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Note

Glass capillary gas chromatography of homologous series of esters

IV. Separation of homologous series of certain halogenopropyl esters of aliphatic carboxylic acids on OV-101

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Systematic studies have recently been published by Korhonen[1–3,5] and Haken *et al.*[4] dealing with gas chromatographic (GC) separation of certain homologous series of halogenoesters on glass and silica WCOT capillary columns coated with Carbowax 20M, SE-30, and OV-351. In our earlier paper[6] we dealt with the influence on the elution of (i) chlorine, bromine and iodine atoms in 2-halogenoethyl esters of aliphatic monocarboxylic acids, C_2–C_{10}, and (ii) the increasing chain length.

In this paper we deal with the GC behaviour of chloropropyl esters of aliphatic monocarboxylic acids on an OV-101 glass capillary column. Model mixtures of homologous series of *n*-propyl esters (PrE), 3-chloropropyl esters (3-ClPrE), 2,3-dichloropropyl esters (2,3-DClPrE), 1,3-dichloroisopropyl esters (1,3-DClisoPrE) and butyl esters (BuE) of aliphatic monocarboxylic acids *n*-C_2–C_{10} and iso-C_4–C_6 have been separated.

EXPERIMENTAL

GC separation of homologous series of chloropropyl esters was carried out on a Fractovap Model 2150 gas chromatograph (Carlo Erba, Italy) equipped with a flame-ionization detector and a home-made glass capillary column (15 m × 0.22 mm I.D.) coated dynamically with OV-101. The column temperature was maintained at 80°C for separation of chloropropyl esters of the lower (*n*-C_2–C_6 and iso-C_4–C_6) and at 200°C for those of the higher (*n*-C_6–C_{16}) aliphatic monocarboxylic acids. The temperatures of the injector and detector were 250°C and 300°C, respectively, for separation of the chloropropyl esters of the higher acids. The model mixtures of propyl and chloropropyl esters of aliphatic monocarboxylic acids were obtained from the individual esters. The esters were prepared by the azeotropic sulphuric acid-catalysed esterification of commercial monocarboxylic acids and alcohols, only 3-chloropropyl alcohol and 2,3-dichloropropyl alcohol were prepared in our laboratory according to the method previously described[7].

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TABLE I

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

Ester	*I*	ΔI_{CH_2}	$\Delta I_{Cl(3\text{-}nC)}$	$\Delta I_{2Cl(2,3\text{-}nC)}$	$\Delta I_{2Cl(1,3\text{-}iC)}$
$PrEC_2$	695.8	–	–	–	–
$PrEC_3$	791.6	95.8	–	–	–
$PrEC_4$	880.1	88.5	–	–	–
$PrEC_5$	978.8	98.7	–	–	–
$PrEisoC_4$	840.7	–	–	–	–
$PrEisoC_5$	932.8	92.1	–	–	–
$PrEisoC_6$	1043.8	111.0	–	–	–
$3\text{-}ClPrEC_2$	922.4	–	226.6	–	–
$3\text{-}ClPrEC_3$	1016.2	93.8	224.6	–	–
$3\text{-}ClPrEC_4$	1103.8	87.6	223.7	–	–
$3\text{-}ClPrEC_5$	1201.3	97.5	222.5	–	–
$3\text{-}ClPrEC_6$	1302.3	101.0	225.5	–	–
$3\text{-}ClPrEisoC_4$	1061.3	–	220.6	–	–
$3\text{-}ClPrEisoC_5$	1155.1	93.8	222.3	–	–
$3\text{-}ClPrEisoC_6$	1264.5	109.4	220.7	–	–
$2,3\text{-}DClPrEC_2$	1042.6	–	–	346.8	–
$2,3\text{-}DClPrEC_3$	1133.7	91.1	–	342.1	–
$2,3\text{-}DClPrEC_4$	1220.2	86.5	–	340.1	–
$2,3\text{-}DClPrEC_5$	1317.3	97.1	–	338.5	–
$2,3\text{-}DClPrEC_6$	1413.5	96.2	–	336.2	–
$2,3\text{-}DClPrEisoC_4$	1177.4	–	–	336.6	–
$2,3\text{-}DClPrEisoC_5$	1271.0	93.7	–	338.2	–
$2,3\text{-}DClPrEisoC_6$	1377.9	106.9	–	334.1	–
$1,3\text{-}DClisoPrEC_2$	1025.5	–	–	–	379.2
$1,3\text{-}DClisoPrEC_3$	1114.4	88.9	–	–	376.9
$1,3\text{-}DClisoPrEC_4$	1200.2	85.8	–	–	374.3
$1,3\text{-}DClisoPrEC_5$	1297.0	96.8	–	–	373.3
$1,3\text{-}DClisoPrEC_6$	1393.7	96.7	–	–	372.0
$1,3\text{-}DClisoPrEisoC_4$	1157.7	–	–	–	375.0
$1,3\text{-}DClisoPrEisoC_5$	1251.9	94.2	–	–	372.4
$1,3\text{-}DClisoPrEisoC_6$	1356.0	94.1	–	–	368.8
$ButEC_2$	796.4	–	–	–	–
$ButEC_3$	890.3	93.9	–	–	–
$ButEC_4$	977.9	87.6	–	–	–
$ButEC_5$	1075.6	97.7	–	–	–
$ButEC_6$	1173.3	97.7	–	–	–
$ButEisoC_4$	937.0	–	–	–	–
$ButEisoC_5$	1030.0	93.0	–	–	–
$ButEisoC_6$	1139.0	109.0	–	–	–

TABLE I *(continued)*

Ester	*I*	ΔI_{CH_2}	$\Delta I_{Cl(3\text{-}nC)}$	$\Delta I_{2Cl(2,3\text{-}nC)}$	$\Delta I_{2Cl(1,3\text{-}iC)}$
isoPrEC$_2$	646.3	–	–	–	–
isoPrEC$_3$	737.5	91.2	–	–	–
isoPrEC$_4$	825.9	88.4	–	–	–
isoPrEC$_5$	923.7	97.8		–	
isoPrEC$_6$	1021.7	98.0	–	–	–
isoPrEisoC$_4$	782.7	–	–	–	–
isoPrEisoC$_5$	879.5	96.8	–		
isoPrEisoC$_6$	987.2	107.7	–	–	–

TABLE II

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

Ester	*I*	ΔI_{CH_2}	$\Delta I_{Cl(3\text{-}nC)}$	$\Delta I_{2Cl(2,3\text{-}nC)}$	$\Delta I_{2Cl(1,3\text{-}iC)}$
PrEC$_6$	1075.1	–	–	–	–
PrEC$_7$	1173.6	98.5	–	–	–
PrEC$_8$	1273.8	100.2	–	–	–
PrEC$_9$	1373.2	99.4	–	–	–
PrEC$_{10}$	1473.0	99.8	–	–	–
3-ClPrEC$_6$	1313.5	–	238.4	–	–
3-ClPrEC$_7$	1412.8	99.3	239.2	–	–
3-ClPrEC$_8$	1512.8	100.0	239.0	–	–
3-ClPrEC$_9$	1612.3	99.5	239.1	–	–
3-ClPrEC$_{10}$	1712.3	100.0	239.3	–	–
2,3-DClPrEC$_6$	1437.8	–	–	362.7	–
2,3-DClPrEC$_7$	1536.7	98.9	–	363.1	–
2,3-DClPrEC$_8$	1635.8	99.1	–	362.0	–
2,3-DClPrEC$_9$	1735.4	99.6	–	362.2	–
2,3-DClPrEC$_{10}$	1835.5	100.1	–	362.5	–
1,3-DClisoPrEC$_6$	1413.2	–	–	–	–
1,3-DClisoPrEC$_7$	1512.0	98.8	–	–	–
1,3-DClisoPrEC$_8$	1610.7	98.7	–	–	–
1,3-DClisoPrEC$_9$	1710.4	99.7	–	–	–
1,3-DClisoPrEC$_{10}$	1810.1	99.7	–	–	–
ButEC$_6$	1171.7	–	–	–	–
ButEC$_7$	1271.4	99.7	–	–	–
ButEC$_8$	1370.3	98.9	–	–	–
ButEC$_9$	1469.5	99.2	–	–	–
ButEC$_{10}$	1569.2	99.7	–	–	–

RESULTS AND DISCUSSION

The influence of chlorine atoms in position 3 (3-nC) and two atoms in positions 2 and 3 (2,3-nC) of *n*-propyl esters and in positions 1 and 3 (1,3-iC) of isopropyl esters, and of increasing chain length and branching of the acid moiety of esters was studied using retention index increments $\Delta I_{Cl(3\text{-nC})}$, $\Delta I_{2Cl(2,3\text{-nC})}$ and $\Delta I_{2Cl(1,3\text{-iC})}$ (see Tables I and II). These increments were calculated as the difference between retention indices for 3-chloro, 2,3-dichloropropyl and 1,3-dichloroisopropyl esters of aliphatic monocarboxylic acids and those for the corresponding unhalogenated esters; *e.g.* the 2,3-dichloropropyl esters of decanoic acid: $\Delta I_{2Cl(2,3\text{-nC})} = I_{2,3\text{-DClPrEC}_{10}} - I_{\text{PrEC}_{10}}$; or the 1,3-dichloroisopropyl esters of hexanoic acid $\Delta I_{2Cl(1,3\text{-iC})} = I_{1,3\text{-DClisoPrEC}_6} - I_{\text{isoPrEC}_6}$. The increments for chlorine atoms, $\Delta I_{Cl(3\text{-nC})}$, $\Delta I_{2Cl(2,3\text{-nC})}$ and $\Delta I_{2Cl(1,3\text{-iC})}$ decrease with increasing carbon chain length of acid moiety of esters for all the homologous series of both chlorated *n*-propyl and isopropyl esters of both the lower branched and unbranched monocarboxylic acids. Those for higher esters do not decrease, but they fluctuate slightly.

Comparison of the retention index increments, $\Delta I_{2Cl(2,3\text{-nC})}$, for 2,3-dichloropropyl esters and, $\Delta I_{2Cl(1,3\text{-iC})}$, for 1,3-dichloroisopropyl esters indicate that the values of the former for two chlorine atoms in 2,3-dichloropropyl esters are greater than those of the latter for two chlorine atoms in 1,3-dichloroisopropyl esters. From interpretation of the retention index increments measured for chlorine in 3-chloropropyl esters, $\Delta I_{Cl(3\text{-nC})}$, and those for two chlorine atoms in 2,3-dichloropropyl esters $\Delta I_{2Cl(2,3\text{-nC})}$, we can expect that the values of the increments for chlorine in 2-chloropropyl esters, $\Delta I_{Cl(2\text{-nC})}$, will be lower than those for chlorine in 3-chloropropyl esters $\Delta I_{Cl(3\text{-nC})}$. This expection is in agreement with the results published by Korhonen[2].

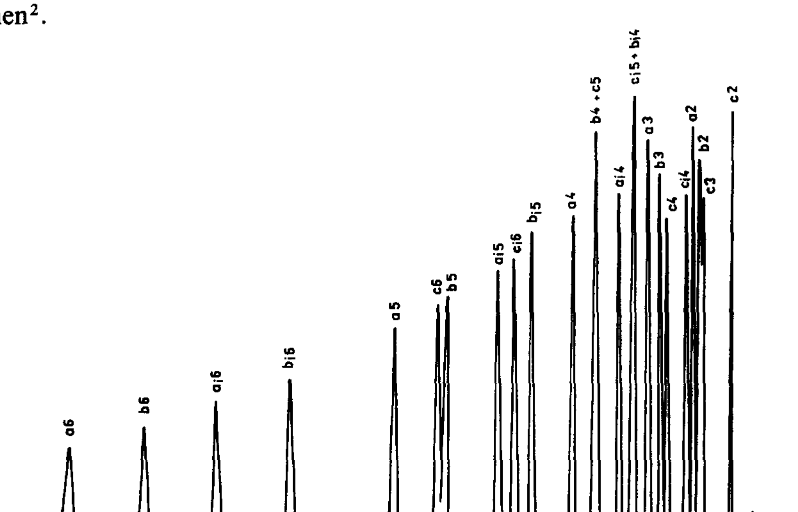

Fig. 1. Chromatogram of the separation of 2,3-dichloropropyl (a2–a6 and ai4–ai6), 1,3-dichloroisopropyl (b2–b6 and bi4–bi6), 3-chloropropyl (c2–c6 and ci4–ci6) of the lower n-C_2–C_6 and iso-C_4–C_6 carboxylic acids using an OV-101 glass capillary column (15 m × 0.22 mm I.D.) at 80°C.

The chromatogram of the separation of 3-chloropropyl, 2,3-dichloropropyl and 1,3-dichloroisopropyl esters of lower aliphatic carboxylic acids is shown in Fig. 1.

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