Separation of C_{11}–C_{14} branched-chain alcohols by high-resolution gas chromatography on a modified β-cyclodextrin stationary phase

J. Krupčík[*,a], I. Špánik[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

The separation of C_{11}–C_{14} branched-chain alcohols and their acetyl derivatives by gas chromatography on a fused-silica capillary column coated with heptakis (6-O-*tert*.-butyldimethylsilyl-2,3-di-O-diacetyl)-β-cyclodextrin dissolved in OV-1701 (1:1) was studied. It is demonstrated that the separation of positional isomers of these alcohols and their acetyl derivatives on this stationary phase is poorer than that on Carbowax 20M. Enantiomers of the alcohols were resolved on this stationary phase at temperatures below 110°C, whereas enantiomers of their acetyl derivatives were not resolved under similar conditions.

1. Introduction

Cyclodextrins (CDs) and their derivatives are used for the separation of both geometric and enantiomeric isomers. The separation of the former depends on the inclusion effects, whereas the separation of the latter on modified CDs can be successful also for molecules with diameters that are substantially larger than the diameters of the CD cavities and therefore inclusion in a cavity is excluded. Fused-silica capillary columns coated with several alkyl and/or acyl α-, β- and γ-CD derivatives are suitable for the enantiomeric separation of a wide variety of volatile compounds of different molecular size and functionality [1]. It has become increasingly evident that not inclusion but reversible diastereomeric

association in the outer sphere of the CD cavity, possibly supported by conformational changes ("induced fit"), is responsible for chiral recognition [2].

The aim of this work was to study the separation of positional and enantiomeric isomers of C_{11}–C_{14} branched-chain alcohols (obtained by hydroformylation of C_{10}–C_{13} *n*-alkenes) by gas chromatography (GC) on a fused-silica capillary column coated with a 1:1 mixture of OV-1701 and heptakis (6-O-*tert*.-butyldimethylsilyl-2,3-di-O-diacetyl)-β-CD.

2. Experimental

GC was performed with a Hewlett-Packard (HP) Model 5890 gas chromatograph equipped with flame ionization detector and a split–split-

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* Corresponding author.

less injection port. Separations were performed on a 25 m × 0.33 mm I.D. fused-silica capillary column coated with a 0.125-μm film of the mixed stationary phase of OV-1701 and heptakis (6-O-*tert.* - butyldimethylsilyl-2,3-di-O-diacetyl)-β-CD (1:1). The GC oven was operated at various temperatures for isothermal experiments from 80 to 140°C in 10°C increments. The chromatograms were registered by an HP 3396 integrator and using Peak 96 software were sent to a PC where they were evaluated with HP Chem software (all products from Hewlett-Packard, Waldbronn, Germany).

The alcohol samples were prepared by hydroformylation of C_{10}–C_{13} *n*-alkenes using a procedure described previously [4]. A summary of the alcohols expected in the hydroformylation products of C_{10}–C_{13} *n*-alkenes and their labelling as used in this paper is given in Table 1.

It is convenient formally to consider the CH_2OH group as the functional group of alcohols in the hydroformylation products. In this way all alcohols obtained by the hydroformylation of *n*-alkenes (except for 1-ols) can be regarded as analogous to secondary alcohols. For instance, 2-butyl-nonanol:

$$CH_3-(CH_2)_3-\underset{\underset{CH_2OH}{|}}{CH}-(CH_2)_6-CH_3$$
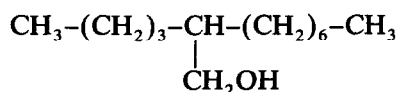
is structurally similar to 5-dodecanol, and we label it as 12–5 to indicate the number of the

carbon atoms in the *n*-alkyl chain by the first number and the position of the CH_2OH group in this chain by the second number.

Acetyl derivatives of the alcohols were prepared by acetylation with an excess of acetyl chloride as described [4].

3. Results and discussion

3.1. Separation of positional isomers

The separation of the alcohols listed in Table 1 by GC on a fused-silica capillary column coated with the mixture of OV-1701 and heptakis (6-O-*tert.*-butyldimethylsilyl-2,3-di-O-diacetyl)-β-CD (1:1) at 120°C is shown in Fig. 1 and the separation of the acetyl derivatives of these alcohols under similar conditions in Fig. 2. From a comparison of these figures, it can be concluded that the separation of alcohols is influenced mainly by hydrogen bonds. The influence of dispersive interactions of the alkyl chain on the separation of isomers of branched-chain alcohols is less pronounced. For acetyl derivatives of alcohols, where the hydrogen atom in the hydroxyl group is replaced by an acetyl group, acetyl derivatives of alcohols cannot interact with the stationary phase with hydrogen bonds. Therefore, the contribution of the shape of the alkyl chain interaction with the stationary phase to the retention substantially influences

Table 1
List and labels of alcohols obtained by hydroformylation of C_{10}–C_{13} *n*-alkenes

| Alcohol	Label	Alcohol	Label
1-Undecanol	10–1	2-Methyl-1-dodecanol	12–2
2-Methyl-1-decanol	10–2	2-Ethyl-1-undecanol	12–3
2-Ethyl-1-nonanol	10–3	2-Propyl-1-decanol	12–4
2-Propyl-1-octanol	10–4	2-Butyl-1-nonanol	12–5
2-Butyl-1-heptanol	10–5	2-Pentyl-1-octanol	12–6
1-Dodecanol	11–0	1-Tetradecanol	13–1
2-Methyl-1-undecanol	11–2	2-Methyl-1-tridecanol	13–2
2-Ethyl-1-decanol	11–3	2-Ethyl-1-dodecanol	13–3
2-Propyl-1-nonanol	11–4	2-Propyl-1-undecanol	13–4
2-Butyl-1-octanol	11–5	2-Butyl-1-decanol	13–5
2-Pentyl-1-heptanol	11–6	2-Pentyl-1-nonanol	13–6
1-Tridecanol	12–1	2-Hexyl-1-octanol	13–7
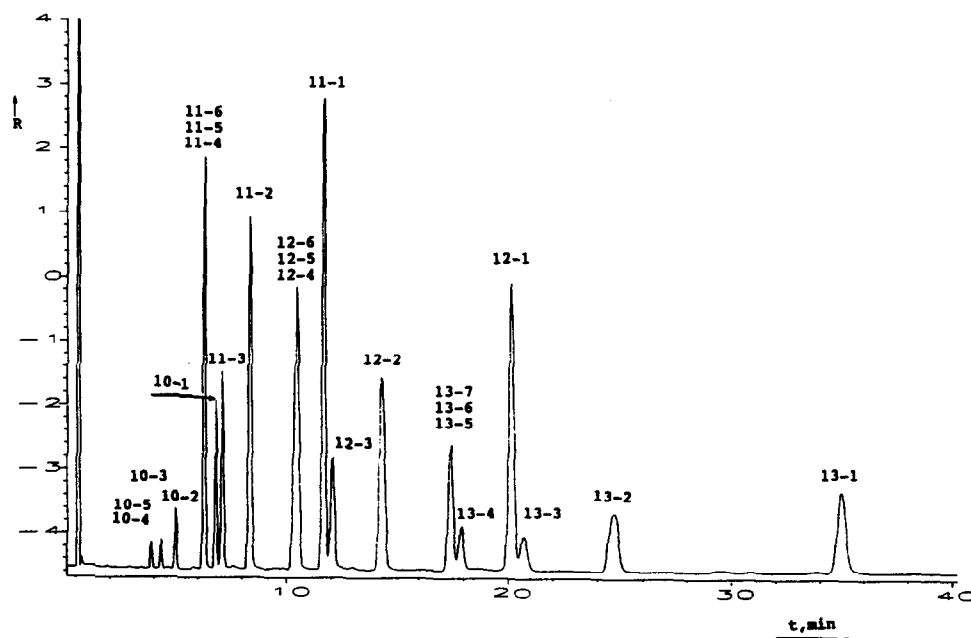
Fig. 1. Separation of alcohols at 120°C. For identification of peaks, see Table 1.
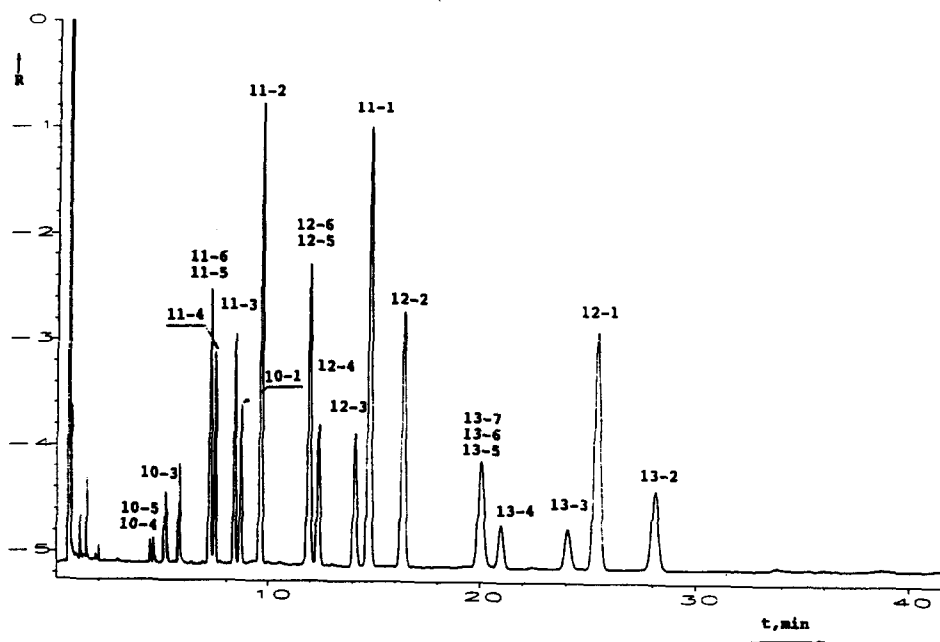
Fig. 2. Separation of acetyl derivatives of alcohols at 120°C. For identification of peaks see Table 1.

the separation. This is the reason why the resolution of positional isomers of acetyl derivatives (Fig. 2) is better than that of alcohols (Fig. 1).

Comparison of Figs. 1 and 2 with the chromatograms obtained for alcohols and their acetyl derivatives on a capillary column coated with Carbowax 20M [4] shows that Carbowax 20M is more suitable for the separation of positional isomers of branched-chain alcohols and their acetyl derivatives. Fig. 1 shows no separation of positional isomers of -4 and -5 compounds, whereas on Carbowax 20M they were fully resolved [4]. Fig. 2 shows no separation of positional isomers of -5 and -6 compounds, whereas on Carbowax 20M they were resolved [4].

The identification of branched-chain alcohols in the hydroformylation products was described previously [4]. In this work, the dependence of $\log t'_R$ on carbon atom number (n) in the alkyl chain was used for the tentative identification of sample constituents, as demonstrated in Fig. 3 for acetyl derivatives of the alcohols at 110°C. Straight lines were found for 1-, 2-, 3-, 4- and 5-positional isomers; with the 5-isomer, how-
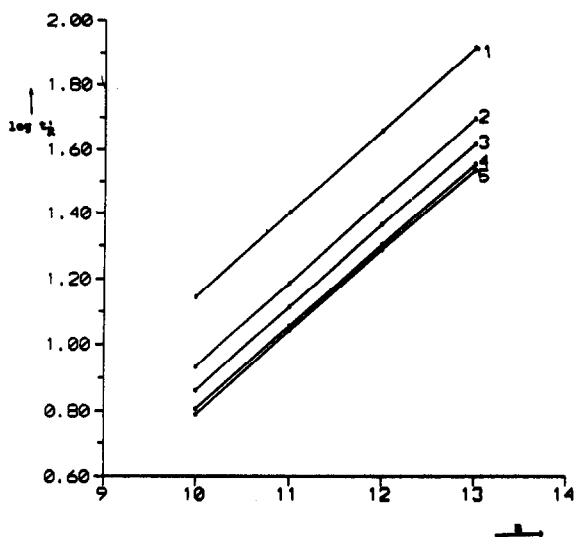
ever, the isomers 6- or 6- + 7-isomers are also eluted.

Separations of branched-chain undecanols and dodecanols and their corresponding acetyl derivatives at 100°C are shown in Figs. 4 and 5. Comparison of Figs. 4 and 5 with Figs. 1 and 2 shows a very small influence of temperature on the separation of the positional isomers for both alcohols and their acetyl derivatives.

3.2. Separation of enantiomeric isomers

In contrast to the small influence of temperature on the separation of the positional isomers of alcohols and their acetyl derivatives, a decrease in temperature significantly improved the separation of enantiomeric alcohols, as follows from a comparison of Figs. 1 and 4 (split peaks 10–3, 10–2, 11–4 and 11–2 in Fig. 4). From Figs. 2 and 5, virtually no influence of a decrease in temperature on the separation of the acetyl derivatives is observed. Further improvement in the separation of enantiomeric pairs is shown in Fig. 6, where branched-chain alcohols are separated at 90°C.

4. Conclusions

The separation of C_{11}–C_{14} branched-chain alcohols and their acetyl derivatives on a fused-silica capillary column coated with heptakis (6-O-tert.-butyldimethylsilyl-2,3-di-O-diacetyl)-β-CD dissolved in OV-1701 (1:1) leads to following conclusions. (i) Acetyl derivatives of positional isomers of branched-chain alcohols are better separated than the parent alcohols at given experimental conditions. (ii) The separation of positional isomers of both branched-chain alcohols and their acetyl derivatives on this chiral column is poorer than that on Carbowax 20M, which indicates that there is no inclusion of solutes on this type of modified cyclodextrin. (iii) The successful separation of enantiomeric pairs of several C_{11}–C_{14} branched-chain alcohols was achieved at 90°C. (iv) No enantiomeric separation of acetyl derivatives of C_{11}–C_{14} branched-chain alcohols was achieved at 70–120°C.

Fig. 3. Dependence of $\log t'_R$ on number of carbon atoms in the n-alkyl chain (n) for acetyl derivatives of alcohols at 110°C.

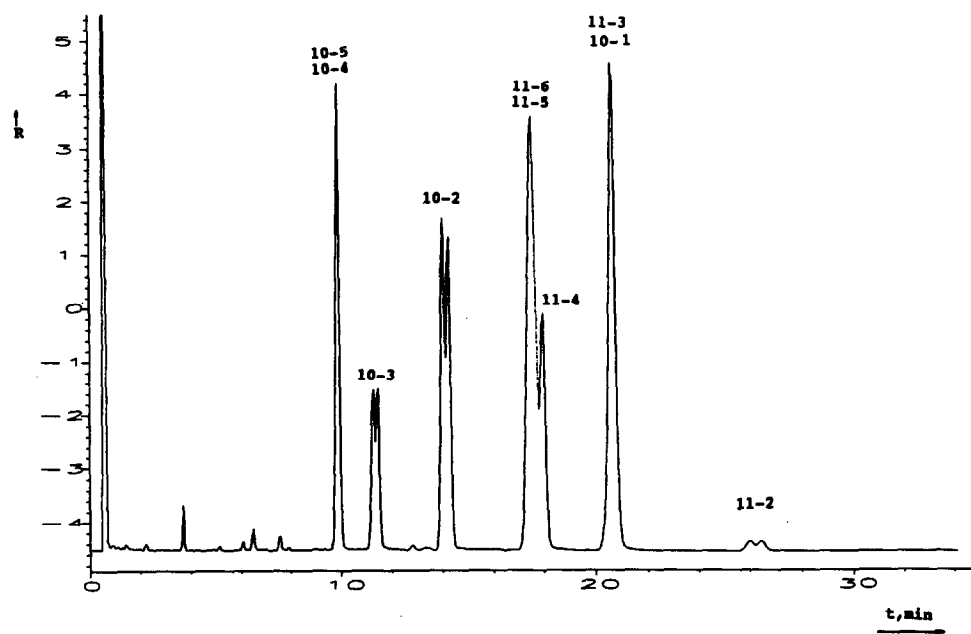*J. Krupčík et al. / J. Chromatogr. A 665 (1994) 163–168*

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Fig. 4. Separation of branched-chain undecanols and dodecanols at 100°C. For identification of peaks, see Table 1.
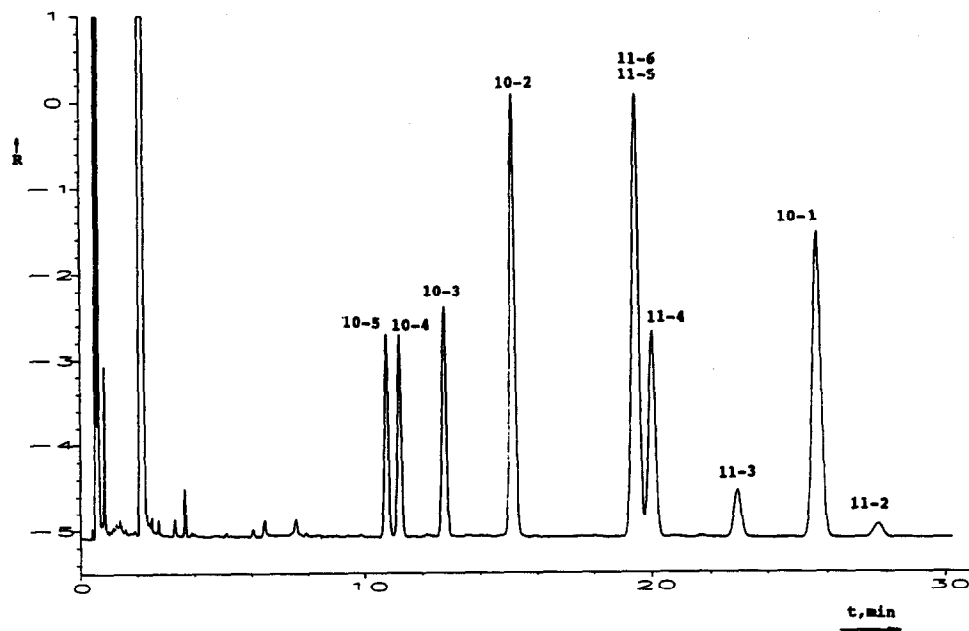

Fig. 5. Separation of acetyl derivatives of branched-chain undecanols and dodecanols at 100°C. For identification of peaks, see Table 1.
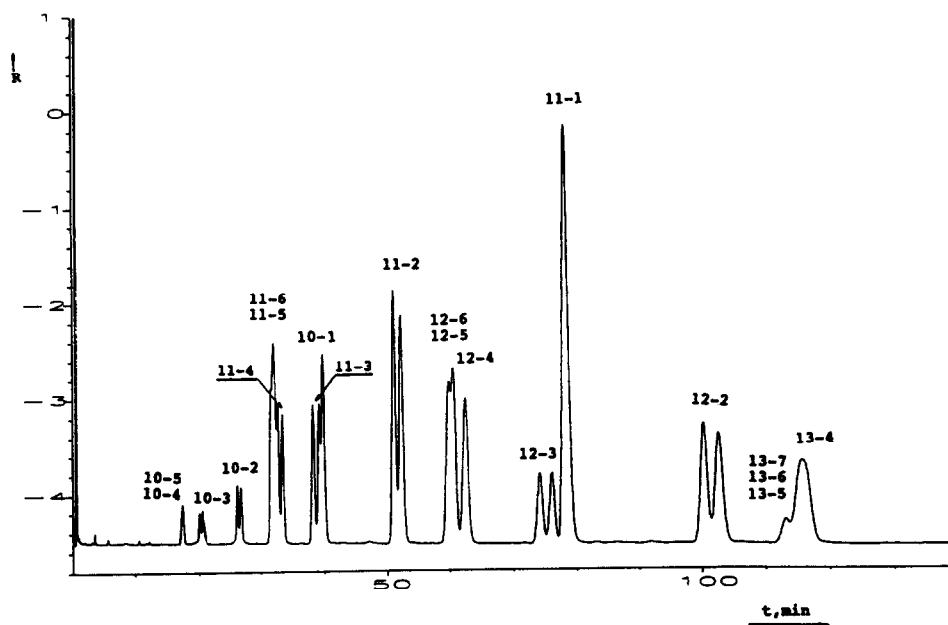
Fig. 6. Separation of C_{11}–C_{14} branched-chain alcohols at 90°C. For identification of peaks, see Table 1.

5. Acknowledgements

6. References

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