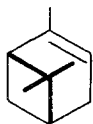


SEPARATION PROCESSES IN GAS-LIQUID CHROMATOGRAPHY BASED ON FORMATION OF
 α -CYCLODEXTRIN - CHIRAL HYDROCARBONS INCLUSION COMPLEXES

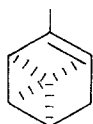
Tomasz Kościelski, Danuta Sybilska, and Janusz Jurczak
Institute of Physical Chemistry
Institute of Organic Chemistry
Polish Academy of Sciences
01-224 Warsaw, Kasprzaka 44/52
Poland

Chromatographic separation of enantiomeric hydrocarbons presents a number of difficulties caused by weak and not very selective intermolecular interactions in the common gas and liquid chromatographic systems. The use of optically active organic stationary phases cannot be realized on the basis of the "three-point-attachment" of Dalgliesh,¹ namely hydrocarbon molecules do not contain any functional groups suitable for forming the necessary hydrogen bonds for specific attachment of the enantiomer to the stationary phase. Chiral metal complexes were applied in RP-HPLC^{2,3} and GLC⁴ for resolution of chiral olefins into enantiomers; however in this case π donor - acceptor interactions being possible only for unsaturated hydrocarbons take place. We have recently discovered that under gas-partition chromatographic conditions, α -cyclodextrin (α -CD) complexation permits very efficient resolution of some terpenoid hydrocarbons (saturated and unsaturated) into enantiomers.⁵ The present paper summarizes our further systematic studies on enantio- and diastereoselective separation of α - and β -pinene, and of four stereoisomers of pinane, whose formulae are shown below:



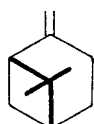
1

(+)- α -Pinene



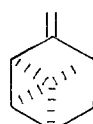
2

(-)- α -Pinene



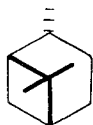
3

(+)- β -Pinene



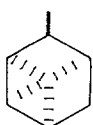
4

(-)- β -Pinene



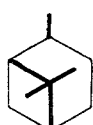
5

(+)-trans-



6

(-)-trans-



7

(+)-cis-



8

(-)-cis-

P i n a n e s

The ability of α - and β -CD complexation to modify the gas-partition chromatography system for separation of terpenoid hydrocarbons is exemplified in Fig. 1 for α -pinene.

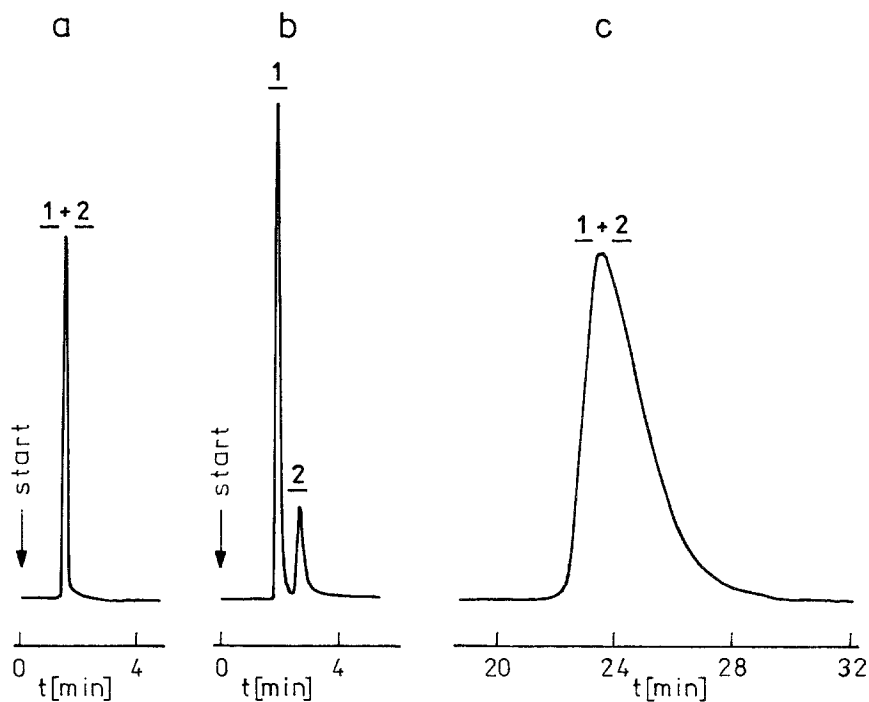


Fig. 1. Chromatograms of a nonracemic mixture of α -pinene, obtained at 50°C on a column packed with Celite covered by: (a) formamide, (b) 1.23 mol% of α -CD in formamide, (c) 1.18 mol% of β -CD in formamide.

As suggested by the chromatograms in Fig. 1, both α - and β -CD form inclusion complexes with α -pinene. Approximative estimation of the stability of CD complexes indicates that β -CD complex is much more stable than that of α -CD (the stability constant of the former complex is by one order greater than that of the latter). However, only α -CD complexation permits substantial chiral recognition of terpenoid hydrocarbons. This stereoselectivity originating from specific interactions between α -CD and guest molecules in inclusion complexes is markedly influenced by temperature and nature of the matrix medium.

So far, formamide is found to be the best matrix medium; its properties can sometimes be improved by addition of ethylene, propylene or tetramethylene glycol, or else of some inorganic salts as lithium or potassium nitrate. On the other hand, addition of diethylene or triethylene glycol or else silver nitrate destroys completely the selectivity of the column. On the basis of the above-presented results, optimal conditions were established for more complex mixtures containing enantiomers of β -pinene and stereoisomeric pinanes (Fig. 2).

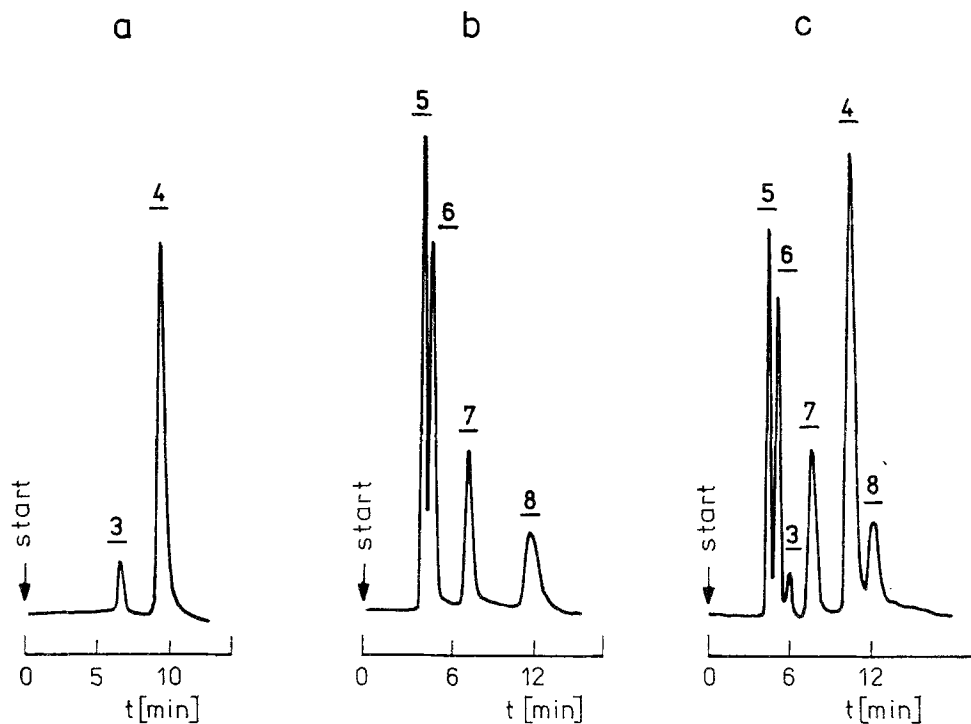


Fig. 2. Chromatograms (obtained at 35°C on a column packed with Celite covered by 0.6 mol% of α -CD in formamide) of mixtures containing: (a) enantiomeric β -pinenes (3, 4), (b) four stereoisomeric pinanes (5, 6, 7, 8), (c) all six above-mentioned compounds.

The results presented in Fig. 2 led to the conclusion that α -CD can readily be applied for gas chromatographic monitoring of the stereochemical course of β -pinene hydrogenation.⁶ An analogous approach has earlier been successfully applied for monitoring of α -pinene hydrogenation.⁷

A simple and very convenient method for the determination of enantiomeric purity of chiral hydrocarbons, recently developed at this Laboratory,⁸ is another interesting application of chromatographic separation of enantiomers *via* inclusion complexes with α -CD.

The present results fully confirm our claim that gas-liquid chromatography systems containing α -CD can be used as an analytical tool for monitoring stereocontrolled organic reactions. Moreover, the method seems to be promising for preparative purposes.

ACKNOWLEDGMENTS. The authors are indebted to Professor J. Szejtli (Chinoin, Budapest, Hungary) for kindly providing the sample of α -CD. Financial support from the Polish Academy of Sciences (Grants CPBR-3.20 and CPBP-01.13) is gratefully acknowledged.

REFERENCES

1. C. E. Dalgliesh, *J. Chem. Soc.*, 3940 (1952).
2. J. Köhler and G. Schomburg, *Chromatographia*, 14, 559 (1981).
3. J. Köhler, A. Deege, and G. Schomburg, *Chromatographia*, 18, 119 (1984).
4. V. Schurig, *Chromatographia*, 13, 263 (1980).
5. T. Kościelski, D. Sybilska, and J. Jurczak, *J. Chromatogr.*, 280, 131 (1983).
6. T. Kościelski, D. Sybilska, S. Belniak, and J. Jurczak, *Chromatographia*, 21, 413 (1986).
7. T. Kościelski, D. Sybilska, S. Belniak, and J. Jurczak, *Chromatographia*, 19, 292 (1984).
8. T. Kościelski, D. Sybilska, and J. Jurczak, *J. Chromatogr.*, 364, 297 (1986).