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Studies of Terpene Mixtures

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Two-component mixtures of the terpenes, Δ^3-carene, *d*-limonene, and α- and β-pinene purified to index homogeneity have been analysed using a micro sorption method. The sorptograms — n_D^{25} plotted against the 5 μl fraction number — are given for these six mixtures. The sensitivity of the analytical method has been studied for the different types of sorptograms.

As an appendix the sorptograms of some commercial samples of terpenes are given. No direct conclusion regarding the general qualities of the samples must be drawn from these sorptograms.

The determination of the purity of terpene hydrocarbons is of fundamental importance for the study of the reactions of individual terpenes. The earlier lack of methods available for testing the homogeneity of the liquid terpene hydrocarbons, used as starting materials for syntheses and isomerizations, has greatly hampered the interpretation of the results obtained. Simonsen [1] gives several examples of this kind in his comprehensive survey of the terpenes.

Collecting the results from a large series of experiments performed at Naval Stores Research Division, USA, O'Connor and Goldblatt [2] have shown it possible to determine the content of isomeric terpenes in some mixtures by infrared spectroscopy, and, from ultraviolet absorption curves, to classify the terpenes into groups. Widmark has, as described in earlier communications [3, 4], purified Δ^3-carene, *d*-limonene, and α- and β-pinene and studied the results obtained with an analytical micro sorption method devised by Blohm[5]. The present authors[6] have investigated the use of this method on oxidized Δ^3-carene.

In this investigation a series of mixtures of the four terpenes purified to index homogeneity (see above) has been analysed by the micro sorption method[5]: One drop (40.0 μl) was displaced with ethanol at pressure (1 atm) through a 25.0 cm long, narrow (i ø 1.4 mm) column filled with active silica gel and 5.0 μl fractions were collected, refractive indices of which were determined. With most of the mixtures very good readings were obtained and small amounts of the other terpenes were detected.

All the samples analysed here have been shown to be free from oxidation products, as even a slight oxidation can give rise to considerable changes in

the sorptograms [6]. A freshly oxidized sample, however, can be restored to its original stage by methanol extraction [3, 4].

The sequence, *e.g.* falling affinity to the gel, of these terpenes on sorption of 50 % mixtures is found to be *d*-limonene, Δ^3-carene, β-pinene, and α-pinene and the sorptograms — n_D^{25} plotted against the 5 μl fraction number — obtained after sorption of the mixtures have different shapes, *cf.* Figs. 1—6. After sorption of a two-component mixture containing one terpene as a minor constituent, the variation can be found in the beginning or at the end of the sorptogram. The method is usually most sensitive for those mixtures giving sorptograms with peaks at the ends. Thus 0.2 % Δ^3-carene can be detected in pure α-pinene. The sorptograms having an upward or downward slope in the beginning, *e.g.* α-pinene in Δ^3-carene, are less sensitive for interpretation purposes, but a few percent can be detected satisfactorily. Small amounts of Δ^3-carene and *d*-limonene in β-pinene give sorptograms with downward slopes at the end and usually less than 5 % cannot be detected in this case. When about 25 % or less β-pinene is present in Δ^3-carene there is a very small separating effect and straight sorptograms can be obtained; *cf.* Hirschler and Amon [7] who elucidate these phenomena in their investigation of separation of petroleum products on gel and carbon. The values of the refractive indices of Δ^3-carene and *d*-limonene are too close to allow good readings of the sorptograms and the sorption fractions have to be investigated with other micro identification methods. These results demonstrate clearly the danger in accepting the sorptogram as the sole criterion of purity.

Isomerization of the terpenes investigated caused by the passage through the active gel has not been observed yet, but the possible occurrence of these reactions will be further studied. The degree of activation is, however, of great importance, especially in the sorption of β-pinene mixtures, where only freshly activated gel will give reproducible results.

As an appendix to this paper, sorptograms of commercial samples of terpenes are given. For several reasons it is impossible to transfer directly the results obtained with the mixtures of the index homogeneous terpenes over to the commercial samples. The usefulness of the analytical method can as yet be considered as unknown for oxygen-containing terpenes and the method has already been found unsuitable for viscous liquids, or mixtures containing a solid compound. Furthermore, reservations have to be made when interpreting the quality of samples of the different manufactures from the sorptograms given here, as it is not known how our samples have been handled at the dealers. Nevertheless some of the examples given demonstrate, when used under controlled conditions, how the quality of terpene samples can be investigated using the sorption method.

EXPERIMENTAL PART

A micro sorption apparatus (column 250 × i ø 1.4 mm), fully conforming to Blohm's [5] instructions, was used. The silica gel (Davison, 922—08—226 through 200 mesh) was activated 2 hours at 140° (15 mm Hg). On reading the refractive indices, a fresh paper, ~ 5 × 5 mm, was used for each determination. The refractometer, Bellingham & Stanley No. 402330, was calibrated against a standard plate n_D 1.5009. The thermostat was

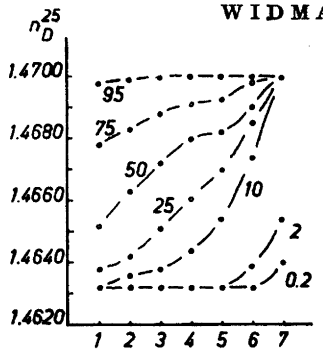

Fig. 1. Sorptograms of Δ^3-carene — α-pinene mixtures. Percent Δ^3-carene is given.

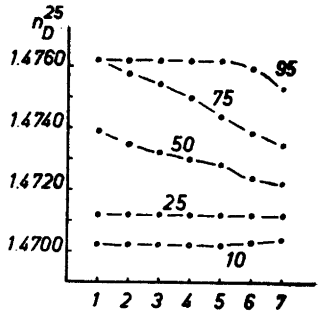

Fig. 2. Sorptograms of Δ^3-carene — β-pinene mixtures. Percent β-pinene is given.

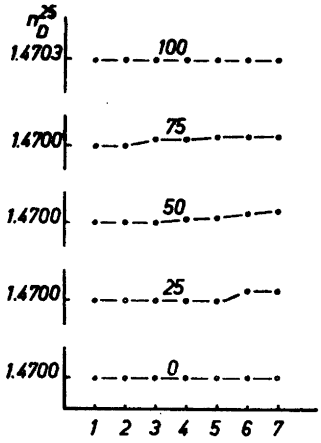

Fig. 3. Sorptograms of Δ^3-carene — d-limonene mixtures. Percent d-limonene is given.

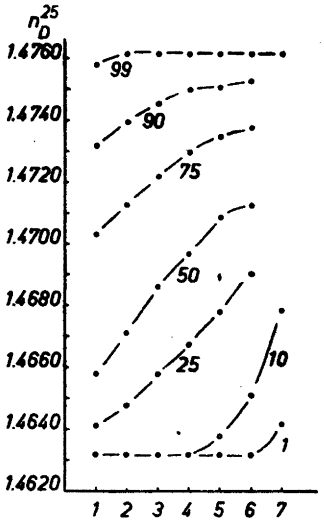

Fig. 4. Sorptograms of α-pinene — β-pinene mixtures. Percent β-pinene is given.

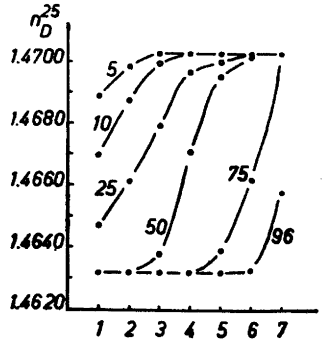

Fig. 5. Sorptograms of α-pinene — d-limonene mixtures. Percent α-pinene is given.

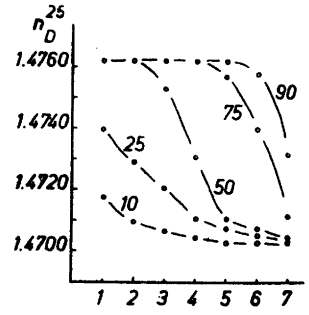

Fig. 6. Sorptograms of d-limonene — β-pinene mixtures. Percent β-pinene is given.

controlled to 25° ± 0.02°. The reproducibility of the sorptograms was found to be ± 0.0001 at the flat parts of the curves and max. ± 0.0005 at the steepest parts.

The terpenes, Δ^3-carene, *d*-limonene, and α- and β-pinene were purified to index homogeneity, *cf.* Widmark [3,4]. The mixtures were prepared by weighing in lots of about 0.5 g and stored in closed, nitrogen-filled tubes in an ice box.

The commercial samples were kept under nitrogen in tightly stoppered bottles, at room temperature and in a dark room, after arrival in the laboratory. No information on time of storing etc. was obtained from the dealers.

Sorptograms of the terpene mixtures are given in Figs. 1—6.

SORPTOGRAMS OF COMMERCIAL SAMPLES

The n_D^{25} values of the sorption are given with the fraction number as index. The value of the unsorbed sample is given US as index.

Fenchene. (Fluka, pract.) 1.4858_{US} 1.4714_{1-2} 1.4770_3 1.4940_4 1.4998_5 1.4874_6.

Dipentene. (Fluka) 1.4567_1 1.4682_2 1.4728_3 1.4745_4 1.4768_5 1.4804_6 1.4788_7; (Hopkins and Williams) 1.4748_1 1.4801_2 1.4809_3 1.4812_{4-6} 1.4817_7; (Schuchardt) 1.4742_{US} 1.4677_1 1.4672_2 1.4692_3 1.4728_4 1.4758_5 1.4807_6 1.4699_7.

d-Limonene (Eastman-Kodak) 1.4703_{US}, $_{1-6}$ 1.4710_7; (E-K tech.) $1,4703_{1-5}$ 1.4706_6 1.4717_7; (Hopkins and Williams) 1.4713_{US} 1.4654_1 1.4703_2 1.4709_3 1.4710_4 1.4715_5 1.4720_6 1.4747_7; (Fluka) 1.4770_{US} 1.4696_1 1.4715_2 1.4742_3 1.4765_4 1.4798_5 1.4763_6; (Schuchardt) 1.4720_{US} 1.4703_1 1.4722_2 1.4728_{3-5} 1.4739_6.

Phellandrene. (Fluka, tech.) 1.4783_{US} 1.4762_1 1.4753_2 1.4758_3 1.4797_4 1.4854_5 1.4832_6

α-Pinene. (Light) 1.4632_{1-5} 1.4637_6 1.4640_7.

p-Cymene. (Eastman-Kodak) 1.4853_1 1.4884_2 1.4883_{3-7}.

Carvone. (Schuchardt) 1.4955_{US} 1.4959_{1-3} 1.4960_{4-6} 1.4708_7.

Citral. (Fluka) 1.4867_{US} 1.4878_{1-3} 1.4865_4 1.4860_{5-6} 1.4690_7.

Citronellal. (Fluka) 1.4501_{US} 1.4518_1 1.4503_2 1.4496_3 1.4506_4 1.4554_5 1.4562_6.

Citronellol. (Fluka) 1.4535_{US} 1.4553_1 1.4532_{2-3} 1.4536_4 1.4541_5 1.4468_6.

Fenchone. (Fluka, purum) 1.4596_{US} 1.4595_1 1.4597_{2-6}.

Geraniol. (Fluka) 1.4692_{US} 1.4743_1 1.4703_2 1.4699_{3-5} 1.4682_6.

α-Ionene. (Fluka) 1.4967_{US} 1.4968_1 1.4965_2 1.4943_3 1.4882_4 1.4818_5 1.4718_6.

β-Ionone. (Fluka) 1.5126_{US} 1.5138_1 1.5131_2 1.5123_3 1.5128_4 1.5032_5 1.4900_6.

Linalool. (Fluka) 1.4597_{US} 1.4596_1 1.4597_2 1.4598_{3-5} 1.4575_6.

Menthone. (Fluka) 1.4492_{US} 1.4478_1 1.4482_{2-4} 1.4492_5 1.4504_6 1.4447_7.

Pseudoionone. (Fluka) 1.5263_{US} 1.5267_1 1.5273_{2-4} 1.5267_5 1.5197_6.

α-Terpineol. (Fluka) 1.4803_{US}, $_{1-4}$ 1.4760_5 1.4700_6.

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