

## Note

### Cyclodextrin as a tool for separating *cis*- and *trans*-decalin by gas-liquid chromatography\*

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Gas chromatographic methods of analysis of the products of naphthalene hydrogenation have been the subject of many publications<sup>1-4</sup>. These include the separation of *cis*- and *trans*-decalins. In our studies, an attempt has been made to resolve the isomers by using gas-liquid chromatography in which inclusion complexes of cyclodextrins may form, thus resulting in a useful selectivity of the chromatographic systems.

Cycloamyloses, commonly called cyclodextrins (CD), are cyclic oligosaccharides, consisting of six, seven or eight glucopyranose units ( $\alpha$ -,  $\beta$ - or  $\gamma$ -cyclodextrin, respectively)<sup>5</sup>. They contain a cylindrical empty inner "cavity" in which suitable guest molecules can be accommodated, thus forming inclusion-type guest CD complexes. A good steric fit in the guest-host cavity is necessary to give stable complexes. Our previous studies have shown that the successful resolution of mixtures of isomers of alkyl derivatives of benzene<sup>6,7</sup> is possible, and efficient analytical procedures were developed. The chiral cavity of CD permits the resolution of optical isomers, even if the guest does not contain a functional group ( $\alpha$ - and  $\beta$ -pinenes and pinanes)<sup>8,9</sup>.

It is of some interest to examine the selectivity of CD towards naphthalene and its hydrogenated products and this was the aim of this study.

## EXPERIMENTAL

### Reagents

$\alpha$ - and  $\beta$ -CD were supplied by Chinoïn (Budapest, Hungary). Commercially available Celite (80-100 mesh) (BDH Chemicals, Poole, U.K.) for gas chromatography, formamide (F) and ethylene glycol (EG) (POCh, Gliwice, Poland) were used. The *cis*- and *trans*-decalins and tetralin were purified by the method described by Chyliński and Stryjek<sup>10</sup>.

### Apparatus and procedure

Chromatographic studies were performed with a Hewlett-Packard 7620A gas

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chromatograph, equipped with dual flame ionization detectors. Glass columns (2 m  $\times$  4 mm I.D.) were used. In all experiments special care was taken to maintain the inlet pressure ( $2.75 \pm 0.05$  atm) and helium flow-rate ( $50 \pm 0.5$  ml/min) constant. The preparation of the stationary phases has been described previously<sup>3</sup>. The mass of coated support in the column was determined by weighing the column before and after packing; the mean value for all the columns was  $10.2 \pm 0.5$  g.

In all experiments two columns were prepared: one with a given solution of  $\alpha$ - or  $\beta$ -CD in F or EG and a reference column, containing the solvents alone, both of them deposited on Celite. The columns thus prepared were operated simultaneous-

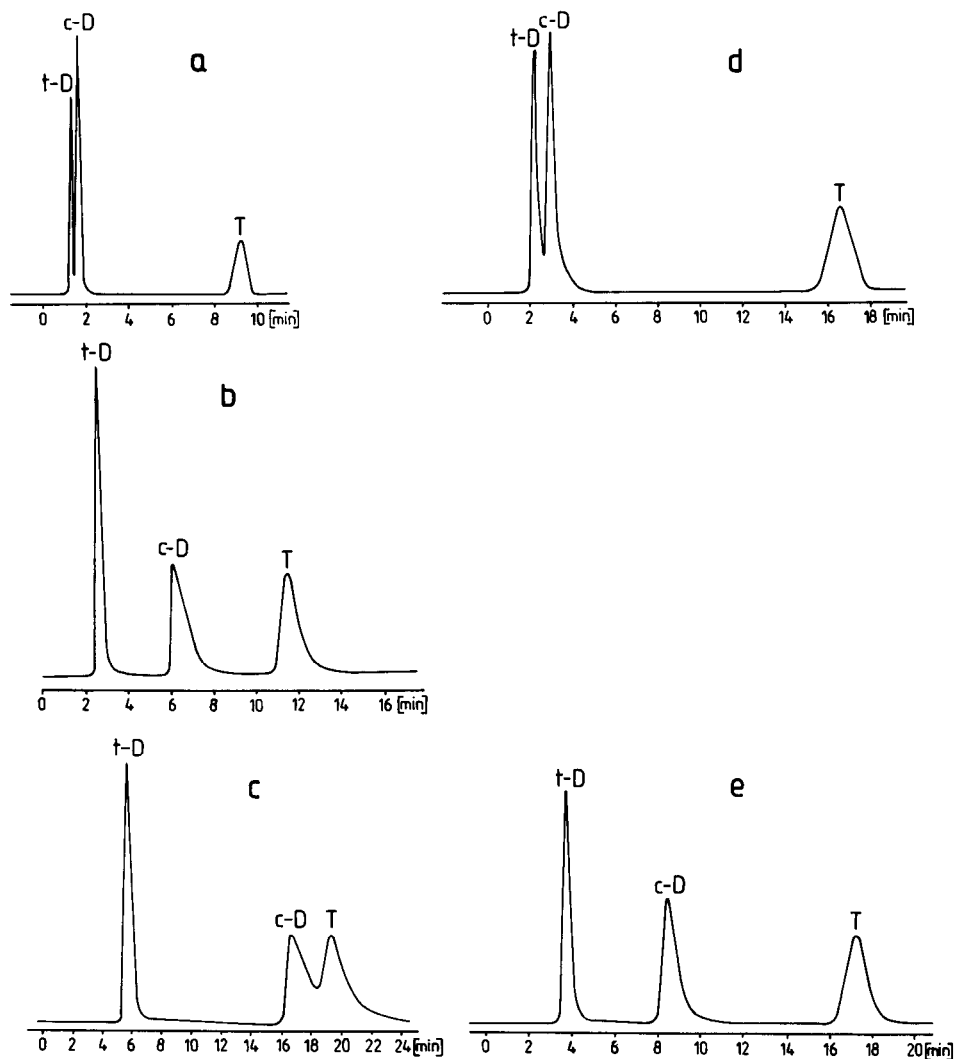


Fig. 1. Chromatograms of a mixture of *trans*-decalin (*t-D*), *cis*-decalin (*c-D*) and tetralin (*T*) at 70°C on columns (2 m  $\times$  4 mm I.D.) packed with (a) 0, (b) 0.10 and (c) 0.30 mol-% of  $\beta$ -CD in formamide solution and (d) 0 and (e) 0.36 mol-% of  $\beta$ -CD in ethylene glycol solution, deposited on Celite (4.54 g of formamide or ethylene glycol per 20 g of Celite). Helium flow-rate:  $50 \pm 0.5$  ml/min.

ly, using two flame ionization detectors. Each injection into the CD-containing column was followed almost immediately by the injection into the reference column. The studies were carried out in the temperature range 50–70°C.

## RESULTS AND DISCUSSION

Fig. 1 shows five chromatograms of a mixture of *cis*- and *trans*-decalin (*c*-D, *t*-D, respectively) and tetralin (T) demonstrating how their separation is influenced by  $\beta$ -CD, dissolved in two different matrix solvents, F and EG. The corresponding chromatograms showing the behaviour of  $\alpha$ -CD are given in Fig. 2.

The separation factors ( $\alpha$ ) of pairs of investigated compounds calculated as the ratios of their adjusted retention times are given in Table I.

Examination of the data leads to the conclusion that only  $\beta$ -CD complexation imposes significant selectivity on the system with respect to the separation of *cis*- and *trans*-decalins. The formation of  $\alpha$ -CD complexes under our experimental conditions is almost imperceptible (see Fig. 2) in the chromatograms.

The  $\beta$ -CD complex with *cis*-decalin is much more stable than that of the *trans*-isomer, in both F and EG solutions, *i.e.*,  $K_{c-D-\beta-CD} > K_{t-D-\beta-CD}$ .

An evaluation of stability constants of  $\beta$ -CD complexes was performed, on the assumption that only complexes of 1:1 stoichiometry are formed, based on the

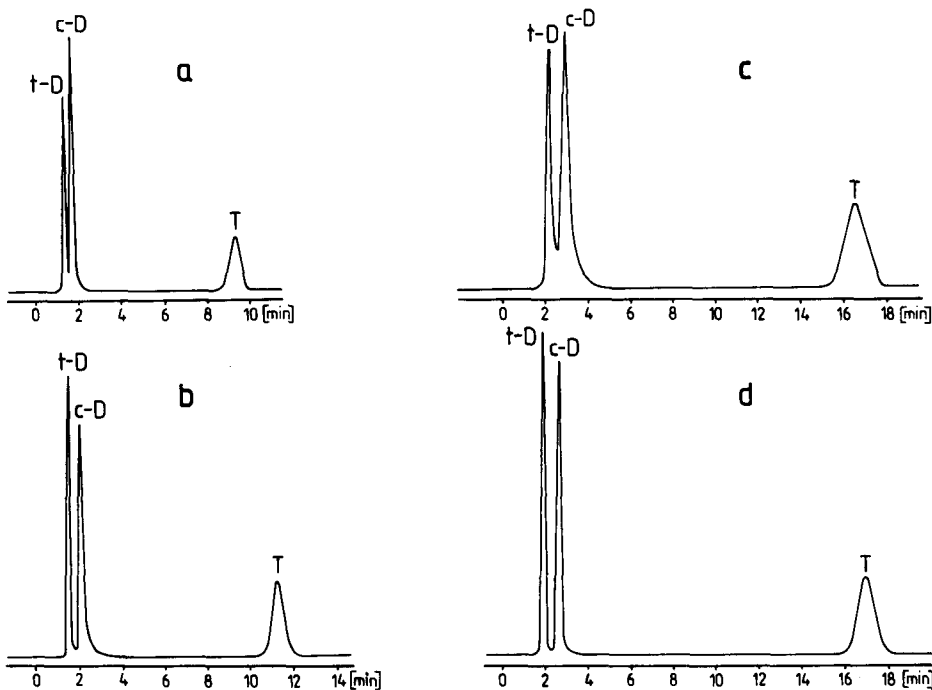


Fig. 2. Chromatograms of a mixture of *trans*-decalin (*t*-D), *cis*-decalin (*c*-D) and tetralin (T) at 70°C on columns (2 m × 4 mm I.D.) packed with (a) 0 and (b) 0.31 mol-% of  $\alpha$ -CD in formamide solution and (c) 0 and (d) 0.42 mol-% of  $\alpha$ -CD in ethylene glycol solution, deposited on Celite (4.54 g of formamide or ethylene glycol per 20 g of Celite). Helium flow-rate: 50 ± 0.5 ml/min.

TABLE I

SEPARATION FACTORS ( $\alpha$ ) AT 70°C FOR COLUMNS WITH DIFFERENT CONCENTRATIONS OF  $\beta$ -CD

Concentration of $\beta$ -CD (mol-%)	$\alpha_{c-D/t-D}$	$\alpha_{T/c-D}$
<i>In formamide</i>		
0.00	1.47	8.63
0.10	2.96	1.78
0.15	3.19	1.52
0.30	3.28	1.17
<i>Ethylene glycol</i>		
0.00	1.92	5.64
0.36	2.11	4.00

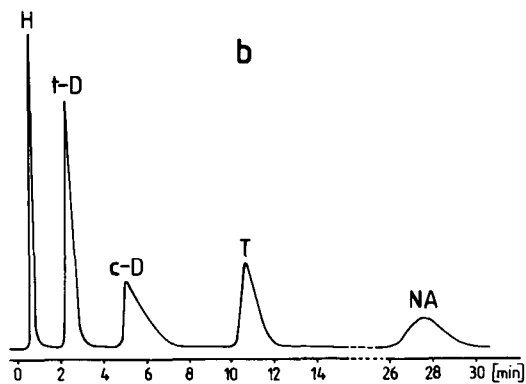
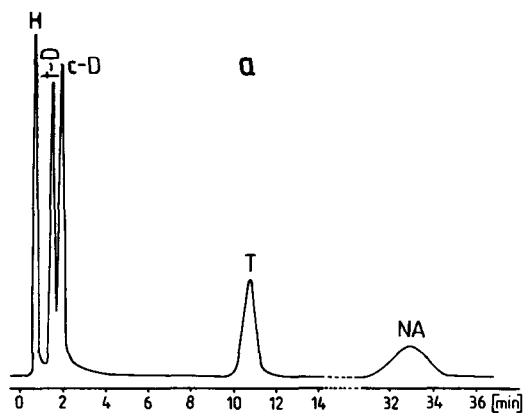


Fig. 3. Chromatograms of a mixture of *trans*-decalin (*t-D*), *cis*-decalin (*c-D*), tetralin (*T*) and naphthalene (*NA*) in heptane (*H*) at 70°C on columns (2 m × 4 mm I.D.) packed with (a) 0 and (b) 0.10 mol-% of  $\beta$ -CD in formamide solution, deposited on Celite (4.54 g of formamide per 20 g of Celite). Helium flow-rate: 50 ± 0.5 ml/min.

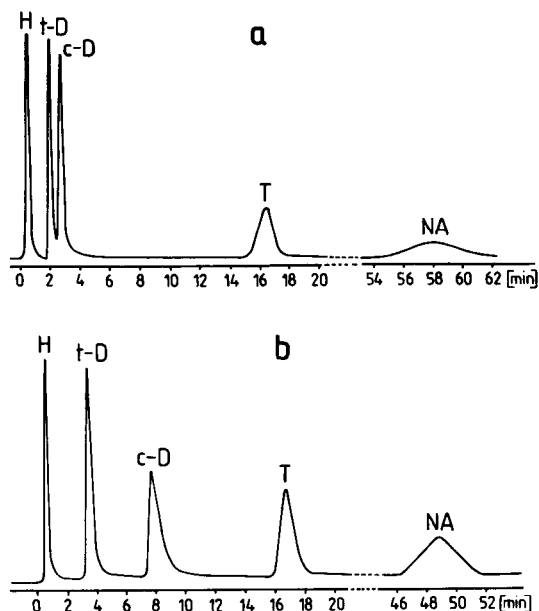


Fig. 4. Chromatograms of a mixture of *trans*-decalin (*t*-D), *cis*-decalin (*c*-D), tetralin (T) and naphthalene (NA) in heptane (H) at 70°C on columns (2 m × 4 mm I.D.) packed with (a) 0 and (b) 0.36 mol-% of  $\beta$ -CD in ethylene glycol solution, deposited on Celite (4.54 g of ethylene glycol per 20 g of Celite). Helium flow-rate: 50 ± 0.5 ml/min.

changes in adjusted retention times<sup>6</sup>. The stability of the T- $\beta$ -CD complex is much lower than that of *cis*-decalin and even of *trans*-decalin in both F and EG solutions:  $K_{cis} > K_{trans} > K_T$ . Hence, for analytical purposes, more dilute solutions of  $\beta$ -CD are recommended. With the more concentrated solutions (see Fig. 1c) the peaks of *cis*-decalin and tetralin partially overlap.

It should be noted that  $\beta$ -CD complexation processes are strongly affected by a temperature change from 50 to 70°C in both F and EG solutions. At 50°C the retention times of the investigated compounds are too long for analytical purposes and there is considerable tailing. A temperature of 70°C is recommended; higher temperatures are not advisable for reasons of column stability.

An example of the separation of a mixture containing naphthalene (NA), tetralin and *cis*- and *trans*-decalin is presented in Fig. 3. It is interesting that the retention time of naphthalene is shorter on the  $\beta$ -CD-containing column than on that with pure F (Fig. 3). The asymmetric shape of the peaks in Fig. 3 observed for the F medium is probably caused by some irreversibility in the complexation process. This effect can be avoided by using EG solutions (Fig. 4).

In conclusion, the system described above, involving the application of  $\beta$ -CD in gas-liquid chromatography, seems to be promising for the design of efficient separations of mixtures containing decalins, tetralin and naphthalene. The stereoselectivity towards *cis*- and *trans*-decalin arising from  $\beta$ -CD complexation in F solutions is remarkable.

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