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Journal of Chromatography A, 665 (1994) 175–184

JOURNAL OF CHROMATOGRAPHY A

Relationship between structure and chromatographic behaviour of secondary alcohols and their derivatives separated by high-resolution gas chromatography with a modified β-cyclodextrin stationary phase☆

J. Krupčík*,[a], E. Benická[a], P. Májek[a], I. Skačáni[a], P. Sandra[b]

[a]*Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovak Republic*

[b]*Department of Organic Chemistry, University of Ghent, Krijgslaan 281, S-4, B-9000 Ghent, Belgium*

Abstract

Low-boiling secondary alcohols (2-butanol, 2-pentanol and 2- and 3-hexanol) and their methyl, pentyl, acetyl and trifluoroacetyl derivatives were separated by gas chromatography on a fused-silica capillary column coated with a mixture of OV-1701 and heptakis (6-O-*tert.*-butyldimethylsilyl-2,3-di-O-acetyl)-β-cyclodextrin (1:1). The retention of these solutes was studied by determining their separation factors (α) and this temperature dependences. The retention of enantiomers was correlated with optical activity and structural data obtained by theoretical calculations. It was demonstrated that the separation of enantiomers on a modified cyclodextrin stationary phase is governed *inter alia* by total molecule asymmetries.

1. Introduction

Fused-silica capillary columns coated with several alkyl and/or acyl α-, β- and γ-cyclodextrin (CD) derivatives are suitable for the enantiomeric separation of a wide variety of volatile compounds of different molecular size and functionality [1]. The gas chromatographic (GC) separation of more than 250 optical isomers has been demonstrated on capillary columns coated with diluted permethylated or perpentylated α-, β- and γ-CDs or heptakis(2,6-di-O-methyl-3-O-acetyl)-β-CD in OV-1701 stationary phase [2]. Schmalzing *et al.* [3] described a method for preparing capillary columns with a chemically bonded permethylated-β-CD stationary phase through polysiloxane linkages on which more than 100 enantiomers including hydrocarbons, alkyl halides, O-isopropyl-N-trifluoroamino acids, ketones, lactones, ethers, underivatized alcohols and diols were successfully separated. Most alcohols have a separation factor $\alpha = 1.04$ that is not dependent on the molecular mass (*e.g.*, pentanol and α-terpineol), but differences were found between similar compounds (*e.g.*, $\alpha = 1.06$ for 4-methyl-2-pentanol and $\alpha = 1.02$ for 4-methyl-3-pentanol). This clearly shows that the shape of the guest molecule plays an important role in chiral recognition expressed as a "shape selectivity" [3].

König and co-workers [4–8] and Li and Arm-

* Corresponding author.

☆ Part of this paper was presented at the *15th International Symposium on Capillary Chromatography, Riva del Garda, May 24–27, 1993.*

0021-9673/94/$07.00
SSDI 0021-9673(93)E1207-G

strong [9] showed that α-, β- and γ-CDs modified with higher alkyl (*e.g.*, penthyl) and/or acetyl groups are liquids suitable as stationary phases in capillary GC with fused-silica capillaries. Li and Armstrong [9] separated more than 150 pairs of enantiomers by GC on capillaries coated with hexakis(2,6-di-O-pentyl-3-O-trifluoroacetyl)-α-CD (DP-TFA-α-CD), heptakis (2,6-di-O-pentyl-3-O-trifluoroacetyl)-β-CD (DP-TMA-β-CD) or octakis(2,6-di-O-pentyl-3-O-trifluoroacetyl)-γ-CD (DP-TFA-γ-CD). Excellent resolutions of secondary alcohols, diols, amino alcohols, α-halocarboxylic acid esters, halohydrocarbons, glycidyl analogues, lactones, bicyclic compounds and pyran and furan derivatives were obtained on columns coated with DP-TFA-γ-CD. (*R*)- and (*S*)-2-chloropropionic acid methyl esters showed an α value of 2.69 on DP-TFA-β-CD, which is unusually large for a GC separation of enantiomers [9].

However, there is a lack of a systematic study on the interaction mechanisms between the "host" CD derivatives and the "guest" enantiomeric solutes. The applications selected to illustrate the enantioselectivity of a CD derivative are the result of trial and error [10].

The host–guest interaction via inclusion complex formation could be an explanation for the chiral resolution obtained with macrocyclic CD derivatives [11]. The CD macrocycle moreover recognizes the chiral host through an induced fit [11]. König *et al.* [11] stated that there are facts opposing inclusion complexes, as the enantiomers of substances that are too large to fit into the macrocyclic cavity can be successfully separated. This indicates that the enantioselective interaction could take place at the outer surface of a molecule [11].

The separation of enantiomers occurs through reversible diastereomer association between the solutes and the chiral environment. However, various kinds of binding interaction may also be involved [12]. The successful enantiomer separation of totally unfunctionalized saturated hydrocarbons on peralkyl derivatives of β- and γ-CD [11,12] demonstrates that Van der Waals interactions are sufficient for chiral recognition.

Armstrong *et al.* [13] observed enantioselective peak reversals for some enantiomeric compounds separated by GC under similar conditions on columns coated with derivatized α-, β- and γ-CD. Peak reversals have been observed between α- and β-CD and between β- and γ-CD, but not between α- and γ-CD, which is evidence that CD are "size-selective" phases.

König *et al.* [11] showed a reversal of the elution order of α-pinene, β-pinene and limonene enantiomers on columns coated with heptakis(6-O-methyl-2,3-di-O-pentyl)-β-CD and octakis(6-O-methyl-2,3-di-O-pentyl)-γ-CD, respectively. On the β-CD derivative all (−)-enantiomers eluted before the (+)-enantiomers, whereas on the γ-CD derivative the elution order was reversed [12]. On γ-CD derivative all the (+)-enantiomers studied by König *et al.* [11] were eluted before corresponding the (−)-derivatives.

König *et al.* [14] found that by GC analysis of terpineols on a capillary column coated with heptakis(2,6-di-O-methyl-3-O-pentyl)-β-CD the retention orders of enantiomeric pairs differing only in stereo configuration, *e.g.*, (+)-terpinen-4-ol eluted before the (−)-enantiomer, whereas (−)-α-terpineol eluted before the (+)-enantiomer. This clearly shows that in addition to other factors, stereo configuration can have a dominant influence on chiral interactions.

From systematic studies of the enantioselectivity of α-, β- and γ-CD derivatives having identical substitution patterns towards certain chiral substrates, it has become increasingly evident that not only inclusion, possibly supported by conformational changes, but also association in the outer sphere of the cyclodextrin cavity are responsible for chiral recognition [15]. The meaning of inclusion of solutes in a CD cavity is, however, often misunderstood. Inclusion in many instances does not mean that the whole molecule is located in the CD cavity. The accommodation of part of the molecule (alkyl or functional group) is also often considered as inclusion.

The investigation of the temperature dependence of separation factors also indicated that conformational parameters play an important role. Separation factors not only dramatically

decrease with increasing column temperature but may result in a reversal of elution order [16]. Reversal of the elution order is, according to Watanabe *et al.* [17], an indication of two different and temperature-dependent modes of diastereomeric host–gest interactions (molecules of the enantiomers with the molecules of the enantiomeric selective stationary phase). This may occur with members of a homologous series too [18].

The aim of this work was to study the separation of low-boiling secondary alcohols (2-butanol, 2-pentanol and 2- and 3-hexanols) and their methyl, acetyl and trifluoroacetyl derivatives by high-resolution (HR) GC on a fused-silica capillary column coated with a mixture of OV-1701 and heptakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-acetyl)-β-CD (1:1). For the derivatization of secondary alcohols similar reactions were used to those generally used for the preparation of modified cyclodextrin stationary phases in HRGC. The separation factors (α) and their temperature dependences were correlated with optical activities of the solutes and data obtained by the theoretical calculations.

2. Experimental

2.1. Gas chromatography

GC was performed with a Hewlett-Packard Model 5890 gas chromatograph equipped with a flame ionization detector and a split–splitless injector. Separations were performed on a 25 m × 0.30 mm I.D. fused-silica capillary column coated with a 0.125-μm film of the mixed stationary phase OV-1701 and heptakis(6-O-*tert.*-butyldimetylsilyl-2,3-di-O-acetyl)-β-CD (1:1) [19]. The GC oven was operated at various temperatures for isothermal experiments from 30 to 70°C in 10°C increments. Several experiments were performed at 15, 20 and 25°C. A volume of 0.05 or 0.1 μl of individual samples with concentrations of 10 mg/ml in diethyl ether was injected, except for 2-butanol trifluoroacetate, which was dissolved in methanol. Hydrogen was used as the carrier gas at an inlet pressure of 200 kPa. The split flow was 100 ml/min and the septum flow 3 ml/min. Nitrogen was used as the make-up gas at a flow-rate of 30 ml/min.

Chromatograms were registered by a HP 3396 integrator and using Peak 96 software were sent to a PC where they were evaluated with HPChem software (all products from Hewlett-Packard, Waldbronn, Germany).

2.2. Analytes

2-Butanol and 2-pentanol were obtained from Merck (Darmstadt, Germany). 2-Hexanol was prepared by hydration of 1-hexene [20].

Acetyl derivatives of the secondary alcohols were prepared by reaction with acetyl chloride or acetic anhydride [21]. Trifluoroacetyl derivatives of the secondary alcohols were prepared by reaction with trifluoroacetic anhydride [22]. Methyl and pentyl ethers of the secondary alcohols were prepared by alkylation with corresponding alkyl iodide [23,24]. A list of the compounds used and their abbreviations is given in Table 1.

Table 1
Abbreviations of analytes used

Compound	Abbreviation
2-Butanol	2-BuOH
2-Pentanol	2-PeOH
2-Hexanol	2-HexOH
3-Hexanol	3-HexOH
2-Butyl acetate	2-BuOCOCH$_3$
2-Pentyl acetate	2-PeOCOCH$_3$
2-Hexyl acetate	2-HexOCOCH$_3$
3-Hexyl acetate	3-HexOCOCH$_3$
2-Butyl trifluoroacetate	2-BuOCOCF$_3$
2-Pentyl trifluoroacetate	2-PeOCOCF$_3$
2-Hexyl trifluoroacetate	2-HexOCOCF$_3$
3-Hexyl trifluoroacetate	3-HexOCOCF$_3$
Methyl 2-butyl ether	Me-2-BuEt
Methyl 2-pentyl ether	Me-2-PeEt
Methyl 2-hexyl ether	Me-2-HexEt
Pentyl 2-butyl ether	Pe-2-BuEt
Pentyl 2-pentyl ether	Pe-2-PeEt
Pentyl 2-hexyl ether	Pe-2-HexEt
Pentyl 3-hexyl ether	Pe-3-HexEt

2.3. Reagents

Diethyl ether, methanol, acetyl chloride and trifluoroacetic anhydride were obtained from Merck (Darmstadt, Germany).

2.4. Theoretical calculations

Conformations corresponding to energy minima of hydroxy, methoxy, pentoxy, acetyl and trifluoroacetyl derivatives of 2-butane, 2-

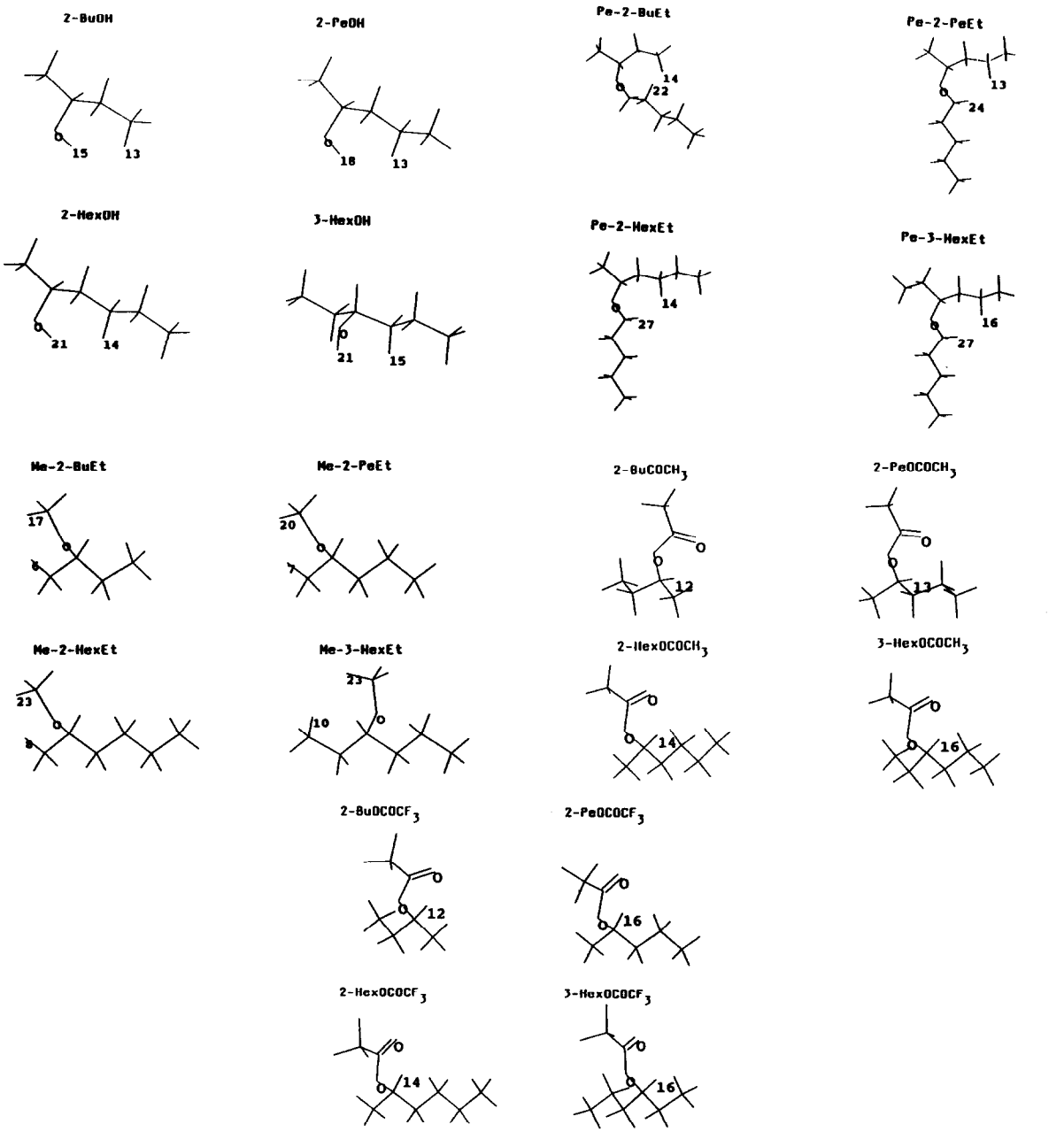

Fig. 1. Stick models of the optimized structures found for the considered molecules by the AM1 method. For illustration oxygen atoms are labelled and atoms with critical intra-atomic distances are numbered.

pentane and 2- and 3-hexane were calculated with HyperChem (trademark of Autodesk Inc.) for Windows Version 2.0. In searching for the optimum conformation of the considered derivatives on the semi-empirical level the AM1 method [25] was used.

Structures of the solutes expressed by conformations of molecules corresponding to energy minima in the gas phase found by AM1 are shown in Fig. 1. Some data that characterize the electronic structure (net charges and dipole moments) of the compounds in optimized conformations are given in Table 2. In the last two columns of Table 2 critical distances (lengths in Å) are given for atoms that substantially influence free rotation along the C–C bond.

The optimum conformation of permethylated-β-CD and heptakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-acetyl)-β-CD shown in Fig. 2 was found by the molecular mechanics calculation MM+ method [26] in the gas phase.

The starting geometries of the considered molecules were designed by the molecular editor which is built in the HyperChem software. The RHF gradient optimization of the model built structure was performed and a value of 0.02 kcal/Å · mol was used as a convergence criterion for the RMS gradient method. The standard parameterization MM+ [26] was used for potentials in the molecular mechanics calculations and the same value of RMS gradient was chosen for the convergence. The energy minima are, however, very flat and often separated by a small rotation energy barrier (several kCal/mol) and consequently local minima can be found with non-expected conformations, as we have found for 2-butylacetate and 2-butyltrifluoroacetate. To avoid this discrepancy different starting structures were designed for all studied compounds. All calculations were performed on a 50-MHz IBM PC/486 computer.

3. Results and discussion

The separation of 2-butanol, 2-pentanol and 2- and 3-hexanols by GC on a fused-silica capillary column coated with the mixture of OV-1701 and

Table 2
Net changes, dipole moments and critical intra-atomic distances found by the AM1 method for molecules of the considered compounds with optimized conformations

Compound	Net charge (e)	Dipole moment (D)	Critical distance	
			Atoms	Length (Å)
2-BuOH	$29.1 \cdot 10^{-3}$	1.64	H13–H15	2.15
2-PeOH	$29.4 \cdot 10^{-3}$	1.66	H13–H18	2.14
2-HexOH	$29.6 \cdot 10^{-3}$	1.67	H14–H21	2.13
3-HexOH	$23.7 \cdot 10^{-3}$	1.53	H15–H21	2.12
2-BuOCOCH$_3$	$35.8 \cdot 10^{-3}$	1.80	O7–H12	2.32
2-PeOCOCH$_3$	$30.8 \cdot 10^{-3}$	1.76	O9–H13	2.23
2-HexOCOCH$_3$	$29.9 \cdot 10^{-3}$	1.74	O10–H14	2.21
3-HexOCOCH$_3$	$31.3 \cdot 10^{-3}$	1.79	O10–H16	2.23
2-BuOCOCF$_3$	$38.7 \cdot 10^{-3}$	3.12	O7–H12	2.38
2-PeOCOCF$_3$	$36.0 \cdot 10^{-3}$	3.15	O9–H16	2.29
2-HexOOCF$_3$	$35.0 \cdot 10^{-3}$	3.11	O10–H14	2.27
2-HexOCOCF$_3$	$35.3 \cdot 10^{-3}$	3.11	O10–H16	2.29
Me-2-BuEt	$25.6 \cdot 10^{-3}$	1.30	H6–H17	2.20
Me-2-PeEt	$26.0 \cdot 10^{-3}$	1.28	H7–H20	2.20
Me-2-HexEt	$26.1 \cdot 10^{-3}$	1.28	H8–H23	2.20
Me-3-HexEt	$26.4 \cdot 10^{-3}$	1.30	H10–H23	2.43
Pe-2-BuEt	$32.2 \cdot 10^{-3}$	1.39	H14–H17	2.28
Pe-2-PeEt	$31.2 \cdot 10^{-3}$	1.24	H13–H23	2.27
Pe-2-HexEt	$31.4 \cdot 10^{-3}$	1.25	H14–H27	2.26
Pe-3-HexEt	$30.4 \cdot 10^{-3}$	1.19	H16–H27	2.29

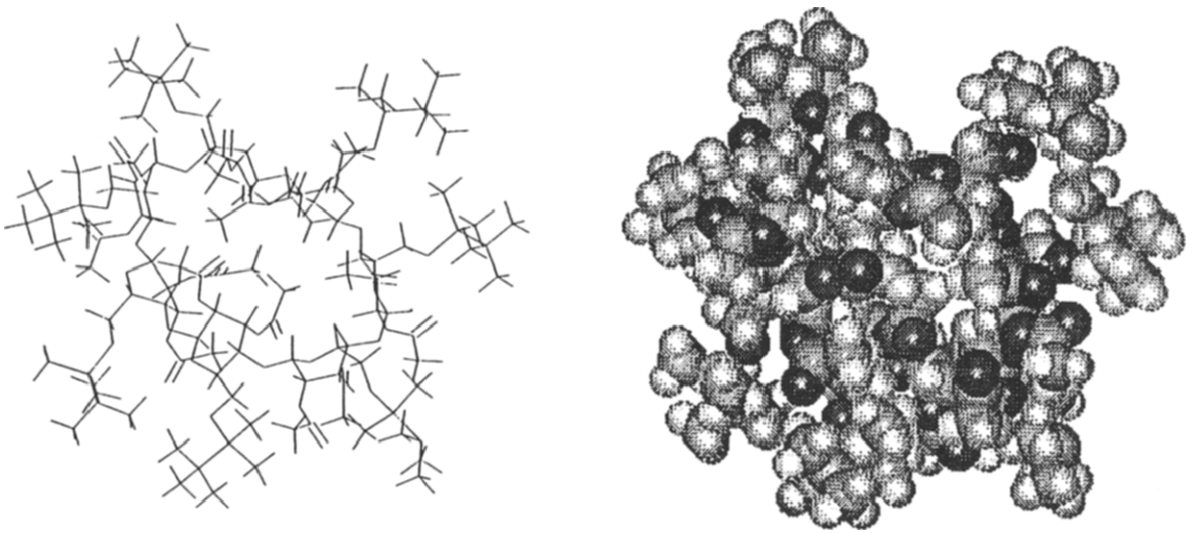

Fig. 2. Stick and spherical models of optimized structure of heptakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-acetyl)-β-CD as found by the MM+ method.

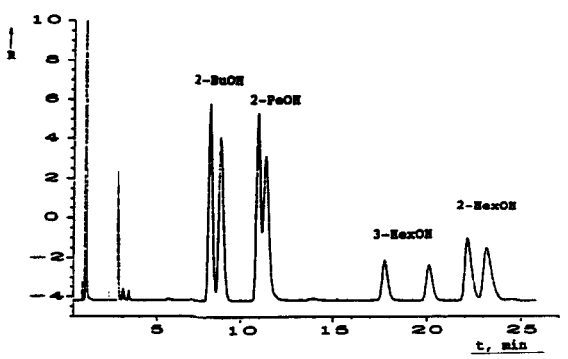

Fig. 3. Separation of enantiomers of 2-butanol, 2-pentanol and 2- and 3-hexanols by capillary GC with heptakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-acetyl)-β-CD at 40°C.

heptakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-acetyl)-β-CD is shown in Fig. 3. A reasonable separation of the enantiomers of 2-butanol and 2-hexanol, an excellent separation of the 3-hexanols and a relatively poor separation of the 2-pentanols is observed. In Table 3, published data for the optical rotation of some secondary alcohols are given. It follows from Table 3 that the chirality of the alcohols decreases with increase in molecular mass and (*R*)-enantiomers turn the polarized light to left (−) and (*S*)-enantiomers to the right (+). Since the optical rotation is a molecular property, a decrease of optical rotation with molecular mass is expected [29]. It is further evident that the separation of alcohols in

Table 3
Optical rotations of some secondary alcohols (from ref. 30)

Compound	Temperature (°C)	[α]	Note
(*R*)-(−)-2-Butanol	20	−13	Neat
(*S*)-(+)-2-Butanol	20	+13	Neat
(*R*)-(−)-2-Pentanol	20	−13	Neat
(*S*)-(+)-2-Pentanol	20	+13	Neat
(*R*)-(−)-2-Hexanol	24	−11	Neat
(*S*)-(+)-2-Hexanol	24	+11	Neat
(*R*)-(−)-3-Hexanol[a]	20	−7.2	Neat
(*S*)-(+)-3-Hexanol[a]	20	+6.8	In chloroform

[a] From ref. 31.

Fig. 3 does not fully correlate with the data in Table 3 as for 2-pentanols and 3-hexanols. The discrepancies in these correlations can be explained by the specific interactions of different shapes of alcohol molecules (see Fig. 1) with a modified cyclodextrin stationary phase. The enantiomers of the alcohols with an ethyl group linked to an optically active carbon atom (2 butanol and 3-hexanol) show a specific molecular shape (a six-membered ring, which hinders free rotation). This asymmetry is, however, enlarged with the interaction of the considered compounds with the modified CD stationary phase and these enantiomers are separated much better in Fig. 3 than those with a longer alkyl chain (2-pentanol and 2-hexanol).

In Table 4 a cyclodextrin derivative exhibits a lower optical activity than the corresponding native compound. As the diastereometric complexes are responsible for the chiral recognition of secondary alcohols, and cyclodextrins turn the light to the right (+), the retention of (*R*)-(−)-enantiomers is higher than that of (*S*)-(+)-enantiomers, which has already been confirmed by analysis of pure enantiomers [27]. As the relationship between the optical properties both solutes and CDs and the separation of solute enantiomers on CDs is very complex and includes *inter alia* the type of interaction, position of interaction and separation temperature, we shall discuss them separately [28].

The enantiomeric resolution of secondary butyl chloride, butyl bromide and butyl iodide, which according to Venema *et al.* [29] can be explained by correlation of retention with the molecular volumes, can also be explained by correlation of the retention with the molecule polarizabilities. This parameter, connected with both the molecular volumes and optical activities for the considered alkyl halides, increases with increase in the relative atomic mass of the halide [*e.g.*, $M_r(I) > M_r(Br) > M_r(Cl)$].

The structures of methyl 2-alkyl ethers do not differ substantially and the separation of their enantiomers is also comparable (Fig. 4). Substitution of hydrogen atoms in the OH groups for cyclodextrin derivatives leads to permethylated cyclodextrins which show lower optical activity than exhibited by the native cyclodextrins (Table 4). This could be a reason why diastereomeric complexes between a given cyclodextrin stationary phase and methyl 2-alkyl ethers are weaker than those with secondary alcohols. The separation in Fig. 4 is not as good as that in Fig. 3. The

Table 4
Optical rotations of α-, β- and γ-cyclodextrins and some of their derivatives [11]

Cyclodextrin derivative	$[\alpha]_D^{22}$ [a]
α-Cyclodextrin	153.0[b]
β-Cyclodextrin	162.0[b]
γ-Cyclodextrin	176.1[b]
Hexakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-pentyl)-α-cyclodextrin	68.0
Heptakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-pentyl)-β-cyclodextrin	65.2
Octakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-pentyl)-γ-cyclodextrin	74.4 ($c = 0.7$)
Hexakis(2,3-di-O-pentyl)-α-cyclodextrin	41.7
Heptakis(2,3-di-O-pentyl)-β-cyclodextrin	108.9
Octakis(2,3-di-O-pentyl)-γ-cyclodextrin	104.6 ($c = 0.7$)
Hexakis(6-O-acetyl-2,3-di-O-pentyl)-α-cyclodextrin	40.8 ($c = 0.8$)
Heptakis (6-O-acetyl-2,3-di-O-pentyl)-β-cyclodextrin	81.1
Hexakis(6-O-butyryl-2,3-di-O-pentyl)-α-cyclodextrin	71.5
Heptakis(6-O-butyryl-2,3-di-O-pentyl-β-cyclodextrin	83.5 ($c = 0.2$)
Octakis(6-O-methyl-2,3-di-O-pentyl)-γ-cyclodextrin	80.9 ($c = 0.7$)

[a] Solvent for optical rotation measurements was chloroform ($c = 1$ unless stated otherwise). Solvent for optical rotation measurements of underivatized CDs was water.
[b] From ref. 30.

substitution of hydrogen atoms in OH groups of secondary alcohols containing the pentyl group leads to pentyl 2-alkyl ethers, which were not separated on the capillary column in the temperature range 30–80°C. Possible reasons why these compounds are not separated are discussed elsewhere [28].

The separations of 2-pentyl and 2-hexyl acetate enantiomers are comparable (Fig. 5). However, the separation of 3-hexyl acetate enantiomers is poorer and 2-butyl acetate enantiomers do not separate under the given conditions. These results correlate with the structures shown in Fig. 1. The enantiomers of 2-butyl acetate were partially resolved at 15 and 100°C, probably with reversal of retention order. The reversal of the retention of 2-butyl acetate enantiomers with temperature is currently under study and will be reported elsewhere [28].

The structures of 2-alkyl trifluoroacetates were similar (see Fig. 1) and the separation of these compounds was also similar (Fig. 6).

The energy of diastereomeric interactions can be found from the differences in the interaction energies of (*R*)-(−)- and (*S*)-(+)-enantiomers with the cyclodextrin stationary phase. This difference can be found from the semi-logarithmic dependence of the selectivity factor (ln α) on the reciprocal of absolute temperature ($1/T$).

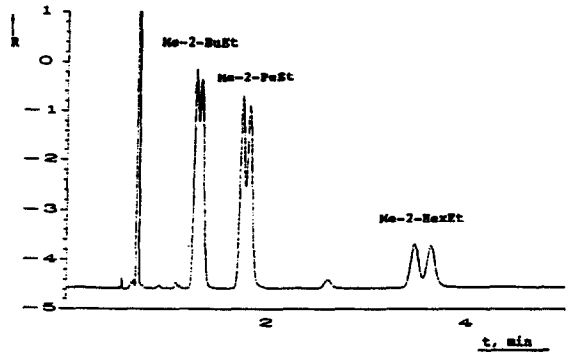

Fig. 4. Separation of enantiomers of methyl 2-butyl, methyl 2-pentyl and methyl 2-hexyl ethers by capillary GC with heptakis(6 - O - *tert.* - butyldimethylsilyl - 2,3 - di - O - acetyl)-β-CD at 40°C.

Linear equations for these dependences are given in Table 5. The correlation coefficients in Table 5 show acceptable linearity. The data for 2-butyl acetate are not included as only poor resolution was obtained in the range 15–100°C.

The slopes of the dependences are characteristic of the homologous series and characterize the differences between the diastereomeric interactions of enantiomeric pairs with the stationary phase. The relationships between the slopes and intercepts of the dependences in Table 5 are under study and will be published elsewhere [28].

Table 5
Semi-logarithmic dependence of separation factor (α) of the considered compounds on temperature ($1/T$)

Compound	Equation	Correlation coefficient
2-BuOH	$\ln \alpha = (92.6/T) - 0.221$	0.9939
2-PeOH	$\ln \alpha = (72.3/T) - 0.190$	0.9998
2-HexOH	$\ln \alpha = (52.8/T) - 0.124$	0.9925
3-HexOH	$\ln \alpha = (210.3/T) - 0.546$	0.9995
2-PeOCOCH$_3$ [a]	$\ln \alpha = (258.7/T) - 0.750$	0.9989
2-HexOCOCH$_3$ [a]	$\ln \alpha = (236.5/T) - 0.705$	0.9951
3-HexOCOCH$_3$ [a]	$\ln \alpha = (188.1/T) - 0.563$	0.9960
2-BuOCOCF$_3$	$\ln \alpha = (194.7/T) - 0.476$	0.9964
2-PeOCOCF$_3$	$\ln \alpha = (202.2/T) - 0.500$	0.9989
2-HexOCOCF$_3$	$\ln \alpha = (201.7/T) - 0.499$	0.9994
Me-2-BuEt[b]	$\ln \alpha = (124.5/T) - 0.344$	–
Me-2-PeEt[b]	$\ln \alpha = (152.8/T) - 0.447$	–
Me-2-HexEt[b]	$\ln \alpha = (171.7/T) - 0.511$	–

[a] Calculated from measurements obtained at 30, 40 and 50°C.
[b] Calculated from measurements obtained at 30 and 40°C.

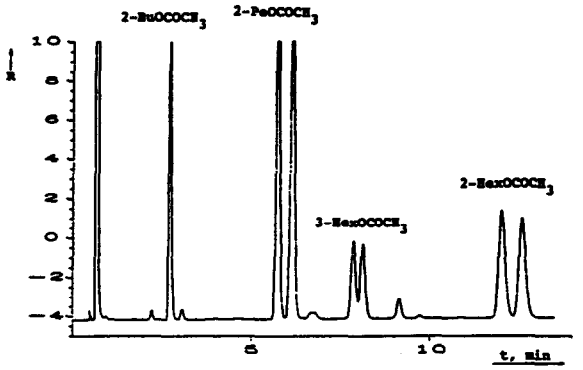

Fig. 5. Separation of enantiomers of 2-butyl, 2-pentyl and 2- and 3-hexyl acetates by capillary GC with heptakis(6-O-*tert.*-butyldimethylsilyl-2,3-di-O-acetyl)-β-CD at 40°C.

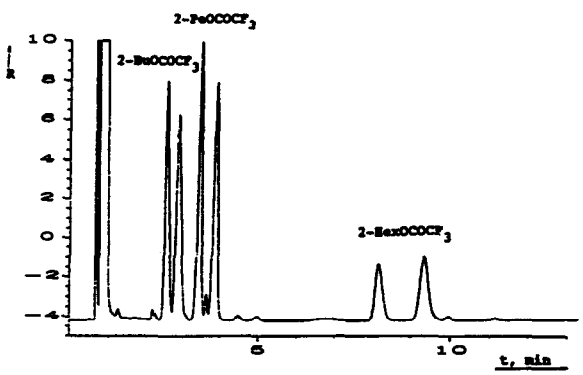

Fig. 6. Separation of enantiomers of 2-butyl, 2-pentyl and 2- and 3-hexyl trifluoroacetates by capillary GC with heptakis (6-O-*tert.*-butyldimethylsilyl-2,3-di-O-acetyl)-β-CD at 40°C.

4. Acknowledgements

The authors thank the European Community for a Tempus Project Grant (JEP-0379-90/2) and the Slovak Ministry of Education for Grant No. 1/990927/92.

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