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Obtaining Essential Oil and Shikimic Acid from Star Anise Fruit *(Illicium verum* Hook*)*

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Abstract. The methods for obtaining simultaneously essential oil and shikimic acid from star anise fruit *(Illicium verum* Hook*)* were investigated. From obtained results, we chose a simple and effective method for desired purpose. With this method, distillation of essential oil and extraction of shikimic acid were simultaneously carried out in the round bottom flask of the Clevenger apparatus. The yield of essential oil and shikimic acid were 9.5% and 5.6% (r.m), respectively as well as the quality of the products is very good.

Keywords: star anise fruit, *Illicium verum* Hook, shikimic acid, essential oil

1. Introduction

Star anise (*Illicium verum* Hook*),* as the name suggests, is star-shaped, native to southern China and northern part of Vietnam, it is now introduced throughout the tropics and subtropical Eastern Asia. Dried star anise fruits have a essential oil content of 8 - 10% and a shikimic acid content of 5–7% [1-3], which are the most valuable compositions of star anise plant. Essential oil from star anise fruits is traditionally obtained by steam distillation, and shikimic acid is extracted from this fruit with alcohol (methanol, ethanol) or water [4,5]. However, there is only a few works researching on the method of obtaining simultaneously essential oil and shikimic acid from star anise fruit. We are, therefore, interested in researching on it in order to increase the value of star anise fruit and reduce the cost of essential oil and shikimic acid products.

2. Material and method

Sample preparation

Star anise (*Illicium verum* Hook) fruits were received from Lang son, which is the largest material area in Vietnam. They had a moisture content of 10.5%, an essential oil content of 9.8 % and a shikimic acid content of 6.2%. Star anise fruits were ground and sieved into a size of 1.59 (1.18-2.00 mm, mesh no. 10)

Equipment

The Clevenger apparatus was used for steam distillation, with a round bottom flask of 500 ml volume. The upper part of the apparatus

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is a condenser and the middle part is a cylindrical tube with a collection bottom of capacity 1ml, graded into 0.1 ml (AOAC, 1984)

GC-MS determining the volatile components of star anise essential oil was performed with HP 6890 couple to detector Agilent 5973. Temp. programme:

40^0C (2min)-5^0C/min-220^0C(5min)-10^0C/min-250^0C

The purity of shikimic acid samples was analyzed on a HPLC (Shimadzu, Japan with SPD-10v detector and Supeleo-H column).

Methods for obtaining simultaneously essential oil and shikimic acid from star anise fruit

Method 1: This method is adapted from the work of Payne and Edmonds (5). It is used to obtain mainly shikimic acid.

Method 2 and 3 were created from result of experimental, especially, we had to research the main factors, which affect on the process of obtaining simultaneously essential oil and shikimic acid from star anise fruits. The factors investigated for method 2 are ratio of material to solvent (w/v), concentration of ethanol (in water), extraction time, and extraction times. The factors researched for method 3 are ratio of material to water (w/w), distillation speed, distillation time, ratio of material to flask volume (w/v).

3. Results and Discussion

For purpose of obtaining simultaneously essential oil and shikimic acid from star anise fruit, we had collected concerning documents and carried out lab experiments to choose the suitable methods such as:

Method 1: (This method is adapted from the work of Payne and Edmonds)

50 g sample of ground star anise fruits was placed into a thimble in the Soxhlet apparatus and heated under reflux with 95% ethanol (250 ml) for 8h. The ethanol from brown coloured filtrate was removed by rotary evaporation. The residue was redissolved in 200 ml of water and extracted with petrol ether (2 x 200ml). The combined ether solution was dried over anhydrous Na_2SO_4, and removed solvent by rotary evaporation to obtain essential oil. The aqueous solution (the bottom layer) was passed through an anion exchange column (Amberlite IRA-400, in acetate form, dry weight 50g). The column was then washed with water (200ml), which was discarded. The column was then eluted with acetic acid (350ml of 25% acetic acid in water) and the yellow eluent was collected. Removal of the acetic acid by rotary evaporation followed by high vacuum pump afforded a brown coloured solid. The solid was recrystallized from methanol and ethyl acetate (1 : 1, v/v) to afford the desired shikimic acid as a bright brown crystalline solid.

Method 2: 50 g sample of ground star anise fruits and 400 ml of 75% ethanol placed in a round bottom flask of 1000 ml volume. This mixture was refluxed for 4h. After separating ethanol solution with filter, the solid part was reextracted another with 300ml 75% ethanol. The combined 75% ethanol solution was concentrated to volume of 200ml, and carried out extraction with petrol ether (2 x 200ml). The combined ether solution was dried over anhydrous Na_2SO_4, and removed solvent by rotary evaporation to obtain essential oil. The aqueous solution (the bottom layer) was concentrated to minimum volume. The residue was extracted (2 times) with methanol : water (8 : 2; v/v). Removal of methanol and water by rotary evaporation followed by high vacuum pump afforded a brown coloured solid. The solid was recrystallized from methanol and

ethyl acetate (1 : 1, v/v) to afford the desired shikimic acid as a bright brown crystalline solid.

Method 3: 50 g sample of ground star anise fruits and 600 ml of water placed in a 1000 ml flask with boiling chips. The distillation was run for 8h until no more oil collected. The electrical heater was regulated to maintain a rate of condensate of 22- 25 drops per min. The oil sample was allowed to cool at room temperature and then the volume of obtained essential oil was read. During distilling essential oil, process of extracting shikimic acid was simultaneously carried out in the distillation flask. After finishing this process, the aqueous solution in the flask was filled to remove solid part and then concentrated to minimum volume. The residue was extracted (2 times) with methanol : water (8 : 2; v/v). Removal of methanol and water by rotary evaporation followed by high vacuum pump afforded a brown coloured solid. The solid was recrystallized from methanol and ethyl acetate (1 : 1, v/v) to afford the desired shikimic acid as a bright brown crystalline solid

Obtaining yield and quality of star anise essential oil as well as shikimic acid obtained by methods N^0 1, N^0 2 and N^0 3 were shown at table 1 and table 2.

Table 1. Obtaining simultaneously essential oil and shikimic acid from star anise fruits by methods N^0 1, N^0 2 and N^0 3

Method	Star anise essential oil		Shikimic acid		
	Obtaining yield (% r.m.)	Anethol content (% e.o.)	Obtaining yield (% r.m.)	Purity (%)	Melting point (^{0}C)
N^0 1	8.6	87.5	5,7	99.4	185-186
N^0 2	9.4	87.2	5.4	98.3	184-185
N^0 3	9.5	89.4	5.6	98.5	184-185

Table 2: Physico-chemical properties of essential oil obtained by methods N^0 1, N^0 2 and N^0 3

Star anise essential oil	Colour	Congealing point,(^{0}C)	Refractive index, (n_D^{20})	Specific gravity, (d_4^{20})	Acid value (mg KOH/g)
From N^0 1	Yellow	13.5	1.5550	0.979	4.8
From N^0 2	Yellow	13.5	1.5548	0.979	4.7
From N^0 3	Greenish-yellow	14.5	1.5552	0.981	4.5

It shows that method N^0 3 is the best for obtaining simultaneously essential oil and shikimic acid from star anise fruits. With this method, obtaining yield of essential oil and shikimic acid respectively are 9.5% and 5.6% (essential oil content and shikimic acid content in raw material are 9.8 % and 6.2%, respectively). Star anise essential oil with anethol content of 89.4% meet quality standard for export, shikimic acid with high purity (98.5%) can be used as material for production of oseltamivir phosphate (tamiflu drug). It is impressed that we had also chosen the way for refining shikimic acid that it more simple and economic than Payne and Edmonds method. In this study, we used methanol : water (8:2) extraction to remove impurities from the crude shikimic acid, while Payne and Edmonds used Amberlite IRA-400 ion exchanged column for it.

4. Conclusions

Method combining of distillation and extraction in the Clevenger apparatus is suitable

for obtaining simultaneously essential oil and shikimic acid from star anise fruits. The yield of essential oil and shikimic acid were 9.5% and 5.6% (r.m), respectively as well as the quality of the products is very good.

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Thu nhận tinh dầu và axit Shikimic từ quả hồi *(Illicium verum* Hook*)*

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Các phương pháp khai thác đồng thời tinh dầu hồi và axit shikimic từ quả hồi Việt Nam *(Illicium verum* Hook*)* đã được nghiên cứu. Từ các kết quả thu được, chúng tôi đã lựa chọn được phương pháp đơn giản và hiệu quả cho mục đích mong muốn. Với phương pháp này, quá trình chưng cất tinh dầu và trích ly shikimic axit được thực hiện đồng thời trong bình cất của thiết bị chưng cất kiểu Clevenger. Hiệu suất thu nhận tinh dầu và axit shikimic đạt lần lượt là 9,5% và 5,6% (so với nguyên liệu), chất lượng các sản phẩm này rất tốt.