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Chromatographic separation of α-pinene isomerization products

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Abstract

In the present work, the chromatographic separation of all monoterpene products formed in the catalytic isomerization of α-pinene, using the capillary column CP-Wax 52 CB, is reported. The retention times and order of appearance for monocyclic, bi- and tricyclic terpene products have been determined. The enantioselective analysis of the α-pinene isomerization products was performed by use of a γ-cyclodextrin capillary column. The order of appearance and the retention times of the separated enantiomers are presented. These analyses provide us with the necessary information about the composition of the isomerization products, which is required for a proper understanding of the reaction mechanism and the selectivity pattern in the catalytic isomerization of α-pinene over natural clinoptilolite.

Keywords: Enantiomer separation; Monoterpenes; Pinenes; Terpenes

1. Introduction

α-Pinene, one of the most widespread bicyclic monoterpenes, is a chiral compound obtained from the turpentine oil [1]. The liquid-phase isomerization of α-pinene over solid catalysts was first reported by Gurvich [2]. It is generally known that in the isomerization of (±)-α-pinene over heterogeneous catalysts, different monoterpene products such as bi- and tricyclic products [ΣTP: (±)-β-pinene, tricyclene, (±)-camphene, etc.] and monocyclic products [ΣMP: (±)-limonene, *p*-cymene, α- and γ-terpinenes, (±)-α- and (±)-β-phellandrenes, etc.] are formed [2–4]; see Fig. 1. The selectivity is highly dependent on the type of the heterogeneous catalyst used in the isomerization reaction [4–9]. Among the catalysts reported were silica-alumina and titanium dioxide [4], synthetic zeolite [5], mineral clay [7], alumina [8], and natural clinoptilolite [9].

However, in these investigations, the separation of the reaction products has been a difficult task. This is why many authors usually report the isomerization products as a sum of monocyclic products and a sum of bi- and tricyclic products. These analysis problems make it impossible to investigate correctly how the selectivity is affected by the reaction conditions such as temperature, pressure and type of the catalyst used. To our knowledge, there has not been any publication reporting on the separation and analysis of the individual enantiomers in the complex (±)-α-pinene isomerization reaction. Yet, thanks to the development of advanced capillary columns for gas

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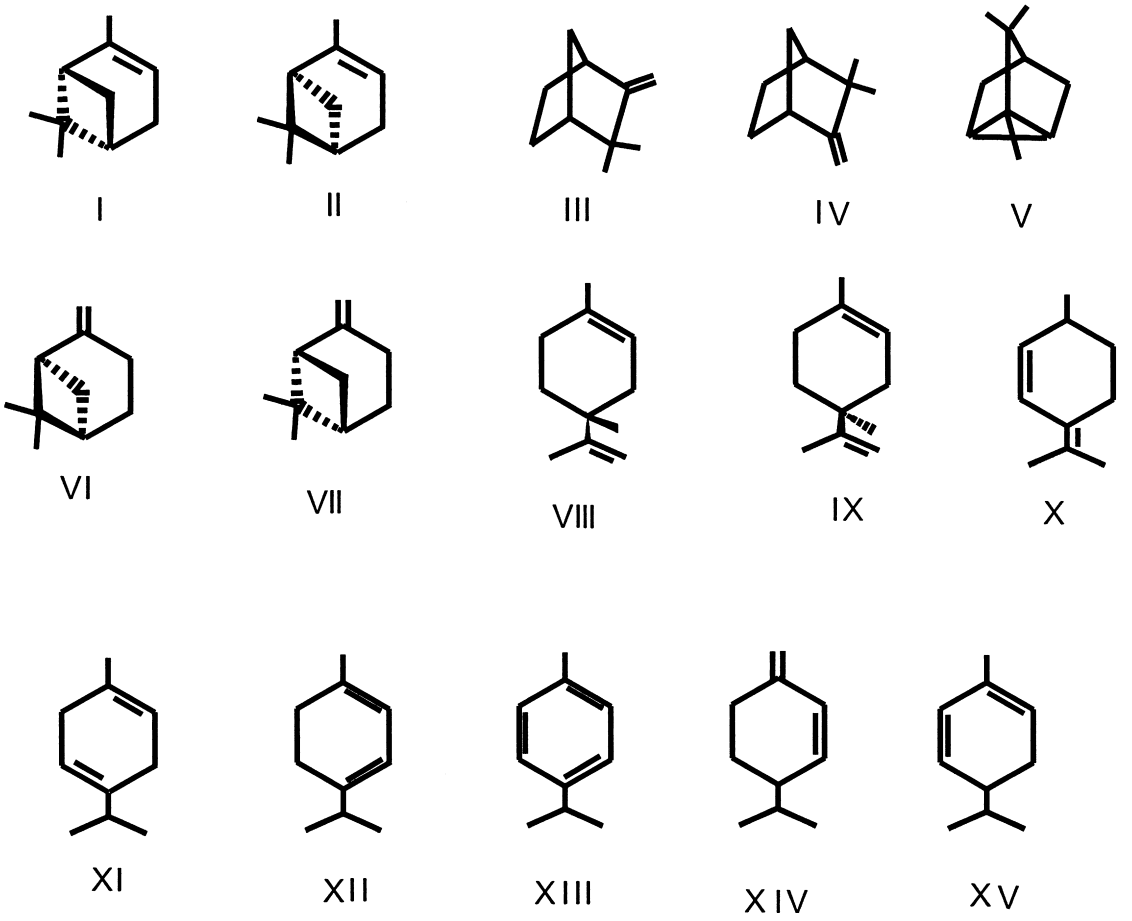

Fig. 1. Structural formulae of some monoterpene compounds. I=(−)-α-Pinene, II=(+)-α-pinene, III=(−)-camphene, IV=(+)-camphene, V=tricyclene, VI=(+)-β-pinene, VII=(−)-β-pinene, VIII=(+)-limonene, IX=(−)-limonene, X=terpinolene, XI=γ-terpinene, XII=α-terpinene, XIII=*p*-cymene, XIV=β-phellanderene, XV=α-phellanderene.

chromatography (GC) in recent years, it has become possible to separate all monoterpene products. Further, it is possible to separate all enantiomers by combining the use of α-, β- or γ-cyclodextrins as stationary phases [10–16].

Cyclodextrins are macrocyclic molecules formed from α-(1→4) linked D-glucopyranose units. These oligomers, composed of six or more glucose unites, adopt a toroid shape. Cyclodextrins and their derivatives, therefore, are useful tools in inducing asymmetric reactions [11] and have been used extensively as stationary phases in chromatographic enantioselective separations of a wide variety of chiral compounds. With γ-cyclodextrin as stationary phase, it is possible to separate and quantify the enantiomers of (±)-α-, (±)-β-pinene, (±)-α-, (±)-β-phellandrenes and (±)-limonene rapidly and with high precision. These monoterpene products are not only natural products from flowers and fruits oils, but can also be produced by synthetic means using different physico–chemical methods.

The enantioselective separation of monoterpene products formed by isomerization of (±)-α-pinene is of interest because there is an industrial need for (+)- and (−)-enantiomers of these molecules, as they show different physico–biological activities. In

the present work, all monoterpene hydrocarbons were separated by gas chromatography with CP-Wax 52 CB as stationary phase. Also, the enantiomers of α-pinene and limonene formed in the isomerization of α-pinene reaction over heterogeneous natural clinoptilolite catalysts were separated using a γ-cyclodextrin derivative as stationary phase.

2. Experimental

2.1. Materials

α-Pinene used as starting material was received from Arizona Chemical (Oulu, Finland). It was obtained from the sulphate monoterpenes formed

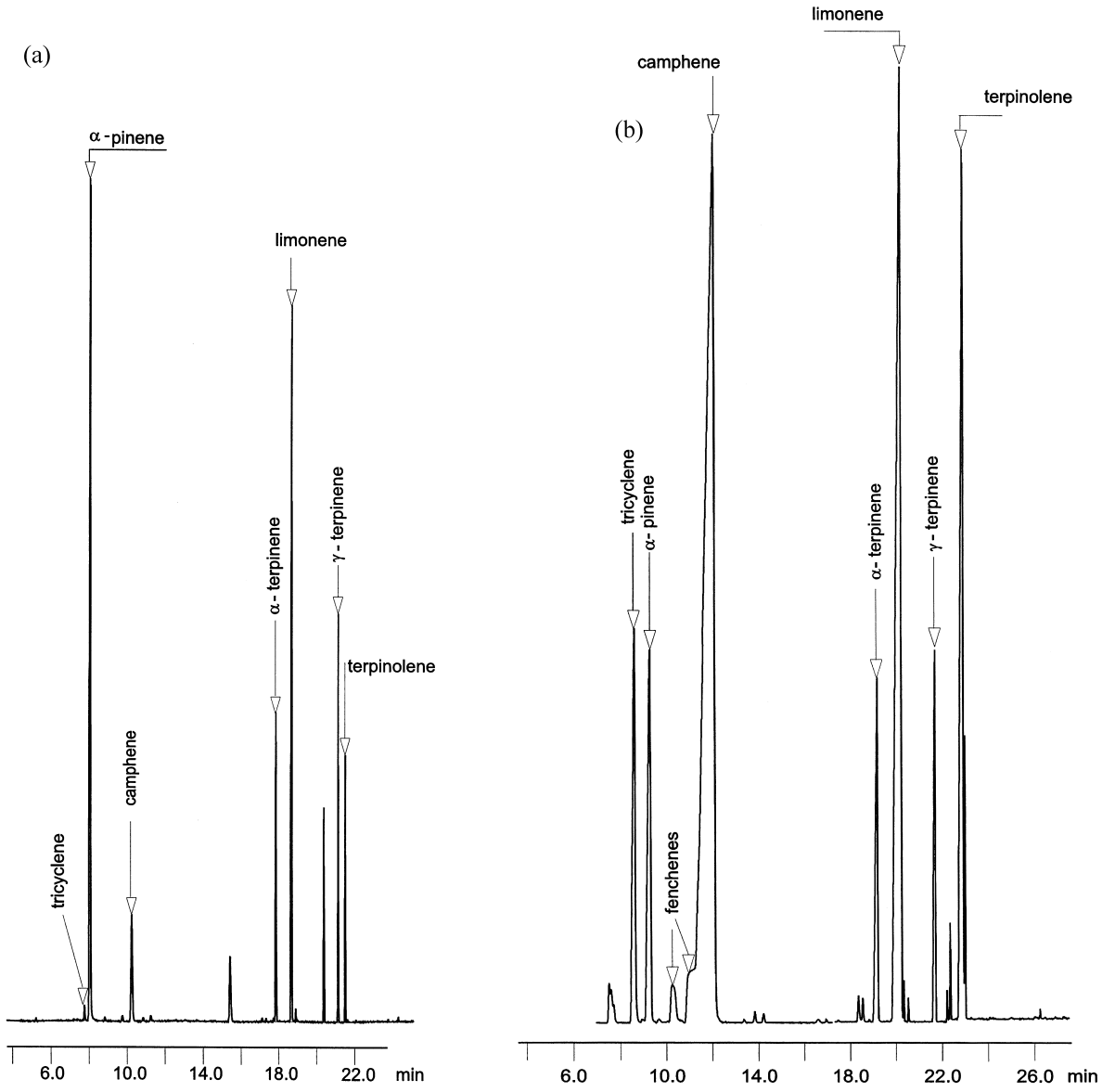

Fig. 2. Chromatograms of (a) the monoterpene standards and (b) reaction products with CP-Wax 52 CB.

during the processing of cedar wood in pulp and paper industries. α-Pinene used in our isomerization studies contained 75% (w/w) (+)-α-pinene and 25% (w/w) (−)-α-pinene. All other standard calibration samples were obtained from Aldrich (Milwaukee, WI, USA) and Fluka (Buchs, Switzerland).

2.2. Apparatus and procedure

A Varian Star 3400 CX gas chromatograph with split–splitless injector and flame ionisation detector was used in the present work. The injector and detector temperatures were 220°C and 250°C, respectively. Hydrogen was used as carrier gas with a split ratio of 100:1.

For the separation of monoterpene products, a capillary column with CP-Wax 52 CB as stationary phase of 60 m×0.25 mm I.D. and a film thickness of 0.25 μm was used (from Chrompack). The temperature programme was as follows: 45°C for 15 min, increase to 180°C at a rate of 15°C/min, and finally 10 min at 180°C. The pressure of the carrier gas, hydrogen, was 15 p.s.i. (1 p.s.i.=6894.76 Pa).

For the enantioselective separation, a capillary column of 25 m×0.25 mm I.D. was used. The stationary phase was Octakis (6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin (with OV 1701, 60:40). The column was obtained from Professor W. König, Hamburg University, Germany. The hydrogen pressure over the column was 5 p.s.i. The temperature programme was initiated with 50°C for 12 min, and then the temperature was increased to 160°C at a rate of 15°C/min, kept for 10 min.

The optical rotations of α-pinene, dissolved in ethanol, were determined in a 1-dm quartz microcell using a Perkin-Elmer 341 LC polarimeter. The wavelength was 589 nm (sodium D-line).

3. Results and discussion

The chiral α-pinene is used for isomerization to obtain bicyclic and monocyclic products. In our investigations of the catalytic isomerization of α-pinene over heterogeneous natural clinoptilolite [9], a fast analytical method had to be developed to determine the product composition with high accuracy. Here we report on the gas chromatographic methods used to determine the relative amount of all monocyclic and bicyclic monoterpenes, including the enantiomeric composition of the isomerization products. By the chromatographic analysis of α-pinene using the γ-cyclodextrin column, it was found that the starting α-pinene contained 75% (w/w) of the (+)- and 25% (w/w) of the (−)-enantiomer.

This result was verified by polarimetry [17]. The specific rotation was determined to be +23.6° which is to be compared with the literature value of +51.28° for pure (+)-α-pinene [18]. This corresponds to a composition of 76.4% (w/w) and 23.6% (w/w) of the (+)- and (−)-α-pinene, respectively, in the industrial α-pinene.

Such a double analysis, i.e., by chromatographic and optical methods, shows that the chromatographic analysis with an injector temperature of 220°C does not cause any racemization and can be regarded as a

Table 1
The elution order and the retention times of α-pinene isomerization products with natural clinoptilolite as catalyst, using the capillary column with CP-Wax 52 CB as stationary phase

Order	Component	Boiling point (°C)	Retention time (min)	
			In standard solution	In reaction mixture
1	Tricyclene	153	8.125	8.216
2	(±)-α-Pinene	156	8.730	8.885
3	Fenchene	139–148	–	–
4	(±)-Camphene	159	10.906	11.686
5	α-Terpinene	175	18.503	18.676
6	(±)-Limonene	176	19.333	19.699
7	*p*-Cymene	176–178	21.042	–
8	γ-Terpinene	182	21.797	21.169
9	Terpinolene	184	22.167	22.392

reliable method. This could also be verified by GC analysis of the α-pinene before and after heating the reactor content in the presence of a heterogeneous catalyst. In both cases the ratio of (+)- and (−)-α-pinene was constant.

3.1. Analysis on the CP-Wax 52 CB column

In Fig. 2a and b, two chromatograms obtained on the capillary column CP-Wax 52 CB are shown. Here, α-pinene isomerization products (with natural clinoptilolite as catalyst) exceeding 1% (w/w) have been identified. From Fig. 2a and b and Table 1, it is obvious that by strictly maintaining the analytical conditions, the order of appearance and the retention times of monoterpene products are unchanged. The results were verified with the help of relative retention times. Furthermore, by use of this column, it

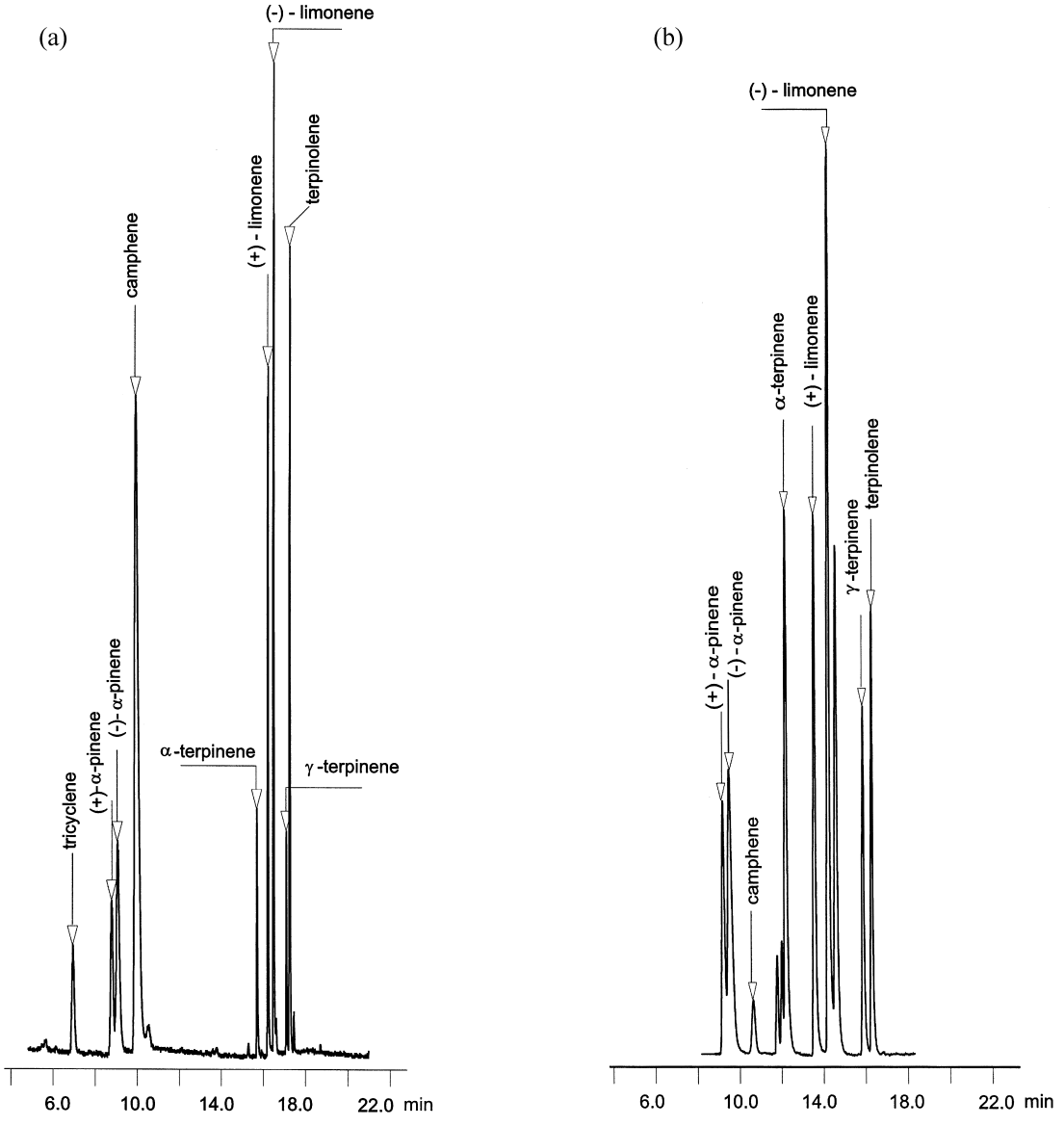

Fig. 3. Chromatograms of (a) the monoterpene standards and (b) reaction products with (6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin.

Table 2
The elution order and the retention times of α-pinene isomerization products with natural clinoptilolite as catalyst, using the capillary column with (6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin as stationary phase

Order	Component	Boiling point (°C)	Retention time (min)	
			In standard solution	In reaction mixture
1	Tricyclene	153	8.075	8.033
2	(+)-α-Pinene	154–156	9.350	9.450
3	(−)-α-Pinene	156–158	9.570	9.668
4	Fenchene	139–148	–	–
5	(±)-Camphene	159–160	10.422	10.330
6	α-Terpinene	175	14.755	14.774
7	(+)-Limonene	176–177	15.159	15.171
8	(−)-Limonene	176–177	15.353	15.374
9	*p*-Cymene	176–178	15.462	–
10	γ-Terpinene	182	15.849	15.852
11	Terpinolene	184	15.968	15.970

is possible to separate fenchenes from camphene, which normally are very difficult to separate. The fenchene peak shown in Fig. 2b was identified by using the boiling temperature correlation method. However, due to their low content in the α-pinene isomerization mixture, fenchenes have not been of interest in this investigation and hence the type of fenchene isomer was not determined.

3.2. Analysis on the γ-cyclodextrin column

Fig. 3a–b shows chromatograms and Table 2 lists the retention times of the monoterpene products run on the chiral stationary phase based on γ-cyclodextrin. The results were verified with help of relative retention times. Since this column can separate most of the monoterpenes, and in addition separate the enantiomers of the chiral α-pinene and limonene, it is possible to follow the stereochemical course of the isomerization reactions. This plays an important role in the development of new synthetic methods to enantiopure monoterpenes. (±)-Camphene was not separated on this column. In the literature a α-cyclodextrin stationary phase is recommended for this purpose [14].

4. Conclusions

The present study describes the first efficient chromatographic method to study the various monoterpene products and their enantiomeric composition obtained in the isomerization of α-pinene during the course of the reaction, using γ-cyclodextrin and CP-Wax 52 CB columns. The polarimetric measurements of the optical rotations of chiral molecules and a comparison between these measurements and the chromatographic results revealed that, at temperatures up to 220°C, there is no risk of enantiomeric isomerization. The enantioselective analysis demonstrated is very important for the future development of methods to obtain enantiopure monoterpene products.

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