Study on Chemical Separation and Purification of Camphor Oil

Aijiang He a, * and Lixiu Liu b

Yibin Vocational & Technical College, Yibin 644003, China

*Corresponding author: 406140056@qq.com, b494661411@qq.com

Abstract. The separation and purification of camphor oil was studied in this paper, using sulfuric acid as the chemical extractant. The effects of sulfuric acid concentration, reactant ratio, temperature and stirring time on the yield and purity of 1,8-eucalyptin in camphor oil were investigated. The results show that the concentration of sulfuric acid, the reactant ratio and temperature have great influence on the extraction effect. When the sulfuric acid concentration is 45%, the reactant ratio is 4:3, the temperature is 50 ℃, and the stirring time is 20 minutes, the purity of eucalyptin reaches 97.8% and the yield gets 57.3% respectively.

Keywords: Camphor oil, separation, chemistry, terpineol.

1. Introduction

Terpineol is widely used in various fields such as ink, chemical industry, light industry, pharmaceutical industry and telecommunication. Terpineol has an aroma and can be used to prepare soap, cosmetics, spices and food additives. China is a big producer of terpineol, with terpineol yield close to 10,000 tons in 2016, 70% of which is exported to foreign countries.

Terpineol is mainly synthesized from α-pinene and β-pinene in turpentine using the traditional two-step synthesis method. With sulfuric acid as a catalyst, α-pinene and β-pinene are synthesized to terpineol through hydration and dehydration [1-2]. Catalytic reaction is the main factor influencing the conversion efficiency and the terpineol quality. Considering the poor controllability of sulfuric acid as a catalyst, scholars replace sulfuric acid with inorganic acids, organic acids, mixed acids and acid-functionalized ionic liquids to improve the yield rate [3-4]. With the advantages of less equipment corrosion, easy separation and purification of products, and controllable environmental pollution, solid acid has become a research hotspot in the synthesis of turpentine. The catalytic synthesis of terpineol by solid acid can improve the reaction selectivity and activity. However, there are still some problems to be solved, such as high catalyst cost and short service life.

Eucalyptol, camphor oil and other essential oil fractions contain high contents of α-pinene, β-pinene and terpineol, and have become important sources of terpineol[5]. With sulfuric acid as the purification medium, this study used chemical purification to explore the influencing factors and process conditions for the separation and purification of terpineol from camphor oil.
2. Experimental methods

2.1. Raw material
The raw material is camphor oil purchased from Yibin Weitu Agricultural Technology Co., Ltd, and the mass fraction of 1,8-eucalyptol is greater than 55%.

2.2. Experimental equipment
Gas chromatograph (Agilent Cerity-6820) manufactured by Agilent Technologies Inc. and 722N visible spectrophotometer manufactured by Shanghai Precision Instrument Co., Ltd. were used in the experiment. Constant temperature water bath was prepared, with the temperature control accuracy of ± 1.0 °C.

2.3. Experimental procedure
100ml of camphor oil was added to a beaker. The magnetic stirrer was started, and a certain volume of sulfuric acid was added and stirred. After standing, the mixture was delaminated, and a separatory funnel was used to place the lower layer of the supernatant in a conical flask. Alkaline solution was added to the conical flask to adjust the pH to neutral and stood in the refrigerator for 8 hours. After filtering, the crystalline substance was placed in a watch glass, which was dried in a desiccator for 24 hours.

3. Discussion of experimental results

3.1. Analysis of components of camphor oil
Gas chromatography was employed to analyze the raw material camphor oil. The contents of the components in camphor oil are listed in Table 1.

| NO. | Name                  | Molecular formula | Molecular weight | Percentage composition% | Note                                      |
|-----|-----------------------|-------------------|------------------|-------------------------|-------------------------------------------|
| 1   | 1,8-eucalyptol        | C_{10}H_{15}O     | 154.25           | 59.18                   | Cyclic ether, boiling point 176~177°C     |
| 2   | Terpineol (α-terpineol)| C_{10}H_{15}O     | 154.25           | 14.36                   | Alcohol, boiling point 214-224°C          |
| 3   | Sabinene              | C_{10}H_{16}      | 136.24           | 9.69                    | Ethylene, boiling point 163-164°C         |
| 4   | α-pinene              | C_{10}H_{16}      | 136.24           | 5.54                    | Ethylene, boiling point 155°C             |
| 5   | β-pinene              | C_{10}H_{16}      | 136.24           | 2.47                    | Ethylene, boiling point 166°C             |
| 6   | Terpinene-4-alcohol   | C_{10}H_{14}O     | 154.25           | 2.43                    | Ethylene, boiling point 212°C             |
| 7   | γ-terpinene           | C_{10}H_{16}      | 136.24           | 1.69                    | Ethylene, boiling point 183°C             |
| 8   | Limonene              | C_{10}H_{16}      | 136.24           | 0.66                    | Ethylene, boiling point 175.44°C          |
| 9   | α-terpinene           | C_{10}H_{16}      | 136.23           | 0.87                    | Ethylene, boiling point 177.2°C           |
| 10  | Isoterpinene          | C_{10}H_{16}      | 136.24           | 0.56                    | Boiling point: 186 ~ 187°C               |
| 11  | p-cymene              | C_{10}H_{14}      | 134.21           | 0.45                    | Boiling point: 177.1°C                   |
| 12  | Other components      |                   |                  | 2.1                     | Ethylene and alcohol                      |
| 13  | Total                 |                   |                  | 100                     |                                           |

As can be seen from Table 1, the contents of 1,8-eucalyptol, Sabinene and terpineol are 56.68%, 14.07%, and 7.64%, respectively. According to the functional groups of the components in the table, the components of camphor oil can be classified into three categories of ether (56.67%), olefin (29.77%) and alcohol (7.64%), as well as a small amount of other substances. α-pinene, β-pinene, terpinene-4-alcohol and γ-terpinene are terpenoids.
3.2. Influence of sulfuric acid concentration on extraction
Sulfuric acid of different concentrations was mixed with camphor oil at the ratio of 1: 1. The mixture was stirred for 10 minutes, and the temperature was controlled at 30 °C. The yield is shown in Fig.1.

![Figure 1. Influence of sulfuric acid concentration on the extraction effect of terpineol](image)

The sulfate generated in esterification reaction of sulfuric acid and terpineol enters the sulfuric acid and is separated from camphor oil. As the sulfuric acid concentration increases, the yield of terpineol increases. The yield is up to 94.6% when the sulfuric acid concentration increases to 20%. As the sulfuric acid concentration continuously increases, since most terpineol has been converted to sulfate, the yield does not significantly increase.

3.3. Reactant ratio
For the optimal extraction of terpineol, the sulfuric acid concentration was 20%, which was taken as the α-terpineol separation concentration, and the mixed reaction was carried out according to the ratio of camphor oil to sulfuric acid of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0. The results are shown in Fig.2.

![Figure 2. Influence of reactant ratio on the separation of terpineol (sulfuric acid concentration 45%, stirring time 10min, temperature 30 °C)](image)

Fig.2. shows that the yield of α-terpineol is maintained at about 95% at the reactant ratio ranging from 0.5 to 2.0. When the amount of crude oil camphor oil is continuously increased, the sulfuric acid is insufficient, and the esterification reaction is incomplete. Consequently, some terpineol cannot be separated into the sulfuric acid phase, leading to a gradual decrease in yield.
3.4. Recrystallization

As terpineol is slightly soluble in water (solubility is 0.71 g/l at 20°C), recrystallization can improve its purity. The obtained α-terpineol was added to water at a mass ratio of 1:50 and heated to 80 °C. After cooling to room temperature, the mixture was cooled in the refrigerator to 5 °C, and the first recrystallization was completed. The purity and quality of the crystals were measured. The results are described in Fig.3.

![Figure 3. Influence of the number of crystallization purifications on the purity and yield of terpineol](image)

As shown in Fig.2, the yield of the product obtained during the first crystallization is up to 105.2%. The product contains other alcohols such as terpineol-4 and nerol, which enter the crystalline product. As a result, the yield is greater than 100%, while the purity is only 87.8%.

After multiple recrystallizations, the purity of the product was gradually improved. After the fourth separation and crystallization, the purity of α-terpineol was up to 99.4%. However, only a small amount of α-terpineol entered the crystallization mother liquor after each recrystallization, resulting in a gradual decrease of yield.

4. Conclusions and recommendations

4.1. Conclusions

Sulfuric acid was taken as the medium to extract crude camphor oil and obtain 1,8-eucalyptol. Sulfuric acid concentration, reactant ratio and reaction temperature have a great influence on the extraction yield. The 1,8-eucalyptol extracted under the optimized conditions is greater than 99%.

Sulfuric acid is used as a chemical extractant and reacts with the components in camphor oil. Some new substances will make eucalyptus colored, which can be adsorbed by activated carbon to achieve a decolorization effect, thus improving the eucalyptus purity.

4.2. Recommendations

This study only investigated the separation and purification of eucalyptol and α-terpineol. It is suggested to study olefins in camphor oil in future studies, especially the synthesis of α-terpineol catalyzed by sulfuric acid of pinene.

Due to side reactions, irreversible reaction between some component like 1,8-eucalyptol in camphor oil and the extraction medium, which reduces the yield. Substances with low oxidability can be used as the separation medium to improve the yield in the future.
Acknowledgments
This work was financially supported by Key scientific research projects of Sichuan Provincial Department of Education(18ZA0549).

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