ACTA CHEMICA SCANDINAVICA 9 (1955) 925—937

# $\Delta^3$-Carene and $\alpha$-Pinene from Swedish Sulfate Turpentine

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$\Delta^3$-Carene and $\alpha$-pinene from Swedish sulfate turpentine have been purified to index homogeneity ($n_D^{25}$ = 1.4700 and 1.4632, respectively) and have been examined by an analytical micro sorption method. The extent of purification effected by vacuum distillation and methanol extraction has been investigated, and the conclusion drawn that only very efficient column distillation will give satisfactory results. $\alpha$-Pinene is isomerized to a small extent on prolonged distillation but the resulting compounds can be removed by extraction.

The products which are formed by autoxidation of $\Delta^3$-carene and $\alpha$-pinene can easily be removed by extraction. This is also found to be the case when some oxygen-containing terpenes are mixed with the two terpenes, but it has been shown that small amounts of terpene hydrocarbons added are not affected by the extractions.

The industrial Swedish turpentine has been analysed by sorption and highly concentrated fractions of $\alpha$-pinene, and $\Delta^3$-carene are found in the first and the last fractions, respectively. The minor constituents in the $\alpha$-pinene fractions are found to be $\Delta^3$-carene and $\beta$-pinene and their content has been determined. The impurities in the $\Delta^3$-carene fractions have been briefly studied.

The presence of $\beta$-pinene has been detected by catalytic Pd-$BaCO_3$ isomerization of $\beta$-pinene to $\alpha$-pinene in connection with sorption analysis. The content of $\beta$-pinene in some fractions has been determined by adding known amounts of pure $\beta$-pinene to the isomerized samples to bring their sorptograms up to their original figures.

Most of the turpentine which is produced in Sweden is prepared at the sulfate pulp mills. At these mills the main source of wood is from *Pinus silvestris* but a smaller amount of wood from *Picea abies* L.* is almost always present, usually in the form of peeled waste from the sulfite mills. As this inferior wood is known to contain much less turpentine than the heart-wood of the pines [1], its influence on the composition of the sulfate turpentine is frequently neglected. It would, however, be interesting to investigate the turpentine prepared from unmixed wood of the two species.

* = *(Picea excelsa.)*

The turpentine is liberated with the steam which is blown off from the boilers at intervals in the heating up period, also during and after the sulfide boiling. Collected from the ring of boilers, the raw turpentine is freed, with the loss of some turpentine, from most of the low boiling sulfur compounds (a) which are burned mostly for the recovery of sulfur. The residue is usually distilled through a column and separated into three fractions; a strongly mercaptan-smelling foreoil (b), the turpentine (c) and a higher boiling fraction (d). The composition of these fractions from the charge of raw turpentine (17 000 l) used for the preparation of the turpentine for this investigation is given below *.

| | | |
|---|---|---|
| a) Fuel oil | 1 150 l = | 6.8 % |
| b) Fore oil | 1 750 l = | 10.3 » |
| c) Turpentine | 8 500 l = | 50.0 » |
| d) "Pine oil" | 2 400 l = | 14.1 » |
| e) Residue | 2 700 l = | 15.9 » |
| Loss | 500 l = | 2.9 » |
| | 17 000 l = | 100 % |

The main constituents of the turpentine fraction from *Pinus silvestris* are known to be $\alpha$-pinene and $\Delta^3$-carene. The presence of $\beta$-pinene has been proved by the preparation of nopinonic acid [2,3], and Bardyshev *et al.*[4] have calculated the content in Siberian balsam turpentine to be 6.36 %. Aschan [2], and Semmler and Schiller [5] have presumed $\Delta^4$-carene to be present but no proof has been given. When, however, discussing the minor constituents in turpentine, several difficulties must be kept in mind. Isomerization can have occurred during the preparation and purification operations. Azeotropic mixtures within a particular distillation fraction can be formed, and derivatives for characterization purposes are usually formed in low yields from terpene mixtures. Last but not least, until very recently there was no method for determination of the homogeneity of the liquid terpenes. An added complication is found in the case of sulfate turpentine which contains sulfur compounds. On the other hand, the alkaline sulfide is believed to have little effect on the isomerization of terpenes.

In this investigation, samples were taken out at intervals from an industrial distillation of the turpentine fraction c — see above. The samples were examined with the usual physical methods, before and after attempts to remove the residual mercaptan-smelling components. The smell was completely removed by storing the samples one week over sodium wire, during which time a brown precipitate was deposited. Alternatively, after five extractions with 90 % methanol, the smell was almost completely removed. As seen from Table 1, there was very little change in the physical constants after these treatments.

Examining the curves in Fig. 1, the three plateaux indicate that three components are present, but the physical values give, of course, no indication

* All the turpentine used in this investigation was kindly supplied by Marma-Långrör Ltd., Marmaverken. I am very much indebted for all help with the samples and industrial information to Ingenjör H. Jansson at this mill.

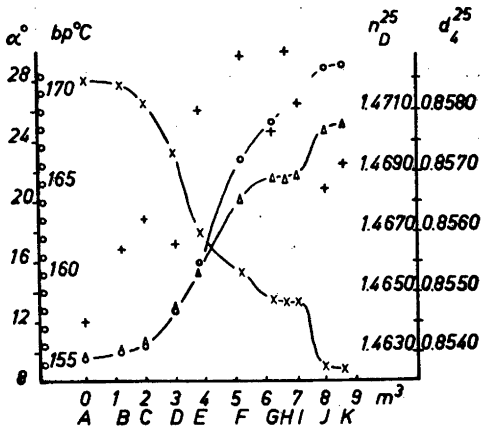


*Fig. 1. Physical values of the fractions A—K from an industrial distillation of turpentine. × = optical rotation (10 cm). △ = refractive index. + = density. ○ = boiling point. The thermometer was unfortunately out of function for the fractions H and I.*

of their homogeneity. However, in this work, the homogeneity of the turpentine fractions has been studied for the first time. The method used was devised by Blohm [6] and involves micro separation on activated silica gel. One drop (40.0 μl) was displaced with ethanol at pressure (1 atm) through a 25.0 cm long, narrow (i. d. 1.4 mm) column and 5 μl fractions were collected, on which refractive indices were determined [7]. The sorptogram, $n_D^{25}$ plotted against sorption fraction number, will give a straight line for a homogeneous sample if no isomerization has been caused by the active gel.

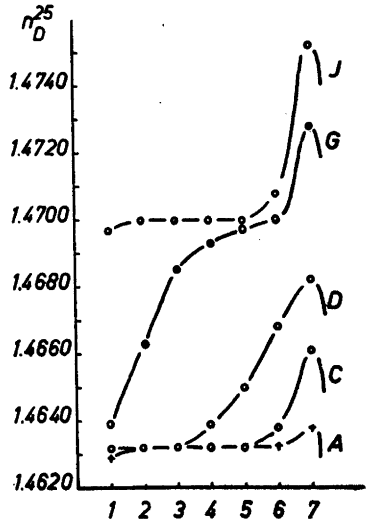


*Fig. 2. Sorptograms of some of the fractions given in Fig. 1.*

*Table 1.* *a) Sorptograms of industrial distillation of the turpentine fraction (c) at 758—760 mm Hg.*
*b) Sorptograms after 5 methanol extractions.*
*c) Sorptograms after 2 weeks with sodium wire.*
*d) Sorptograms after Pd-$BaCO_3$ isomerization.*
*e) Sorptograms after addition of known amounts of pure β-pinene to the isomerized sample, fraction C 1 %, E 12 % and I 13 %.*

| Fraction | Refractive indices of sorptograms, $n_D^{25}$ 1. . . . . |
|---|---|
| A | a) $4631_{US}$* $4630_1$ $4632_{2-5}$ $4633_6$ $4638_7$ |
| | b) $4631_{US}$ $4632_{1-6}$ $4642_7$ |
| | c) $4632_{1-5}$ $4633_6$ $4641_7$ |
| | d) $4632_{US}$ $4627_1$ $4630_2$ $4632_{3-6}$ $4637_7$ |
| B | a) $4632_{US}$ $4630_1$ $4632_{2-6}$ $4643_7$ |
| | b) $4631_{US}$ $4632_{1-6}$ $4641_7$ |
| | c) $4632_{1-6}$ $4652_7$ |
| | d) $4632_{US,\ 1-6}$ $4650_7$ |
| C | a) $4636_{US}$ $4631_1$ $4632_{2-5}$ $4638_6$ $4661_7$ |
| | b) $4632_{US}$ $4632_{1-5}$ $4638_6$ $4661_7$ |
| | c) $4632_{1-5}$ $4638_6$ $4660_7$ |
| | d) $4633_{US}$ $4630_1$ $4632_{2-5}$ $4633_6$ $4649_7$ |
| | e) $4632_{1-6}$ $4659_7$ |
| D | a) $4648_{US}$ $4632_{1-3}$ $4638_4$ $4650_5$ $4668_6$ $4682_7$ |
| | b) $4650_{US}$ $4632_{1-4}$ $4635_5$ $4672_6$ $4700_7$ |
| | c) $4632_{1-4}$ $4638_5$ $4653_6$ $4685_7$ |
| | d) $4640_{US}$ $4628_1$ $4631_2$ $4632_{3-5}$ $4642_6$ $4670_7$ |
| E | a) $4662_{US}$ $4632_{1-3}$ $4647_4$ $4670_5$ $4690_6$ $4704_7$ |
| | b) $4662_{US}$ $4632_{1-3}$ $4644_4$ $4680_5$ $4693_6$ $4706_7$ |
| | c) $4632_{1-3}$ $4634_3$ $4650_4$ $4677_5$ $4690_6$ $4700_7$ |
| | d) $4650_{US}$ $4630_1$ $4632_2$ $4633_{3-4}$ $4642_5$ $4668_6$ $4682_7$ |
| | e) $4629_1$ $4631_2$ $4642_3$ $4658_4$ $4678_5$ $4690_6$ $4702_7$ |
| F | a) $4684_{US}$ $4638_1$ $4653_2$ $4677_3$ $4689_4$ $4697_5$ $4700_6$ $4710_7$ |
| | b) $4683_{US}$ $4632_1$ $4652_2$ $4678_3$ $4689_4$ $4698_5$ $4700_6$ $4713_7$ |
| | c) $4632_1$ $4646_2$ $4675_3$ $4688_4$ $4692_5$ $4698_6$ $4712_7$ |
| | d) $4682_{US}$ $4632_1$ $4653_2$ $4672_3$ $4686_4$ $4690_5$ $4710_6$ |
| G | a) $4690_{US}$ $4645_1$ $4666_2$ $4682_3$ $4691_4$ $4698_5$ $4700_6$ $4722_7$ |
| | b) $4689_{US}$ $4640_1$ $4663_2$ $4685_3$ $4693_4$ $4698_5$ $4700_6$ $4728_7$ |
| | c) $4638_1$ $4668_2$ $4683_3$ $4692_4$ $4700_{5-6}$ $4721_7$ |
| | d) $4698_{US}$ $4642_1$ $4663_2$ $4685_3$ $4695_4$ $4699_5$ $4703_6$ $4753_7$ |
| H | a) $4690_{US}$ $4646_1$ $4667_2$ $4682_3$ $4691_4$ $4700_{5-6}$ $4722_7$ |
| | b) $4690_{US}$ $4647_1$ $4670_2$ $4688_3$ $4697_4$ $4699_5$ $4708_6$ $4730_7$ |
| | c) $4641_1$ $4661_2$ $4680_3$ $4692_4$ $4698_5$ $4700_6$ $4718_7$ |
| | d) $4690_{US}$ $4648_1$ $4672_2$ $4689_3$ $4692_4$ $4700_5$ $4703_6$ $4742_7$ |
| I | a) $4684_{US}$ $4637_1$ $4653_2$ $4682_3$ $4693_4$ $4700_{5-6}$ $4710_7$ |
| | b) $4688_{US}$ $4637_1$ $4661_2$ $4683_3$ $4693_4$ $4700_{5-6}$ $4729_7$ |
| | c) $4632_1$ $4654_2$ $4679_3$ $4689_4$ $4692_5$ $4700_6$ $4714_7$ |
| | d) $4671_{US}$ $4627_1$ $4640_2$ $4662_3$ $4678_4$ $4682_5$ $4688_6$ $4703_7$ |
| | e) $4626_1$ $4640_2$ $4669_3$ $4688_4$ $4693_5$ $4698_6$ $4704_7$ |
| J | a) $4709_{US}$ $4697_1$ $4700_{2-5}$ $4710_6$ $4752_7$ |
| | b) $4710_{US}$ $4693_1$ $4699_2$ $4700_{3-5}$ $4711_6$ $4753_7$ |
| | c) $4692_1$ $4698_2$ $4700_{3-5}$ $4708_6$ $4748_7$ |
| | d) $4708_{US}$ $4681_1$ $4692_2$ $4693_{3-4}$ $4695_5$ $4710_6$ $4756_7$ |
| K | a) $4710_{US}$ $4700_{1-5}$ $4709_6$ $4748_7$ |
| | b) $4710_{US}$ $4700_{1-4}$ $4701_5$ $4717_6$ $4757_7$ |
| | c) $4696_1$ $4700_{2-5}$ $4708_6$ $4747_7$ |
| | d) $4710_{US}$ $4697_1$ $4700_{2-5}$ $4705_6$ $4748_7$ |

* see p. 935, note **.

With the aid of this method it was shown (*cf.* Table 1 and Fig. 2) that the first plateau consisted of a rather homogeneous $\alpha$-pinene, the last plateau was a somewhat less pure $\Delta^3$-carene and the middle one was a more complex mixture. At every sorption analysis the last fractions had higher refractive indices and obviously contained terpenes of more complex nature, thus giving the sorptogram a peak before the fall to the ethanol level. For $\alpha$-pinene, the obvious explanation is that small amounts of $\Delta^3$-carene and $\beta$-pinene are present in the mixture (see below), but in the case of $\Delta^3$-carene there is no simple explanation. To study the problems concerning this subject it is necessary to find methods for the purification of other terpenes which can be presumed to be present in the mixture, either as natural compounds of the wood, or formed by isomerization during the sulfide boiling or on oxidation. Furthermore, the general conditions and the sensitivity of the analytical method cannot be examined until more terpenes have been purified to index homogeneity.

## Purification of $\Delta^3$-carene

In agreement with Rao and Simonsen [3] on their investigation of Swedish turpentine, the purest $\Delta^3$-carene was found in the last fractions of the distillation. To find the best raw material for the purification of $\Delta^3$-carene, samples in the region of sample K from several industrial distillations were examined. There was a rather wide distribution of the sorptograms with different heights of the peaks. The last fractions were without any slope of $\alpha$-pinene in the beginning of the sorptograms, but as the composition of the "pine oil" (d) is rather uncertain (compare Rao and Simonsen [3] who have isolated *l*-cadinene) a fraction containing some percent $\alpha$-pinene was used as starting material for the purification. After standing for two weeks over sodium, the brown

*Table 2. Distillation of 1.5 l $\Delta^3$-carene, sample $K_3$, in a laboratory column (a) at 13 mm Hg. Boiling temperature 55.8—57.4°. Reflux ratio 14:15. Time 85 h.*

| Fraction No. | Volume ml | Refractive indices of sorptograms, $n_D^{25}$ 1. .... |
|---|---|---|
| 1 | 50 | $4691_1$ $4694_2$ $4697_{3-4}$ $4700_5$ $4703_6$ $4728_7$ |
| 2 | 50 | $4692_1$ $4697_2$ $4700_{3-5}$ $4708_6$ $4735_7$ |
| 3 | 50 | $4695_1$ $4698_2$ $4700_{3-5}$ $4708_6$ $4734_7$ |
| 4 | 50 | $4706_{US}$ $4700_{1-4}$ $4701_5$ $4712_6$ $4726_7$ |
| 5 | 50 | $4700_{1-4}$ $4702_5$ $4708_6$ $4729_7$ |
| 6—7 | 100 | $4703_{US}$ $4700_{1-4}$ $4702_5$ $4705_6$ $4728_7$ |
| 8 | 50 | $4700_{1-4}$ $4702_5$ $4706_6$ $4725_7$ |
| 9 | 50 | $4700_{1-4}$ $4701_5$ $4703_6$ $4728_7$ |
| 10 | 50 | $4700_{1-6}$ $4703_7$ $4729_8$ |
| 11—19 | 525 | $4702\text{-}3_{US}$ $4700_{1-6}$ $4727\text{-}30_7$ |
| 20 | 50 | $4704_{US}$ $4700_{1-6}$ $4738_7$ |
| 21 | 50 | $4707_{US}$ $4700_{1-5}$ $4702_6$ $4745_7$ |
| 22 | 50 | $4709_{US}$ $4703_{1-2}$ $4704_{3-4}$ $4710_5$ $4732_6$ $4763_7$ |
| (23)—24 | 100 | $4732_{US}$ $4702_1$ $4703_2$ $4713_3$ $4730_4$ $4748_5$ $4763_6$ $4771_7$ |
| 25 | 35 | $4758_{US}$ |
| Residue | 120 | $4772_{US}$ $4761_{1-2}$ $4770_3$ $4782_4$ $4792_5$ $4797_6$ $4775_7$ |

*Table 3. Distillation of 35 ml $\Delta^3$-carene, sample $K_2$, in a spinning band column [14] at 20 mm Hg. Fractions 2 to 10 boiling at 70.0°.*

| Fraction No. | Volume total % | Refractive indices of sorptograms, $n_D^{25}$ 1. . . . . |
|---|---|---|
| 1 | 7.5 | $4707_{US}$ $4688_1$ $4697_2$ $4700_{2-5}$ $4705_6$ $4728_7$ |
| 2 | 15 | $4709_{US}$ $4698_1$ $4700_{2-5}$ $4702_6$ $4736_7$ |
| 3 | 22.5 | $4706_{US}$ $4698_1$ $4700_{2-6}$ $4732_7$ |
| 4 | 30 | $4703_{US}$ $4698_1$ $4700_{2-6}$ $4730_7$ |
| 5 | 38 | $4703_{US}$ $4698_1$ $4700_{2-6}$ $4708_7$ $4732_8$ |
| 6—7 | 53 | $4704_{US}$ $4698_1$ $4700_{2-5}$ $4726_7$ |
| 8 | 60.5 | $4704_{US}$ $4699_1$ $4700_{2-5}$ $4736_7$ |
| 9 | 68 | $4708_{US}$ $4700_{1-6}$ $4748_7$ |
| 10 | 75.5 | $4710_{US}$ $4700_{1-5}$ $4709_6$ $4765_7$ |
| 11 | 83.5 | $4711_{US}$ $4700_{1-5}$ $4726_6$ $4798_7$ |
| 12 | 89 | $4736_{US}$ $4700_{1-3}$ $4722_4$ $4757_5$ $4779_6$ $4803_7$ |

deposit was filtered off and the liquid was used in the next purification stage. Further treatment with sodium gave no more precipitate, unless the sample became oxidized in the meantime.

In order to remove the most hydrophilic components — after vacuum distillation — the liquid was shaken several times with 10 % of its volume of 90 % methanol. This treatment had an effect on the peak, and the first extractions reduced the peak more than the subsequent ones. After 60—70 extractions there was no further reduction, and the peak remained constant with 9 units in the last figure above the level. As carene is somewhat soluble in 90 % methanol only a very small amount of the terpene was left after all these extractions.

The only way found to purify $\Delta^3$-carene to index homogeneity was by vacuum distillation using a fractionating column. An ordinary laboratory column, 40 cm high, with reflux ratio 14:15 and a spinning band column [8] both operating in vacuum, gave no marked reduction in the peak (Tables 2 and 3). When distilled up a 6′ high Podbielniak column, there was a consider-

*Table 4. Distillation of 2.0 l $\Delta^3$-carene, sample $K_2$, in a 6′ Podbielniak column (e) at 19.5 mm Hg. Fractions 4 to 24 boiling at 66.5°. Reflux ratio fractions 1—8, 199:200; fraction 9—24, 299:300. Time 24 days.*

| Fraction No. | Volume total % | Refractive indices sorptograms, $n_D^{25}$ 1..... | Optical rotation (10 cm) |
|---|---|---|---|
| 5 | 17.5 | $4699_{US}$ $4693_1$ $4696_2$ $4698_3$ $4700_{4-6}$ $4708_7$ | 13.28° |
| 6 | 22.5 | $4699_{US}$ $4700_{1-6}$ $4708_7$ | 13.73° |
| 7—13 | 45 | $4699_{US}$ $4700_{1-6}$ $4705-3_7$ | (10) 13.84° |
| 14 | 48.5 | $4700_{US}$ $4700_{1-6}$ $4703_7$ | 14.49° |
| 15—16 | 55.5 | $4700_{US}$ $4700_{1-6}$ $4701_7$ | (15) 14.80° |
| 17—19 | 65 | $4700_{US}$ $4700_{1-7}$ | (18) 15.22° |
| 20—22 | 79.5 | $4700_{US}$ $4700_{1-6}$ $4702_7$ | (20) 15.27° |
| 23 | 82.5 | $4700_{US}$ $4700_{1-6}$ $4703_7$ | (22) 15.25° |
| 24 | 85.5 | $4700_{1-5}$ $4707_6$ $4763_7$ | 12.78° |

able reduction, but index-homogeneous fractions were obtained only when the reflux ratio was raised to 299:300 (equal to 100—140 TP). As seen from Table 4, most fractions, in spite of the high efficiency of the column, had small peaks and it was only found possible to reduce them a little by methanol extraction.

The physical constants found for index-homogeneous $\Delta^3$-carene are $[\alpha]_D^{25} = +17.6°$; $d_4^{25} = 0.8635$; $n_D^{25} = 1.4700$; as the refractive index by the sorption analysis has become the most important constant it has been determined at different temperatures giving a decrease of 0.0023 per 5° in the range of +15° to +30°.

The nature of the peak constituents has been briefly investigated, but a closer study cannot be made until the supposed constituents have been prepared to index homogeneity. From the sorptograms of mixtures of the two terpenes [9] $\beta$-pinene and *d*-limonene, purified to index homogeneity, it can be seen, that they can be almost excluded as peak constituents. When pure carene was mixed with 5 % of inhomogeneous — in spite of vacuum distillation — $\alpha$-terpinene, terpinolene and "sylvestrene", peaks were obtained, which did not change after methanol extractions. The peak which is formed when $\Delta^3$-carene is oxidized (*cf.* Blohm and Widmark [10]) is easily removed by 2—3 extractions. If, however, the oxidized carene is stored in a sealed glass ampoule for several months, the nature of the peak changes, and becomes as difficult to remove as in the case of the industrial sample.

## Purification of $\alpha$-pinene

Several industrial charges of turpentine were examined and an $\alpha$-pinene fraction ($A_6$) with a very low peak was selected for further purification. After the first few extractions with methanol, or after sodium treatment, there was an increase in the height of the peak. This was most probably due to the removal of some hydrophilic sulfur compounds with low refractive index. Further extractions gave no changes in the peak, even after 60 extractions.

Vacuum distillation using the laboratory column (Table 5) gave a reduction of the peak, and with a higher column the peak remained only in the first

*Table 5. Distillation of 405 ml α-pinene, sample $A_3$, in a laboratory column (a) at 15.0 mm Hg. Boiling temperature 46.1°—46.7°. Reflux ratio 17:18. Time 20 h.*

| Fraction No. | Volume ml | Refractive indices of sorptograms, $n_D^{25}$ 1. .... |
|---|---|---|
| 1 | 20 | $4630_{US}$ $4629_1$ $4631_3$ $4632_{3-5}$ $4634_6$ $4637_7$ $4657_8$ |
| 2 | 30 | $4630_{US}$ $4631_1$ $4632_{3-5}$ $4637_6$ $4650_7$ |
| 3 | 30 | $4629_{US}$ $4632_{1-5}$ $4635_6$ $4645_7$ |
| 4 | 30 | $4630_{US}$ $4632_{1-5}$ $4634_6$ $4644_7$ |
| 5—7 | 90 | $4631_{US}$ $4632_{1-5}$ $4634_6$ $4644_7$ |
| 8—9 | 60 | $4631_{US}$ $4632_{1-5}$ $4635_6$ $4645_7$ |
| 10 | 30 | $4632_{US,\ 1-4}$ $4637_5$ $4640_6$ $4656_7$ |
| 11 | 20 | $4632_{US,\ 1-3}$ $4634_4$ $4639_5$ $4644_6$ $4662_7$ |
| Residue | 75 | $4670_{US}$ $4642_1$ $4653_3$ $4663_3$ $4672_4$ $4685_5$ $4692_6$ $4690_7$ |

*Table 6. Distillation of 275 g α-pinene, sample $A_6$, in a 2 m column (d) (60 mm Hg). Boiling temperature 77.0°–77.5°. Reflux ratio 24:25. Time 12 h.*

| Fraction No. | Volume ml | Refractive indices of sorptograms, $n_D^{25}$ 1. . . . . |
|---|---|---|
| 1 | 41.1 | $4628_1$ $4629_2$ $4630_{3-5}$ $4632_6$ $4633_7$ |
| 2 | 35.7 | $4629_{US}$ $4632_{1-7}$ |
| 3 | 59.0 | $4629_{US}$ $4632_{1-7}$ |
| 4 * | 11.7 | $4629_{US}$ $4632_{1-7}$ |

* By accident no more fractions were obtained.

of 4 fractions (Table 6). However, there was a difference in refractive index between the unsorbed sample and the plateau in the sorptogram; $n_D^{25} = 1.4629$ and 1.4632, respectively, probably depending on compounds of low index which were mixed up with the displacer during the sorption. Distilled through the Podbielniak column all fractions had small peaks (Table 7), most likely formed by isomerization on prolonged distillation. Methanol extractions removed these peaks, and after washing and drying, the plateau and the unsorbed sample both had the same refractive index 1.4632.

The values found for α-pinene are

$$[\alpha]_D^{25} = +\ 34.9°;\quad d_4^{25} = 0.8571;\quad n_D^{25} = 1.4632$$

with a decrease of 0.0023 per 5° in the range of +15° to 30°. The value for the rotation is lower than those reported for *e. g.* Greek *d*-α-pinene. This could be explained by the content of *l*-α-pinene in our turpentine resulting from contamination of the pine wood by fir wood. However, α-pinene extracted from American wood [11] gives a rotation similar to ours.

In agreement with the findings in the case of $\Delta^3$-carene, oxygen compounds added to pure α-pinene could be removed by methanol extractions, but the peaks which were formed by adding small amounts of $\Delta^3$-carene and β-pinene were almost unaffected by extractions. Sorptograms similar to the ones for fractions A to C were formed when sorbing mixtures [9] of pure α-pinene with small amounts of $\Delta^3$-carene or β-pinene; fraction A corresponded to 0.4 % $\Delta^3$-carene or 1 % β-pinene, B to 1.5 % or 3 % and C 2 % or 5 %, respectively.

*Table 7. Distillation of 800 ml α-pinene, sample $A_6$, in a 6′ Podbielniak column (e) (42.1–42.6 mm Hg). Boiling temperature 68.0–68.5°. Reflux ratio 299:300.*

| Fraction No. | Volume total % | Refractive indices of sorptograms, $n_D^{23}$ 1. . . . . |
|---|---|---|
| 1 | 7 | $4628_{US}$ $4623_1$ $4630_2$ $4631_3$ $4632_{4-7}$ |
| 2 | 14 | $4629_{US}$ $4628_1$ $4630_2$ $4632_{3-7}$ |
| 3 | 25 | $4630_{US}$ $4632_{1-6}$ $4635_7$ |
| 4 | 32.5 | $4631_{US}$ $4632_{1-6}$ $4637_7$ |
| 5–9 | 77 | $4632_{US,\ 1-6}$ $4636-8_7$ |

As seen from the following paragraph, the peaks consisted of a mixture of the two terpenes, and the numbers above thus give the maximum content in the peaks.

## Presence of $\beta$-pinene

Bardyshev *et al.*[4] have calculated the content of $\beta$-pinene in Siberian turpentine to be about 6 %. They have identified $\beta$-pinene by oxidation to nopinonic acid and explain earlier failures to detect $\beta$-pinene by demonstrating the difficulties in preparing nopinonic acid from $\beta$-pinene mixtures. To overcome this difficulty, an indirect method, catalytic conversion of $\beta$-pinene, was chosen for this investigation.

Richer and Wolff[12] have reported the catalytic isomerization of $\beta$-pinene to $\alpha$-pinene by palladium-black in ether solution in the presence of hydrogen. Here, the more practical Pd-$BaCO_3$-catalyst was used without any solvent, on a half micro scale. In a following communication[13] clear evidence will be given to show that this reaction is quantitative, and that the reaction is almost always followed by a little hydrogenation and a second isomerization, which are found to be low in the case of $\alpha$-pinene and $\Delta^3$-carene. However, these side reactions hamper the interpretation of the sorptograms and smaller amounts than, *e. g.*, 1 % $\beta$-pinene in $\alpha$-pinene cannot usually be detected. Furthermore, the activity of the catalyst and its ability to cause side reactions with other participating terpenes has to be investigated before each analysis.

One ml samples of the fractions A to K were shaken with about 50 mg of a 5 % Pd-$BaCO_3$ catalyst in small stoppered test tubes filled with hydrogen ($\sim$ 2 ml gas). The time, usually 1 to 2 hours, for full conversion was determined by simultaneous tests with index-homogeneous $\beta$-pinene. The presence of $\beta$-pinene or, more improbably, terpenes reacting in the same way, could be detected in the fractions B to I (*cf.* Table 1). For the fraction J, a sorptogram was obtained which differs from any isomerization tests with mixtures of $\Delta^3$-carene and $\alpha$- and $\beta$-pinene, and gives indications of more terpenes in our turpentine mixture.

In order to calculate roughly the content of $\beta$-pinene, known amounts of this terpene in index-homogeneous form were added to some of the isomerized samples to bring their sorptograms up to the original figures. From these experiments the content of $\beta$-pinene was found to be: fraction C 1—2 %, E 12 %, and I 13 %. Comparing the curves after isomerization with those from $\alpha$-pinene-$\Delta^3$-carene mixtures[9] one can calculate the content of $\Delta^3$-carene to be in fraction B and C 1 %, D 3 %, and E 5 %.

## Investigation of the middle fractions

The figures from the sorptograms of the fractions E to I differed from those obtained by mixing index-homogeneous $\Delta^3$-carene and $\alpha$- and $\beta$-pinene[9], not only in presence of peaks but also by the slope of the curves. After isomerization, there was still a difference which could not be explained only by the side reactions of the compounds mentioned. It is, of course, difficult to obtain perfectly reproducible sorptograms here with such steep curves as, *e. g.*, small variations in the 5 $\mu$l volumes can cause considerable variations in

*Table 8. Distillation of sample H (150 ml) in a laboratory column a at 756 mm Hg. Reflux ratio 15:16. Time 4.30 h. 15 ml fractions were collected.*

| Fraction No. | Temp. °C | Refractive indices of sorptograms, $n_D^{25}$ 1. . . . . |
|---|---|---|
| 1 | 162.1 | $4662_{US}$ $4627_1$ $4632_{2-3}$ $4651_4$ $4675_5$ $4691_6$ $4707_7$ |
| 2 | 162.9 | $4662_{US}$ $4628_1$ $4630_2$ $4632_3$ $4659_4$ $4678_5$ $4696_6$ $4702_7$ |
| 3 | 164.5 | $4670_{US}$ $4630_1$ $4633_2$ $4647_3$ $4668_4$ $4684_5$ $4698_6$ $4707_7$ |
| 4 | 165.4 | $4678_{US}$ $4630_1$ $4648_2$ $4671_3$ $4689_4$ $4699_5$ $4704_6$ $4718_7$ |
| 5 | 167.0 | $4688_{US}$ $4640^1$ $4650_2$ $4673_3$ $4682_4$ $4692_5$ $4700_6$ $4709_7$ |
| 6 | 168.8 | $4691_{US}$ $4656_1$ $4675_2$ $4689_3$ $4699_4$ $4700_5$ $4704_6$ $4719_7$ |
| 7 | 170.4 | $4700_{US}$ $4670_1$ $4689_2$ $4700_3$ $4704_4$ $4708_5$ $4728_6$ |
| 8 | 170.0 | $4702_{US}$ $4688_1$ $4700_{2-4}$ $4703_5$ $4705_6$ $4728_7$ |
| 9 | 170.0 | $4708_{US}$ $4690_1$ $4700_{2-5}$ $4705_6$ $4740_7$ |
| Residue | | $4760_{US}$ |

the index values. However, the discrepancy given above cannot be explained by non-reproducibility of the sorptograms, as from experience these are found to be much more reproducible. This gives additional evidence for more terpenes being present in the turpentine. Owing to the discrepancy it is not found possible to calculate, by comparison, the content of $\Delta^3$-carene in the fractions F to J.

In order to examine briefly the presence of other terpenes, fraction H (the middle plateau in Fig. 1) was distilled through a column both at atmospheric pressure and under vacuum. The very poor separation at ordinary pressure (Table 8) gave an indication of an azeotropic mixture. On vacuum distillation (Table 9) there was a separation into two fractions of almost pure $\alpha$-pinene, a middle fraction and finally two fractions ($H_4$ and $H_5$) which from their sorptograms could be $\Delta^3$-carene with small amounts of $\beta$-pinene and $\alpha$-pinene. However, when the $\beta$-pinene was removed by isomerization, sorptograms

*Table 9. a) Distillation of sample H (50 ml) in a 60 cm column (c) at 10—12 mm Hg. Reflux ratio 9:10. Time 4 h. b) Sorptograms after Pd-$BaCO_3$ isomerization for 3 hours.*

| Fraction No. | Volume ml | Temp. °C | Refractive indices of sorptograms, $n_D^{25}$ 1. . . . . |
|---|---|---|---|
| 1 | 5.6 | 40.0 | a) $4634_{US}$ $4629_1$ $4631_2$ $4632_{3-6}$ $4646_7$<br>b) $4632_{1-5}$ $4633_6$ $4648_7$ |
| 2 | 7.1 | 43.8 | a) $4636_{US}$ $4632_{1-5}$ $4638_6$ $4663_7$<br>b) $4632_{1-5}$ $4640_6$ $4664_7$ |
| 3 | 5.5 | 51.0 | a) $4654_{US}$ $4632_1$ $4642_2$ $4661_3$ $4687_4$ $4702_5$ $4712_6$ $4722_7$<br>b) $4632_1$ $4641_2$ $4662_3$ $4691_4$ $4707_5$ $4713_6$ $4718_7$ |
| 4 | 6.0 | 52.7 | a) $4712_{US}$ $4700_1$ $4707_2$ $4709_3$ $4712_4$ $4714_{5-7}$<br>b) $4695_1$ $4708_2$ $4710_3$ $4711_{4-6}$ $4717_7$ |
| 5 | 3.0 | 53.1 | a) $4710_{US}$ $4699_1$ $4703_2$ $4705_3$ $4708_4$ $4710_5$ $4711_6$ $4714_7$<br>b) $4693_1$ $4702_2$ $4704_{3-5}$ $4705_6$ $4709_7$ |
| Residue | 18 | | a) $4718_{US}$ $4709_1$ $4703_2$ $4700_{3-6}$ $4724_7$<br>b) $4700_{1-6}$ $4755_7$ |

were obtained which were different from those from $\alpha$-pinene-$\Delta^3$-carene mixtures [9]. This discovery will be further investigated with aid of a more effective vacuum column.

## EXPERIMENTAL PART

### Equipment

*Refractometer*, Bellingham & Stanley No. 402330. Calibrated against standard plate $n_D$ 1.5009. A thermostat controlled the temperature to 25 ± 0.02° C.

*Polarimeter*, Bellingham & Stanley No. 36291, 20.0 cm tubes being used. All values are calculated for 10 cm.

*Pycnometers.* Two types were used: Ostwald-Sprengel (type E) [14] for the more accurate determination of the pure terpenes and a usual density bottle for the industrial samples. The procedure given by Bauer [14] has been followed.

*Sorption apparatus.* An apparatus, fully observing Blohm's instructions, was used. The silica gel (Davison, 922—08—226 through 200 mesh) was activated 2 hours at 15 mm Hg. On reading the indices the aluminium setting [7] was omitted, and a fresh paper (~ 5 × 5 mm) was used for each determination.

*Columns.* a) 40 cm laboratory column resembling Quickfit No. FC 11/23 filled with 3 mm Fenske steel helices. Refluxhead Quickfit No. FC 15/12 and Thiele receiver; b) Spinning-band column (*cf.* Björkman and Olavi [8]); c) 60 cm column (i. d. 17 mm) electrically compensated, filled with Fenske glass helices, Quickfit No. FC 8/45. Refluxhead modified Quickfit No. FC 15/122. Thiele receiver; d) 2 m column (i. d. 25 mm) filled with steel springs, circulating liquid compensation. Electronic receiver; e) Podbielniak column, Hyper-Cal Apparatus, Cat. No. HC-701-A, Ser. "D", 6′ high, inner diameter 25 mm *. All columns were filled with an inert gas, nitrogen or carbon dioxide, before the distillations and the fractions were changed without disturbing the vacuum.

### Experiments

One liter samples were taken out at the intervals given in Fig. 1, the outlet tube first being cleaned by tapping out several liters of the corresponding turpentine. The samples were stored and transported in full, air free, bottles.

For selecting the best industrial sample of $\Delta^3$-carene and $\alpha$-pinene for purification and synthetic work, carboys of 30 liter capacity were filled at about 300 liters intervals in the region under investigation from several charges. A few ml from each carboy were sent for analysis. The best sample was then sent in tin containers to the laboratory where it was poured immediately into glass bottles. Sodium wire (d. 0.2 mm) — about 2 g per liter — was pressed into the liquid and the samples stored air tight in a dark cellar.

The sorptograms **, after Na-treatment of the used samples were, *$\Delta^3$-carene* ($K_3$) $1.4706_{US}$ $1.4698_1$ $1.4700_{2-5}$ $1.4716_6$ $1.4750_7$, *$\alpha$-pinene* ($A_6$) $1.4630_{US}$ $1.4632_{1-5}$ $1.4633_8$ $1.4638_{7}$, and ($A_3$) $1.4632_{US, 1-4}$ $1.4634_5$ $1.4639_6$ $1.4645_7$ for a preliminary investigation.

### Methanol extractions

*$\Delta^3$-Carene*, 25 ml of fraction 11—19 (Table 2), was shaken 3 minutes with about 10 % of its volume with 90 % methanol in a joint test tube ***. After separation (15—30 minutes) the methanol layer was suctioned off and some of the loss of turpentine can be explained by emulsion formation. After 70 extractions only 3 ml were left.

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* The two distillations with this column have been performed by Mo and Domsjö, Ltd., Örnsköldvik. I am very much indebted to Dr. B. Weibull and Mr. B. Nycander for all help with the distillations.

** In order to simplify the printing of the sorptograms and to avoid too many printed figures 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.

*** The minimal amount of grease was used, and 1 % grease in pure $\Delta^3$-carene gave no change of the sorptogram.

| | | | |
|---|---|---|---|
| 7 extractions | $1.4700_{1-5}$ | $1.4702_6$ | $1.4726_7$ |
| 23 » | $1.4700_{1-6}$ | $1.4721_7$ | |
| 33 » | $1.4700_{1-6}$ | $1.4715_7$ | |
| 45 » | $1.4700_{1-6}$ | $1.4711_7$ | |
| 55 » | $1.4700_{1-6}$ | $1.4710_7$ | |
| 70 » | $1.4700_{1-6}$ | $1.4709_7$ | |

*$\Delta^3$-Carene*, 6 ml of fraction 7 (Table 4), was extracted 15 times which brought the peak down to 1.4702. Extracting fraction 14 (peak 1.4703) a peak of 1.4702 remained even after 20 shakes.

*Freshly oxidized $\Delta^3$-carene.* 3 ml of index-homogeneous carene was stored 2 days in an open flask giving the sorptogram a peak, due to oxidation: $1.4712_{US}$ $1.4700_{1-5}$ $1.4712_6$ $1.4758_7$. After 3 extractions the peak was fully removed.

*Stored, oxidized $\Delta^3$-carene.* A 4 ml sample of pure carene was oxidized by accident, before it was sealed in an ampoule. After storing for several months it gave the sorptogram: $1.4701_{US}$ $1.4700_{1-6}$ $1.4709_7$. When extracted, the peak was reduced with difficulty.

| | | |
|---|---|---|
| 6 extractions | $1.4700_{1-6}$ | $1.4706_7$ |
| 12 » | $1.4700_{1-6}$ | $1.4703_7$ |

*α-Pinene.* 75 ml α-pinene, sorptogram $1.4632_{US}$ $1.4632_{1-5}$ $1.4639_6$ $1.4646_7$, was extracted 30 times with 90 % methanol but there was no change in the peak. The same negative result was obtained by extraction with 50 % ethanol.

α-Pinene, obtained on prolonged vacuum distillation (fraction 3, Table 7) was extracted 5 times and gave then the sorptogram $1.4632_{US, 1-7}$.

*Freshly oxidized α-pinene.* 2 ml index-homogeneous α-pinene, stored in an open flask for 5 days, gave the sorptogram $1.4632_{1-4}$ $1.4636_5$ $1.4639_6$ $1.4642_7$. Three methanol extractions restored the α-pinene to index homogeneity.

## Extraction of mixtures

*$\Delta^3$-Carene and β-pinene in α-pinene.* One percent $\Delta^3$-carene in α-pinene and 1 % β-pinene in α-pinene gave the sorptograms $1.4632_{1-5}$ $1.4635_6$ $1.4649_7$ and $1.4632_{1-5}$ $1.4634_6$ $1.4649_7$, respectively. There was very little change after 30 extractions.

*Verbenone in α-pinene.* Two percent of carefully vacuum distilled verbenone; sorptogram: $1.4818_1$ $1.4850_2$ $1.4863_3$ $1.4869_4$ $1.4874_{5-6}$ $1.4672_7$ were added to pure α-pinene forming the sorptogram $1.4632_{US, 1-6}$ $1.4645_7$. The peak was removed after 10 extractions.

*α-Terpinene, terpinolene, and "sylvestrene" in $\Delta^3$-carene.* Up to now there has been no success in purifying the available amounts of these terpenes to index homogeneity. After vacuum distillation the terpenes had the following sorptograms:

*α-Terpinene* $1.4760_{US}$ $1.4747_1$ $1.4752_2$ $1.4770_3$ $1.4781_4$ $1.4783_5$ $1.4784_6$ $1.4785_7$;
*Terpinolene* $1.4757_{US}$ $1.4791_1$ $1.4797_2$ $1.4800_3$ $1.4802_{4-5}$ $1.4803_6$;
*"Sylvestrene"* $1.4810_{US}$ $1.4856_1$ $1.4848_2$ $1.4837_3$ $1.4825_4$ $1.4803_5$ $1.4802_6$ $1.4793_7$

Five percent of these samples in pure carene gave the sorptograms:

*α-Terpinene:* $1.4703_{US}$ $1.4700_{1-4}$ $1.4701_5$ $1.4715_6$ $1.4729_7$;
*Terpinolene* $1.4704_{US}$ $1.4703_{1-2}$ $1.4701_{3-4}$ $1.4700_{5-6}$ $1.4720_7$;
*"Sylvestrene"* $1.4708_{US}$ $1.4700_{1-3}$ $1.4705_4$ $1.4713_5$ $1.4722_6$ $1.4738_7$.

After 20 methanol extractions of these mixtures there were no marked changes in the sorptograms.

*α-Terpineol in $\Delta^3$-carene.* α-Terpineol was only very slowly forced through the column giving the sorptogram: $1.4800_{US}$ $1.4805_1$ $1.4798_2$ $1.4780_3$ $1.4720_4$ $1.4632_5$. In 5 % mixture the sorption also proceeded slowly giving $1.4700_{US, 1-5}$ $1.4698_6$ $1.4684_7$. Three extractions gave $1.4700_{US, 1-7}$.

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Received April 4, 1955.