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Note

Separation of α - and β -pinene into enantiomers in gas-liquid chromatography systems via α -cyclodextrin inclusion complexes

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Chromatographic separation of enantiomeric unsaturated hydrocarbons presents a number of difficulties caused by weak and not very selective intermolecular interactions in the common gas and liquid chromatographic systems. Use of optically active organic stationary phases cannot be realized on the basis of the "three-point-attachment concept" of Dalglish¹; olefinic molecules do not contain any functional groups suitable for forming the necessary hydrogen bonds for a specific attachment of the enantiomer to the molecules of the stationary phase. Charge-transfer interactions with optically active acceptor molecules as parts of a stationary phase can be assumed to be too weak to separate olefins into their enantiomers².

Recently we reported the successful resolution of mandelic acid³ and its derivatives⁴ into enantiomers using β -cyclodextrin (β -CD) as a chiral component of the mobile phase in reversed-phase high-performance liquid chromatographic systems. On the other hand, we found that β -CD works very well as a selective agent for the separation of *o*-, *m*- and *p*-xylenes and an ethylbenzene mixture in a gas-liquid chromatographic system using formamide as a matrix medium⁵.

These results prompted us to investigate CDs as potential optically active selective agents for a chromatographic separation of non-polar chiral olefins into enantiomers. The aim of this work was to determine the applicability of CDs for the resolution of the useful terpenoid olefins α - and β -pinene into their enantiomers.

EXPERIMENTAL

Supplies of α - and β -CD were obtained from Chinoin (Budapest, Hungary). Celite (80–120 mesh) for gas chromatography was from B.D.H. (Poole, U.K.), α - and β -pinene were commercial products (Glidden Organics, U.S.A.) having the following optical rotations: (+)- α -pinene, $[\alpha]_D^{20} + 20.8^\circ$; (–)- α -pinene, $[\alpha]_D^{20} - 35.0^\circ$; (–)- β -pinene, $[\alpha]_D^{20} - 16.9^\circ$. All other materials were of analytical or reagent grade and were used without further purification.

Chromatographic studies were performed using a Hewlett-Packard 7620A gas chromatograph equipped with dual flame ionization detectors. Glass columns (2 m \times 4 mm I.D.) were used. During the course of all experiments, special care was taken to maintain fixed values for the inlet pressure (2.75 atm) and helium flow-velocity (50

ml/min). Samples (0.2 μ l) were injected with Hamilton microsyringes. The retention time of each compound was determined as the mean value (relative error < 0.5%) from each of the series of six injections. Column packings, *i.e.* celite covered with formamide solution of α - or β -CD were prepared according to the procedure described earlier⁵. In all experiments two columns were used: the first contained formamide solution of a given concentration of α - or β -CD and the second, containing only formamide, was used as a reference. This two-column system enabled us to perform comparative measurements and excluded many sources of error. The studies were carried out in the temperature range 50–70°C.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the chromatograms of samples enriched in (+)- α -pinene and (-)- β -pinene, respectively. Examination of the chromatograms shown (Figs. 1 and 2) indicates that both α - and β -CD dissolved in formamide form inclusion complexes with α - and β -pinene. Comparison of the values of the adjusted retention times (*e.g.* at 50°C, t' for α -pinene- α -CD = 2 min 42.4 sec; α -pinene- β -CD = *ca.* 23.5 min; β -pinene- α -CD = 3 min 1.2 sec; β -pinene- β -CD = *ca.* 40 min) shows that the β -CD complexes are more stable than those of the corresponding α -CD or that the stoichiometry of the complexes formed is different for both CDs (*i.e.* more rich in β -CD molecules). A distinct asymmetry of the elution curves in the case of the β -CD containing column (at 50°C) is also observed.

The remarkable fact is that molecular inclusion in α -CD molecules exhibits enantioselectivity both towards α - and β -pinene. The values of the separation factor evaluated for the conditions given in Figs. 1 and 2 are $\alpha_{+/-}$ = 1.76 (α -pinene) and

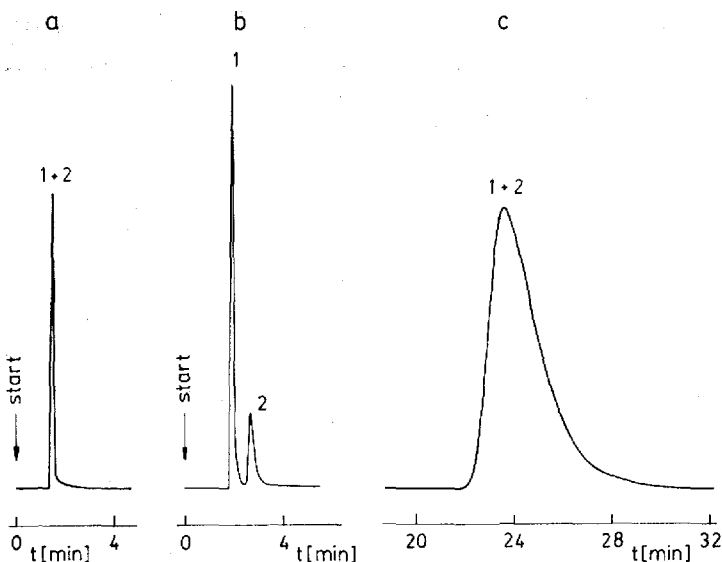


Fig. 1. Chromatograms of (+)- α -pinene ($[\alpha]_D^{20} + 20.8^\circ$) obtained at 50°C on columns filled with Celite covered by (a) formamide, (b) 1.23 mol % α -CD in formamide, (c) 1.18 mol % β -CD in formamide. Peaks 1 = (+)- α -pinene; 2 = (-)- α -pinene.

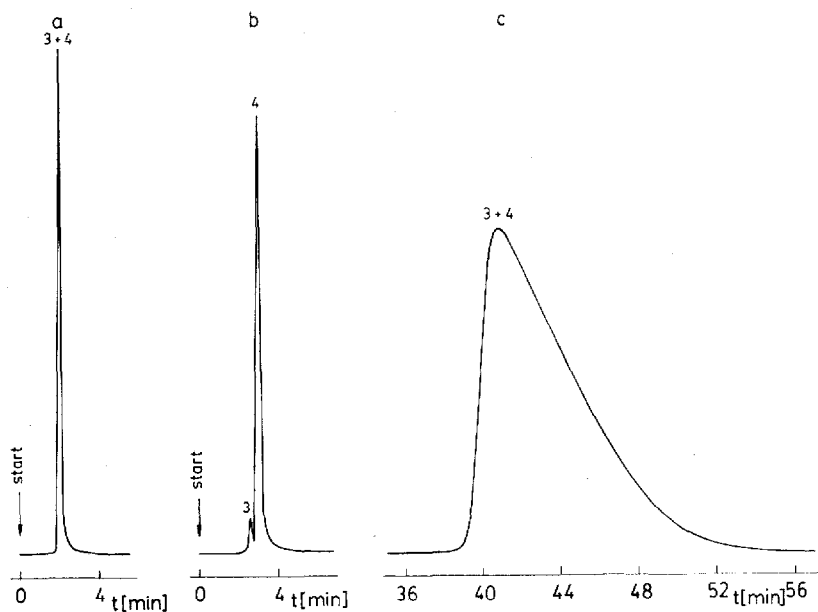


Fig. 2. Chromatograms of $(-)\text{-}\beta\text{-pinene}$ ($[\alpha]_D - 16.9^\circ$) obtained under the same conditions as indicated in Fig. 1. Peaks: 3 = $(+)\text{-}\beta\text{-pinene}$; 4 = $(-)\text{-}\beta\text{-pinene}$.

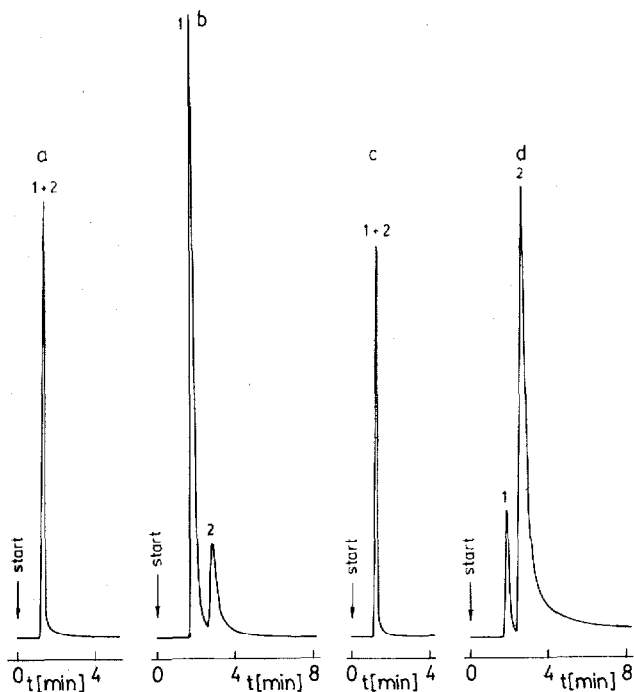


Fig. 3. Chromatograms of $(+)\text{-}\alpha\text{-pinene}$ ($[\alpha]_D + 20.8^\circ$) (curves a, b) and $(-)\text{-}\alpha\text{-pinene}$ ($[\alpha]_D - 35.0^\circ$) (curves c, d) obtained at 50°C on columns filled with Celite covered by (a, c) formamide, (b, d) 1.84 mol % $\alpha\text{-CD}$ in formamide. Peaks: 1 = $(+)\text{-}\alpha\text{-pinene}$; 2 = $(-)\text{-}\alpha\text{-pinene}$.

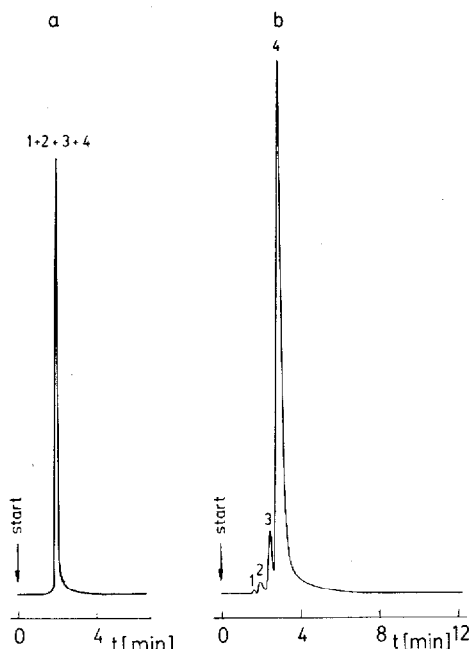


Fig. 4. Chromatograms of $(-)\text{-}\beta\text{-pinene}$ in admixture with $\alpha\text{-pinene}$, obtained under the same conditions as indicated in Fig. 3. Peaks: 1 = $(+)\text{-}\alpha\text{-pinene}$; 2 = $(-)\text{-}\alpha\text{-pinene}$; 3 = $(+)\text{-}\beta\text{-pinene}$; 4 = $(-)\text{-}\beta\text{-pinene}$.

$\alpha_{+/-} = 1.17$ ($\beta\text{-pinene}$). These values are slightly greater for the more concentrated formamide solutions of $\alpha\text{-CD}$ (Figs. 3 and 4).

Taking into account that the factors found correspond to neutral molecules of hydrocarbons, one can conclude that the observed enantioselectivity is of importance; the examples given in Figs. 3 and 4 confirm this opinion. The first shows a separation of two $\alpha\text{-pinene}$ samples of different optical rotation, and the second shows a chromatogram of $\beta\text{-pinene}$ mixed with $\alpha\text{-pinene}$. It should be noted that these separations were obtained on relatively short columns (2 m).

The results presented above demonstrate that $\alpha\text{-CD}$ can be used for the preparation of gas chromatography systems for the efficient separation of chiral non-polar hydrocarbons into their enantiomers. As the course of the straight-line isotherm is high in partition chromatography, such systems should also be promising for preparative gas chromatography.

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