

Purification of *d*-Limonene and  $\beta$ -Pinene

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By methanol extraction *d*-limonene and  $\beta$ -pinene have been purified to index homogeneity ( $n_D^{25} = 1.4703, 1.4762$  respectively) when analysed for purity using a micro sorption method. *l*-Limonene, isolated from cones of *Abies alba* and purified on a micro scale gave the same sorptogram as *d*-limonene 1.4703<sub>US 1-7</sub> and the same sorptogram as dipentene prepared by mixing the antipodes.

In an earlier communication<sup>1</sup> the author has studied the purification of  $\Delta^8$ -carene and  $\beta$ -pinene from Swedish turpentine. It was found that only a combination of prolonged column distillation under vacuum and methanol extraction gave index-homogeneous products when analysed for purity with a micro sorption method devised by Blohm<sup>2</sup>.

In this investigation, commercial samples of *d*-limonene and  $\beta$ -pinene were purified to index homogeneity and it was found that only one of the methods mentioned above, methanol extraction, was needed to bring these samples to index homogeneity.

The physical values for the two index homogeneous terpenes are as follows:

	$[\alpha]_D^{25}$	$d_4^{25}$	$n_D^{25}$
<i>d</i> -limonene	+ 123.3°	0.8409	1.4703
$\beta$ -pinene	- 21.5°	0.8684	1.4762

In the range of +15° C to 30° C there is a decrease in refractive index of 0.0023 per 5° C.

Several attempts to reach the same stage of purity with samples of dipentene have been unsuccessful. An indirect way was chosen to study the eventual isomerization of dipentene caused by the active gel which is used in the analyses. Cones of *Abies alba* Mill. were extracted and a small amount of a turpentine was obtained, too small to distil through an efficient vacuum column. On displacement chromatography of 120  $\mu$ l of the extract, about 40  $\mu$ l index-homogeneous *l*-limonene were obtained. When mixed with *d*-limonene the dipentene obtained was shown to be index-homogeneous on sorption analysis, thus demonstrating that the purification of dipentene can be followed with the analytical sorption method.

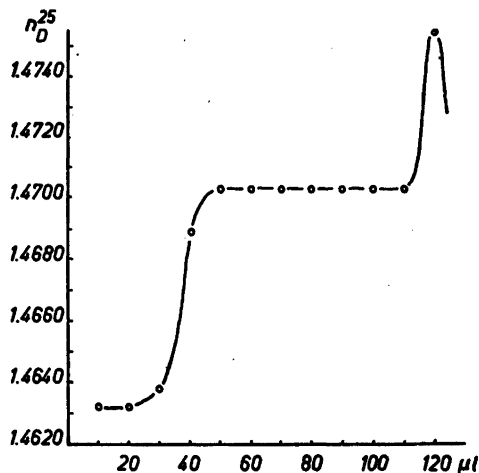


Fig. 1. Turpentine from cones of *Abies alba* separated by displacement chromatography.

#### EXPERIMENTAL PART

A micro sorption apparatus (column  $250 \times$  i. d. 1.4 mm), fully conforming to Blohm's instructions, was used. The silica gel (Davison, 922, 08, 226, through 200 mesh) was activated for 2 hours at  $140^\circ$  and 15 mm Hg. The refractometer, Bellingham & Stanley No. 402330, was calibrated against a standard plate  $n_D$  1.5009. The thermostat was controlled to  $25^\circ \pm 0.02^\circ$ . For reading the refractive indices, a fresh paper  $\sim 5 \times 5$  mm was used for each determination.

The optical rotations were measured without any solvent in 20 cm tubes; polarimeter Bellingham & Stanley No. 36291. The densities were determined according to Bauer<sup>3</sup>, using Ostwald-Sprengel pycnometers with small cups (type E).

Commercial samples of *d*-limonene (Eastman, Kodak No. 1980) and  $\beta$ -pinene (Light & Co., unnumbered) gave the sorptograms —  $n_D^{25}$  plotted against the  $5 \mu$  fraction number — 1.4704<sub>US</sub>, 1.4703<sub>1-6</sub>, 1.4710<sub>7</sub>, and 1.4764<sub>US</sub>, 1.4762<sub>1-5</sub>, 1.4763<sub>6</sub>, 1.4771, respectively\*.

Ten extractions with 90 % methanol, the methanol portions being 10 % of the terpene volume, removed the "peaks", and after washing with water and drying ( $\text{Na}_2\text{SO}_4$ ) index-homogeneous sorptograms were obtained, 1.4703<sub>US, 1-7</sub> and 1.4762<sub>US, 1-7</sub>. There was no change after vacuum distillation through an effective column. Measured at different temperatures the refractive indices were:  $n_D^{15.8}$  1.4742 and 1.4805,  $n_D^{20}$  1.4725 and 1.4788, and  $n_D^{30}$  1.4656 and 1.4718, respectively.

Samples of dipentene, both commercial and those prepared in the laboratory, gave no indication of index homogeneity upon sorption analysis even after prolonged fractional distillation. A further sample of dipentene was then prepared by mixing *d*- and *l*-limonene. The *l*-limonene was prepared in the following way. Ten cones of *Pinus alba* Mill. which, according to Brühl<sup>4</sup>, contains *l*-limonene were extracted with ether and the turpentine collected

\* In order to simplify the printing of the sorptograms and to avoid printed figures the  $n_D^{25}$  values of the sorption are given with the fraction number as index. The value of the unsorted sample is given with US as index.

( $\sim 4$  ml) was distilled through a micro column under vacuum. 4 fractions were obtained giving the sorptograms:

I	1.3898 <sub>US</sub>	1.4658 <sub>1</sub>	1.4350 <sub>2</sub>	1.3568 <sub>3</sub>	1.3503 <sub>4</sub>	1.3503 <sub>5</sub>	1.3530 <sub>6</sub>	1.3560 <sub>7</sub>
II	1.4630 <sub>US</sub>	1.4632 <sub>1</sub>	1.4640 <sub>2</sub>	1.4656 <sub>3</sub>	1.4682 <sub>4-5</sub>	1.4700 <sub>6</sub>	1.4702 <sub>7</sub>	1.4703 <sub>8</sub>
III	1.4689 <sub>US</sub>	1.4632 <sub>1</sub>	1.4652 <sub>2</sub>	1.4688 <sub>3</sub>	1.4702 <sub>4</sub>	1.4703 <sub>5-7</sub>		
IV	1.4722 <sub>US</sub>	1.4695 <sub>1</sub>	1.4702 <sub>2</sub>	1.4709 <sub>3-5</sub>	1.4712 <sub>6</sub>	1.4756 <sub>7</sub>		

120  $\mu$ l of fraction III were displaced with ethanol through a 50 cm column (i. d. 1.5 mm) packed with activated gel and 10  $\mu$ l fractions were collected. Refractive indices were determined on 5  $\mu$ l aliquots of the fractions giving the enlarged sorptogram with an *l*-limonene plateau  $n_D^{25} = 1.4703$  (Fig. 1). The residual 5  $\mu$ l samples of *l*-limonene were mixed with the same amount of *d*-limonene and analysed by sorption in the usual way, giving the sorptogram for dipentene 1.4703<sub>US, 1-7</sub>. — The optical rotation of the sample of *l*-limonene was determined on a micro scale using a 5 cm tube, volume 0.33 ml. 10  $\mu$ l index-homogeneous sample were dissolved in 0.4 ml ethanol, giving  $[\alpha]_D^{25} = -100$ , assuming the density to be 0.80.

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