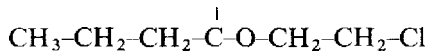
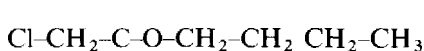
0

0



0

0



etc. Looking at the formulae of pairs of halogenated esters with the same molecular weights, a "mirror" arrangement of the carbon atoms and the positions of the halogen atoms in the acid and the alcohol chains is evident to when imagining the mirror at the location of the alcohol oxygen.

We have previously dealt with the GC separation of these pairs of halogenated esters on packed columns under isothermal conditions⁺⁺. The GC separation of various types of unhalogenated homologous series of lower esters on packed columns was studied in great detail by **Haken** and co-workers⁹.

A better separation efficiency is achieved on capillary columns, so we used an appropriate glass capillary column under isothermal conditions for the GC separation of halogenated esters^{10,11}. Because of the imperfect separation of halogenated esters, capillary CC with temperature programming coupled with mass spectrometry was used¹². Recently, a systematic GC separation of homologous series of various chlorinated esters on glass and silica capillary columns with temperature programming was reported by **Korhonen**¹³⁻¹⁵, and **Haken** and co-workers^{16,17}, who compared the retentions of homologous esters with the same carbon number in the alcohol and the acid chains.

In this work, model mixtures of homologous series of C₁-C₁₆ n-alkyl and C₃-C₅ isoalkyl acetates (Ac), monochloroacetates (MClAc), dichloroacetates (DClAc), trichloroacetates (TClAc), monobromoacetates (MBrAc), monoiodoacetates (MIAc) and trifluoroacetates (TFAc) and methyl esters (MetE), ethyl esters (EtE), 2-chloroethyl esters (MClEtE), 2,2,2-trichloroethyl esters (TClEtE), 2-bromo-

ethyl esters (BrEtE) and 2-iodoethyl esters (IEtE) of n -C₂-C₁₆ and iso-C₄-C₆ aliphatic monocarboxylic acids have been separated.

EXPERIMENTAL

GC separations were carried out on a Fractovap Model 2 150 gas chromatograph (Carlo Erba, Milan, Italy) equipped with a flame-ionization detector and an SP-400 glass capillary column. This column was made in our laboratory from soft Unihost soda-lime glass etched with methyl 2-chloro-1,1,2-trifluoroethyl ether vapour, statically silylated with dimethyldichlorosilane vapour and dynamically coated with SP-400 silicone stationary phase. The column efficiency was found to be: capacity ratio, $k = 2.94$ and number of theoretical plates, N , per metre = 4020 for n -decane, with "Trennzahl", $TZ = 40.5$ for n -nonane and n -decane.

First, all of the homologous series of lower halogenated esters were separated on a 37 m \times 0.16 mm I.D. column, then the column was divided into two lengths of 16 and 21 m. All of the homologous series of the higher halogenated esters were separated on the shorter 16-m column. Nitrogen was used as the carrier gas at a flow-rate 10 100 cm³/sec with a splitting ratio of 1:100. The column temperature was maintained at 80°C for the separation of the lower C₁-C₆ n -alkyl and C₃-C₅ isoalkyl halogenoacetates and 2-halogenoethyl esters n -C₂-C₆ and iso-C₄-C₆ monocarboxylic acids, and at 200°C for those of the higher C₆-C₁₆ n -alkyl halogenoacetates and 2-halogenoethyl esters of n -C₂-C₁₆ monocarboxylic acids. The temperatures of the injector and the detector were 250 and 300°C, respectively, for the separation of the higher halogenated esters. The dead time was determined by the injection of methane.

Model mixtures of the lower and higher halogenated esters were obtained from the individual esters. Unhalogenated esters were prepared by the usual sulphuric acid-catalysed esterification and halogenated esters by azeotropic esterification.

RESULTS AND DISCUSSION

The influence of chlorine, bromine and iodine atoms introduced into the alcohol chain of 2-halogenoethyl esters of n -C₂-C₁₆ and iso-C₄-C₆ carboxylic acids, the increasing length or branching of the acid carbon chain of esters, the influence of these on the acid chain of C₁-C₁₆ n -alkyl and C₃-C₅ isoalkyl halogenoacetates and the increasing length or branching of the alcohol carbon chain of esters was studied for "mirror image" halogenated esters with the same molecular weight using retention index increments (see Tables I-IV).

The retention index increments, $\Delta I_{\bar{X}}, \Delta I_{3\bar{X}}^*$, for chlorine, bromine, iodine and three chlorine atoms were calculated as the differences between the retention indices for 2-chloro-, 2-bromo-, 2-iodo- and 2,2,2-trichloroethyl esters of aliphatic carboxylic acids and those for the corresponding unhalogenated ethyl esters, such as for 2-bromoethyl esters of propionic acid, $\Delta I_{\bar{Br}} = I_{BrEtEC_3} - I_{EtEC_3}$. The retention index increments, ΔI_X for chlorine, bromine and iodine atoms, ΔI_{2X} for two chlorine atoms and ΔI_{3X} for three chlorine and fluorine atoms, were calculated as the differences in

* The increments marked with a bar belong to halogen atoms and methylene groups in the alcohol chain of the esters.

TABLE I

RETENTION INDICES. I , OF C_1C_6 ALKYL ESTERS AND INCREMENTS OF RETENTION INDICES FOR METHYLENE AND HALOGEN GROUPS AT $80^\circ C$

<i>Ester</i>	<i>I</i>	ΔI_{CH_2}	$\Delta I_{X,2X,3X}$	ΔI_{Cl}	ΔI_{HCl}	ΔI_{HCl}
AcC ₁	526.28	—	—	—	—	—
AcC ₂	607.32	81.04	—	—	—	—
AcC ₃	708.33	101.01	—	—	—	—
AcC ₄	808.80	100.47	—	—	—	—
AcC ₅	909.83	101.03	—	—	—	—
AcC ₆	1009.69	99.86	—	—	—	—
AcisoC ₃	657.26	—	—	—	—	—
AcisoC ₄	169.72	112.56	—	—	—	—
AcisoC ₅	873.28	103.56	—	—	—	—
MClAcC ₁	149.74	—	223.46	223.46	—	—
MClAcC ₂	826.37	76.63	219.05	219.05	—	—
MClAcC ₃	921.88	95.51	213.55	213.55	—	—
MClAcC ₄	1021.18	99.30	212.38	212.38	—	—
MClAcC ₅	1121.04	99.86	211.21	211.21	—	—
MClAcisoC ₃	868.41	—	211.25	211.25	—	—
MClAcisoC ₄	978.56	110.15	208.84	208.84	—	—
MClAcisoC ₅	1082.96	104.40	209.68	209.68	—	—
MBrAcC ₁	815.25	—	288.97	288.97	—	—
MBrAcC ₂	897.18	81.93	289.86	289.86	—	—
MBrAcC ₃	986.94	89.76	278.62	278.62	—	—
MBrAcC ₄	1089.32	102.38	280.52	280.52	—	—
MBrAcC ₅	1187.55	98.28	277.72	277.72	—	—
MBrAcisoC ₃	937.36	—	280.20	280.20	—	—
MBrAcisoC ₄	1048.15	110.79	278.43	278.43	—	—
MBrAcisoC ₅	1150.49	102.34	271.21	271.21	—	—
MIAcC ₁	889.62	—	363.34	363.34	—	—
MIAcC ₂	982.25	93.63	374.93	374.93	—	—
MIAcC ₃	1082.07	98.82	312.74	372.74	—	—
MIAcC ₄	1178.60	97.3	369.80	369.80	—	—
MIAcC ₅	1275.07	96.47	365.24	365.24	—	—
MIAcisoC ₃	1024.47	—	367.30	367.30	—	—
MIAcisoC ₄	113X.38	113.92	368.66	368.66	—	—
MIAcisoC ₅	1237.65	99.27	364.37	364.37	—	—
DClAcC ₁	831.65	—	305.37	—	81.91	—
DClAcC ₂	902.67	71.02	295.35	—	76.30	—
DClAcC ₃	995.72	93.08	287.39	—	73.84	—
DClAcC ₄	1092.41	96.69	283.61	—	71.23	—
DClAcC ₅	1189.68	97.27	279.83	—	68.64	—
DClAcC ₆	1288.53	98.85	278.84	—	—	—
DClAcisoC ₃	940.28	—	283.12	—	71.87	—
DClAcisoC ₄	1050.35	110.07	280.63	—	71.79	—
DClAcisoC ₅	1151.15	100.80	277.87	—	68.19	—
TClAcC ₁	911.81	—	385.53	—	—	80.16
TClAcC ₂	978.60	64.79	371.28	—	—	75.93

TABLE I (continued)

<i>Ester</i>	<i>I</i>	ΔI_{CH_2}	$\Delta I_{X,2X,3X}$	ΔI_{ICl}	ΔI_{IIcI}	ΔI_{IIIcI}
TClAcC ₃	1069.09	90.39	360.76	—	—	73.37
TClAcC ₄	1162.91	93.82	354.11	—	—	70.50
TClAcC ₅	1258.76	95.85	348.53	—	—	69.08
TClAcisoC ₃	1012.12	—	354.96	—	—	71.84
TClAcisoC ₄	1121.65	109.53	351.93	—	—	71.30
TClAcisoC ₅	1220.81	99.16	341.53	—	—	69.66
TFAcC ₃	576.20	—	-132.13	—	—	—
TFAcC ₄	671.41	95.21	-137.39	—	—	—
TFAcC ₅	768.34	96.93	-141.49	—	—	—
TFAcC ₆	866.25	97.91	-143.44	—	—	—
TFAcisoC ₃	529.67	—	-127.49	—	—	—
TFAcisoC ₄	630.30	100.63	-139.42	—	—	—
TFAcisoC ₅	731.99	101.69	-141.29	—	—	—

the retention indices for halogenoacetates and those for the corresponding unhalogenated acetates, such as for *n*-propyl monobromoacetate, $\Delta I_{Br} = I_{MBrAcC_3} - I_{AcC_3}$. The retention increments, ΔI_{IIcI} for the second chlorine atom introduced into the monochloroacetate molecule and ΔI_{IIIcI} for the third chlorine atom introduced into the dichloroacetate molecule, were calculated as the differences in the retention indices of the corresponding dichloroacetates and monochloroacetates, and trichloroacetates and dichloroacetates, such as for ethyl dichloroacetate, $\Delta I_{IIcIc_2} = I_{DClAcC_2} - I_{MClAcC_2}$, and for ethyl trichloroacetate, $\Delta I_{IIIcIc_2} = I_{TClAcC_2} - I_{DClAcC_2}$.

The retention index increments ΔI_X , ΔI_{2X} , ΔI_{3X} , $\Delta I_{\bar{X}}$ and $\Delta I_{3\bar{X}}$ decrease with increasing length of the alcohol or acid chains for all the homologous series of the lower halogenated esters. The decreases in these increments are greater and sharper for *n*-C₁-C₆ alkylhalogenoacetates, whereas those for 2-halogenoethyl esters of *n*-C₂-C₆ carboxylic acids are smaller and more gradual. A gradual and small decrease in retention index increments for halogen atoms is observed for both types of homologous series of lower halogenated esters with branched carbon chains. The retention index increments for chlorine atoms gradually decrease in the order alkyl monochloroacetates (ΔI_X), alkyl dichloroacetates (ΔI_{2X}) and alkyl trichloroacetates (ΔI_{3X}). The decreases in the retention index increments, ΔI_X , for homologous series of C₁-C₆ *n*-alkyl monochloroacetates, monobromoacetates and monoiodoacetates are approximately the same (10-12 units).

The decreases in retention index increments $\Delta I_{\bar{Cl}}$ and $\Delta I_{3\bar{Cl}}$ increase for homologous series of 2-halogenoethyl esters of C₂-C₆ carboxylic acids with increasing number of chlorine atoms in the ester molecules, i.e., they are higher for 2,2,2-trichloroethyl esters than for 2-chloroethyl esters. The decreases in retention index increments $\Delta I_{\bar{X}}$ for homologous series of 2-chloroethyl esters, 2-bromoethyl esters and 2-iodoethyl esters of C₂-C₆ carboxylic acids are approximately the same (1-6 units). For both types of homologous series of higher halogenated esters, the retention index increments do not change very much. The absolute values of the retention index increments ΔI_{3X} for fluorine atoms decrease for the whole homologous series of trifluoroacetates.

TABLE 11

RETENTION INDICES, I , OF HALOGENOETHYL ESTERS OF LOWER CARBOXYLIC ACIDS AND INCREMENTS OF RETENTION INDICES FOR METHYLENE AND HALOGEN GROUPS AT 80°C

<i>Ester</i>	I	ΔI_{CH_2}	$\Delta I_{\text{x,3x}}$	$\Delta I_{3x} - \Delta I_x$
EtEC ₂	607.32	—	—	—
EtEC ₃	705.59	98.27	—	—
EtEC ₄	795.30	89.71	—	—
EtEC ₅	896.35	101.05	—	—
EtEC ₆	995.61	99.26	—	—
EtEisoC ₄	754.54	—	—	—
EtEisoC ₅	850.02	95.48	—	—
EtEisoC ₆	962.26	112.24	—	—
MCIEtEC ₂	825.40	—	218.08	—
MCIEtEC ₃	920.64	95.24	215.05	—
MCIEtEC ₄	1010.48	89.84	215.18	—
MCIEtEC ₅	1110.14	99.66	213.79	—
MCIEtEisoC ₄	967.12	—	212.58	—
MCIEtEisoC ₅	1063.48	96.34	213.46	—
MCIEtEisoC ₆	1174.27	110.79	212.01	—
BrEtEC ₂	902.16	—	294.84	—
BrEtEC ₃	994.87	94.71	291.28	—
BrEtEC ₄	1087.43	90.56	292.13	—
BrEtEC ₅	1185.67	98.24	289.32	—
BrEtEC ₆	1284.57	98.90	288.96	—
BrEtEisoC ₄	1043.53	—	288.99	—
BrEtEisoC ₅	1138.95	95.42	288.93	—
BrEtEisoC ₆	1249.38	110.43	287.12	—
IEtEC ₂	988.45	—	381.13	—
IEtEC ₃	1089.08	100.63	383.45	—
IEtEC ₄	1177.82	88.74	382.52	—
IEtEC ₅	1276.70	98.88	380.35	—
IEtEC ₆	1375.16	98.44	379.55	—
IEtEisoC ₄	1135.66	—	381.12	—
IEtEisoC ₅	1229.95	94.29	379.93	—
IEtEisoC ₆	1343.56	113.61	381.30	—
TCIEtEC ₃	981.61	—	374.29	156.21
TCIEtEC ₃	1074.47	92.86	368.88	153.83
TCIEtEC ₄	1162.30	87.83	367.00	151.82
TCIEtEC ₅	1258.00	95.70	361.65	147.86
TCIEtEisoC ₄	1119.48	—	364.94	152.36
TCIEtEisoC ₅	1213.80	94.32	368.78	150.22
TCIEtEisoC ₆	1321.98	108.18	359.72	147.71
MetEC ₂	524.69	—	—	—
MetEC ₃	625.94	101.35	—	—
MetEC ₄	717.85	91.91	—	—
MetEC ₅	819.85	102.00	—	—
MetEC ₆	920.36	100.51	—	—
MetEisoC ₄	680.99	—	—	—
MetEisoC ₅	773.78	92.79	—	—
MetEisoC ₆	887.78	113.92	—	—

TABLE III

RETENTION INDICES, I , OF C_6 - C_{16} ALKYL ESTERS AND INCREMENTS OF RETENTION INDICES FOR METHYLENE AND HALOGEN GROUPS AT 200°C

<i>Ester</i>	I	δI_{CH_2}	$\Delta I_{X,2X,3X}$	ΔI_{ICl}	ΔI_{HCl}	ΔI_{HCl}
AcC ₆	1005.99	—	—	—	—	—
AcC ₇	1106.28	100.29	—	—	—	—
AcC ₈	1203.98	97.70	—	—	—	—
AcC ₉	1304.56	100.60	—	—	—	—
AcC ₁₀	1402.81	98.33	—	—	—	—
AcC ₁₂	1600.94	198.13	—	—	—	—
AcC ₁₄	1803.29	202.35	—	—	—	—
AcC ₁₆	2004.68	201.39	—	—	—	—
MClAcC ₆	1225.65	—	219.66	219.66	—	—
MClAcC ₈	1423.86	198.21	219.88	219.88	—	—
MClAcC ₉	1524.44	100.58	219.86	219.86	—	—
MClAcC ₁₀	1625.44	101.00	222.63	222.63	—	—
MBrAcC ₆	1307.19	—	301.20	301.20	—	—
MBrAcC ₇	1405.46	98.27	299.18	299.18	—	—
MBrAcC ₈	1503.01	97.5s	299.03	299.03	—	—
MBrAcC ₉	1606.34	102.35	301.76	301.76	—	—
MBrAcC ₁₀	1703.61	97.27	300.80	300.80	—	—
MIAcC ₆	1400.70	—	394.81	394.8 †	—	—
MIAcC ₇	1504.53	103.83	398.25	398.25	—	—
MIAcC ₈	1609.03	104.50	403.05	403.05	—	—
MIAcC ₉	1712.87	103.84	408.29	408.29	—	—
DCIAcC ₆	1307.89	—	301.90	—	82.24	—
DCIAcC ₇	1405.20	97.31	298.92	—	—	—
DCIAcC ₈	1505.26	100.06	301.28	—	81.40	—
DCIAcC ₉	1603.67	98.41	299.09	—	79.23	—
DCIAcC ₁₀	1701.26	97.61	298.37	—	75.84	—
TClAcC ₆	1384.13	—	378.14	—	—	76.24
TClAcC ₇	1482.38	99.25	376.10	—	—	77.18
TClAcC ₈	1581.75	99.37	377.77	—	—	76.49
TClAcC ₉	1680.23	98.48	375.65	—	—	76.56
TClAcC ₁₀	1778.13	97.90	375.32	—	—	76.85
TClAcC ₁₂	1978.12	199.99	377.18	—	—	—
TFAcC ₆	830.48	—	—175.51	—	—	—
TFAcC ₇	930.26	99.78	—176.02	—	—	—
TFAcC ₈	1027.23	96.97	—176.75	—	—	—
TFAcC ₉	1125.44	98.21	-179.14	—	—	—
TFAcC ₁₀	1225.46	100.02	—177.3s	—	—	—
TFAcC ₁₂	1423.17	197.71	—177.77	—	—	—
TFAcC ₁₄	1622.89	199.72	—181.40	—	—	—
TFAcC ₁₆	1822.87	199.98	-181.81	—	—	—

Special attention was paid to halogenoesters with the same molecular weights but differing as molecular “mirror image” at the carbon atoms and the positions of the halogen atoms in the alcohol and the acid chains. To determine the influence of the number and position of individual halogen atoms in these types of halogenated esters, we calculated differences, D , between retention indices for pairs of alkyl halo-

TABLE IV

RETENTION INDICES, I , OF HALOGENOETHYL ESTERS OF HIGHER CARBOXYLIC ACIDS AND INCREMENTS OF RETENTION INDICES FOR METHYLENE AND HALOGEN GROUPS AT 200°C

<i>Ester</i>	I	ΔI_{CH_2}	$\Delta I_{\text{x,3x}}$	$\Delta I_{3x} - \Delta I_x$
EtEC ₆	991.55	—	—	—
EtEC ₇	1090.22	98.67	—	—
EtEC ₈	1189.17	98.95	—	—
EtEC ₉	1290.24	101.07	—	—
EtEC ₁₀	1389.21	98.97	—	—
EtEC ₁₂	1589.75	200.54	—	—
EtEC ₁₄	1789.77	200.02	—	—
EtEC ₁₆	1989.63	199.96	—	—
MCIEtEC ₆	1214.83	—	223.28	—
MCIEtEC ₇	1315.77	100.94	225.55	—
MCIEtEC ₈	1416.23	100.46	227.06	—
MCIEtEC ₉	1516.36	100.13	226.12	—
MCIEtEC ₁₀	1617.08	100.72	227.87	—
BrEtEC,	1306.37	—	314.82	—
BrEtEC,	1405.38	99.01	315.16	—
BrEtEC,	1505.78	100.40	316.61	—
BrEtEC,	1605.14	99.36	314.90	—
BrEtEC ₁₀	1705.20	100.06	315.99	—
IEtEC ₆	1411.35	—	419.80	—
IEtEC ₇	1509.92	98.57	419.70	—
IEtEC ₈	1609.29	99.37	420.12	—
IEtEC ₉	1710.55	101.26	420.3 1	—
IEtEC ₁₀	1808.86	98.3 I	419.65	—
TCIEtEC ₆	1382.05	—	390.50	167.22
TCIEtEC,	1479.47	97.42	389.25	163.70
TCIEtEC,	1578.53	99.06	389.36	162.30
TCIEtEC ₉	1677.67	99.15	387.44	161.32
TCIEtEC,,	1777.50	99.82	388.29	160.42
MetEC,	922.36	—	—	—
MetEC,	1025.50	103.14	—	—
MetEC,	1121.84	96.34	—	—
MetEC,	1223.44	101.60	—	—
MetEC ₁₀	1320.04	96.60	—	—
MetEC, 1	1419.37	99.33	—	—
MetEC 12	1520.53	101.16	—	—
MetEC ₁₄	1720.78	200.25	—	—

genoacetates and 2-halogenoethyl esters carboxylic acids (Tables V and VI). In the tables, values of D calculated from our earlier papers^{5-8,10,11} are compared with those calculated from the paper of Haken and Srisukh⁹. With increasing number of chlorine atoms or atomic weights of the halogen atoms in the pairs of halogenated esters, the differences, D , decrease on the stationary phases used. The separations of these pairs of esters decrease on capillary columns under isothermal conditions.

As expected, the application of capillary columns of medium length did not

TABLE V

CALCULATED DIFFERENCES, IN RETENTION "INDICES" OF "MIRROR" PAIRS OF LOWER HALOGENATED ESTERS

"Mirror" pair	Capillary columns		Packed columns			
	OV-101 ^{10,11}	SP-400	Silicone_QF-1 ⁶⁻⁸ SE-30 ⁹		Silar 10C ⁹	
AcC ₃ -EtEC ₃	2.1	2.74	2	32	4.99	16.11
AcC ₄ -EtEC ₄	14.4	13.50	10	43	7.44	-1.11
AcC ₅ -EtEC ₅	14.0	13.48	13	44	3.09	17.50
AcC ₆ -EtEC ₆	15.0	14.08	—	—	-4.09	24.37
AcisoC ₄ -EtEisoC ₄	13.0	15.18	13	63	—	—
AcisoC ₅ -EtEisoC ₅	22.2	23.26	21	61	—	—
MClAcC ₂ -MClEtEC ₂	-19.0	0.97	-2	12	—	—
MClAcC ₃ -MClEtEC ₃	0.7	1.24	0	29	—	—
MClAcC ₄ -MClEtEC ₄	10.8	10.70	9	38	—	—
MClAcC ₅ -MClEtEC ₅	13.3	10.90	8	36	—	—
MClAcC ₆ -MClEtEC ₆	13.5	—	—	—	—	—
MClAcisoC ₄ -MClEtEisoC ₄	10.5	11.44	11	34	—	—
MClAcisoC ₅ -MClEtEisoC ₅	19.0	19.48	20	39	—	—
TCIAcC ₂ -TCIEtEC ₂	-3.4	-3.01	-4	-24	—	—
TCIAcC ₃ -TCIEtEC ₃	-5.8	-5.38	-3	-9	—	—
TCIAcC ₄ -TCIEtEC ₄	0.5	0.61	2	-1	—	—
TCIAcC ₅ -TCIEtEC ₅	0.8	0.76	3	0	—	—
TCIAcC ₆ -TCIEtEC ₆	3.5	—	—	—	—	—
TCIAcisoC ₄ -TCIEtEisoC ₄	1.5	2.17	33	15	—	—
TCIAcisoC ₅ -TCIEtEisoC ₅	8.1	7.01	10	14	—	—
MBrAcC ₂ -BrEtEC ₂	-8.4	-4.98	-9	-34	—	—
MBrAcC ₃ -BrEtEC ₃	-5.8	-9.93	-6	-10	—	—
MBrAcC ₄ -BrEtEC ₄	3.6	2.89	1	1	—	—
MBrAcC ₅ -BrEtEC ₅	4.1	1.88	-1	0	—	—
MBrAcC ₆ -BrEtEC ₆	4.8	—	—	—	—	—
MBrAcisoC ₄ -BrEtEisoC ₄	2.9	5.62	3	22	—	—
MBrAcisoC ₅ -BrEtEisoC ₅	10.8	11.54	14	21	—	—
MIAcC ₂ -IEtEC ₂	-7.1	-6.20	-11	-54	—	—
MIAcC ₃ -IEtEC ₃	-6.2	-8.01	-9	-30	—	—
MIAcC ₄ -IEtEC ₄	2.1	0.78	-2	-22	—	—
MIAcC ₅ -IEtEC ₅	2.1	-1.63	-2	-24	—	—
MIAcC ₆ -IEtEC ₆	1.8	—	—	—	—	—
MIAcisoC ₄ -IEtEisoC ₄	0.8	2.72	3	—	—	—
MIAcisoC ₅ -IEtEisoC ₅	6.8	7.70	9	—	—	—

substantially increase the differences, D , in comparison with our earlier results on packed columns. The comparison of retention index increments for halogen atoms in "mirror" pairs of halogenated esters, ΔI_X , ΔI_{3X} and $\Delta I_{3\bar{X}}$ (Tables I-IV), show that the values of $\Delta I_{\bar{X}}$ and $\Delta I_{3\bar{X}}$ are higher than the values of ΔI_X and ΔI_{3X} for both the lower and the higher esters, **i. e.** a halogen atom added to the alcohol chain of esters

TABLE VI

CALCULATED DIFFERENCES, *D*, IN RETENTION INDICES OF "MIRROR" PAIRS OF HIGHER HALOGENATED ESTERS

"Mirror" pair	Capillary columns		Packed columns	
	<i>OV-101</i> ^{10,11}	SP-400	<i>Silicone grease QF-1</i> ⁶⁻⁸	
AcC ₆ -EtEC ₆	10.4	14.44	16	47
AcC ₇ -EtEC ₇	11.1	16.06	16	52
AcC ₈ -EtEC ₈	12.6	14.81	17	51
AcC ₉ -EtEC ₉	13.0	14.34	18	48
AcC ₁₀ -EtEC ₁₀	13.1	13.M)	17	48
AcC ₁₂ -EtEC ₁₂	—	11.19	18	51
AcC ₁₄ -EtEC ₁₄	—	13.52	20	48
AcC ₁₆ -EtEC ₁₆	—	15.05	15	48
MClAcC ₆ -MClEtEC ₆	8.2	10.82	9	22
MClAcC ₇ -MClEtEC ₇	6.1	—	7	23
MClAcC ₈ -MClEtEC ₈	5.1	7.63	7	19
MClAcC ₉ -MClEtEC ₉	6.6	8.08	7	21
MClAcC ₁₀ -MClEtEC ₁₀	7.5	8.36	8	20
TClAcC ₆ -TClEtEC ₆	3.0	2.08	- 2	- 1
TClAcC ₇ -TClEtEC ₇	3.3	2.91	1	- 6
TClAcC ₈ -TClEtEC ₈	3.1	3.22	2	- 6
TClAcC ₉ -TClEtEC ₉	3.3	2.55	2	- 7
TClAcC ₁₀ -TClEtEC ₁₀	3.0	0.63	2	- 6
MBrAcC ₆ -BrEtEC ₆	2.1	0.82	- 2	- 10
MBrAcC ₇ -BrEtEC ₇	2.2	0.08		- 10
MBrAcC ₈ -BrEtEC ₈	1.9	-2.77		- 14
MBrAcC ₉ -BrEtEC ₉	2.4	1.20	0	- 17
MBrAcC ₁₀ -BrEtEC ₁₀	2.5	-1.59	- 1	- 17
MIAcC ₆ -IEtEC ₆	- 1.4	- 10.65	3	- 14
MIAcC ₇ -IEtEC ₇	- 1.9	- 5.39	0	- 15
MIAcC ₈ -IEtEC ₈	- 2.1	- 0.25	3	- 13
MIAcC ₉ -IEtEC ₉	- 1.9	2.32	1	- 11
MIAcC ₁₀ -IEtEC ₁₀	- 1.7	—	4	- 12

has a greater influence on the retention than the same halogen atom added to the acid chain.

The differences, which are 10–15 units for unhalogenated "mirror" pairs of esters, decrease with increasing number and atomic weights of halogen atoms in the alcohol chain of halogenated esters, in spite of the fact that the acid carbon number increases (see Tables V and VI).

These results are in agreement with those of Haken and Srisukh⁹ and Korhonen¹³.

REFERENCES

- 1 N. D. Cheronis and T. S. Ma, *Organic Functional Group Analysis by Micro and Semimicro Methods*, Wiley, New York, 1964.
- 2 J. Drozd, *Chemical Derivatization in Gas Chromatography*, Elsevier, Amsterdam, 1981.
- 3 J. Gasparič and J. Churáček, *Paper and Thin-Layer Chromatography*, Ellis Horwood, Chichester, 1978.

- 4 D. J. Pasto and C. R. Johnson, *Organic Structure Determination*, Prentice-Hall, Englewood Cliffs, NJ, 1969.
- 5 J. Churáček, K. Komárek and H. Komárková, *Collect. Sci. Pap. Univ. Chem. Technol. Pardubice*, **27** (1972) 17.
- 6 K. Komarek, J. Churáček, K. Bořecký and M. Timarova, *Collect. Sci. Pap. Univ. Chem. Technol. Pardubice*, **38** (1978) 11.
- 7 K. Komarek, A. Čapek and J. Churáček, *Collect. Sri. Pap. Univ. Chem. Technol. Pardubice*, **14** (1981) 47.
- 8 K. Komarek, K. Bořecký, B. Dadák and J. Churáček, *Collect. Sci. Pap. Univ. Chem. Technol. Pardubice*, **44** (1981) 65.
- 9 J. K. Haken and D. Srisukh, *J. Chromatogr.*, **219** (1981) 45; and references cited therein.
- 10 K. Komarek, L. Hornová and J. Churáček, *J. Chromatogr.*, **244** (1982) 142.
- 11 K. Komarek, L. Hornová and J. Churáček, *J. Chromatogr.*, **252** (1982) 293.
- 12 J. Churáček, A. Horna, K. Komarek and O. Dufka, *J. Chromatogr.*, in press.
- 13 I. O. O. Korhonen, *J. Chromatogr.*, **246** (1982) 241; and references cited therein.
- 14 I. O. O. Korhonen, *J. Chromatogr.*, **248** (1982) 69; and references cited therein.
- 15 I. O. O. Korhonen, *Chromatographia*, **15** (1982) 505 and 635; and references cited therein.
- 16 J. K. Haken, *J. Chromatogr.*, **253** (1982) 264; and references cited therein.
- 17 J. K. Haken, B. G. Madden and I. O. O. Korhonen, *J. Chromatogr.*, **256** (1983) 221; and references cited therein.