Resin purification from Dragons Blood by using sub critical solvent extraction method

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Abstract. Jernang resin (dragon blood) is the world's most expensive sap. The resin obtained from jernang that grows only on the islands of Sumatra and Borneo. Jernang resin is in demand by the State of China, Hong Kong, and Singapore since they contain compounds that have the potential dracohordin as a medicinal ingredient in the biological and pharmacological activity such as antimicrobial, antiviral, antitumor and cytotoxic activity. The resin extracting process has conventionally been done by drizzly with maceration method as one way of processing jernang, which is done by people in Bireuen, Aceh. However, there are still significant obstacles, namely the quality of the yield that obtained lower than the jernang resin. The technological innovation carried out by forceful extraction process maceration by using methanol produced a yield that is higher than the extraction process maceration method carried out in Bireuen. Nevertheless, the use of methanol as a solvent would raise the production costs due to the price, which is relatively more expensive and non-environmentally friendly. To overcome the problem, this research proposed a process, which is known as subcritical solvent method. This process is cheap, and also abundant and environmentally friendly. The results show that the quality of jernang resins is better than the one that obtained by the processing group in Bireuen. The quality of the obtained jernang by maceration method is a class-A quality based on the quality specification requirements of jernang (SNI 1671: 2010) that has resin (b/b) 73%, water (w/w) of 6.8%, ash (w/b) 7%, impurity (w/w) 32%, the melting point of 88°C and red colours. While the two-stage treatment obtained a class between class-A and super quality, with the resin (b/b) 0.86%, water (w/w) of 6.5%, ash (w/w) of 2.8%, levels of impurities (w/w) of 9%, the melting point of 88 °C and dark-red colours.

1. Introduction
Dragon blood is the most expensive resin in the world and most needed in the pharmaceutical world. Since the resin has Dracohordyn compounded, which is plays an important role in the pharmaceutical world. Drachordyn is the main constituent found in dragon blood and included as anthocyanin compound and used as an effective pharmaceutical element since its biology and pharmacology activities such as an anti-microbe, anti-virus, antitumor, and cytotoxic activities [1].

Dragon blood is a resin from secretion process of rattan fruit. It adheres and covers the outside of rattan fruit. Thus, the extraction of the fruit is needed to get the resin out. The dragon blood traditionally is utilized as medicine. It is also used as a dye to paint varnish stuff.
The main chemical component of dragon blood is Esther resin and dracoresino tannol (57-82%). Moreover, red resin also contains compounds such as dracoresene (14%), dracoalban (up to 2.5%), insoluble resin (0.3%), residue (18.4%), benzoic acid, benzoilasetat acid, dracohodin and some of pigments especially nordracorhodin and nordracorubin [2].

This research is related to the efficiency process in extracting the resin of anthocyanin derivation from a raw material of dragon blood. The combined methods between maceration and infundation are used since the engineering of water, as the solvent provides no negative effect to health, the waste gained was environmentally friendly, therefore, it is also lowly cost and has rapid extraction process, which leads to the saving of production cost. Generally, the best solvent used is methanol, however, its price and the effect given to the waste make methanol is reconsider to be used. Alternatively, the extraction using infundation method becomes the most appropriate method to be applied to the people that process the dragon blood.

The using of solvent in conventional processing by the people in Bireuen in extracting the resin were in huge amount compared to the dragon blood weight in order to extract the resin completely and this process was moderately ineffective. This research analysed resin, water, and ashes content and also the melting point of the resin after being extracted. Thus the result was adapted accordance to SNI.

2. Material and method

2.1 Material and equipment

The material used in this research was dragon blood, and Aquades as the solvent to be extracted in beaker glass 1000 ml. The extraction process was conducted in two methods; firstly by using maceration method and secondly by using simulant maceration under subcritical water in the autoclave at 900 °C and atmospheric pressure.

2.2 Method

A 200-gram of crushed jernang, put into a beaker glass and soaked (maceration) for 1 hour, using a solvent (methanol and water) with the ratio of 1:1, 1:2, 1:3, respectively. It is then fed into the autoclave for 60 minutes based on the critical point of methanol and water. Then the separation of the dregs from the solvent mixture (water or methanol) is carried out. The mixture is then distilled to obtain the resin; finally, the resin is analysed by testing the physio-chemical properties of jernang.

Figure 1. Dragon blood fruit.
2.3 Extraction of critical solvent using water
The result of extraction process with maceration method was dried in autoclave with 90 °C for 30 minutes before it was filtered. The result of the extraction, which in lump form was separated from the liquid then it. It had to be dried then analysed.

2.4 Determining the yield of the resin
In determining the content of resin, the analysed sample should be sufficiently dry and usually, the used sample was taken from determined of the used sample for water content. If the sample was still wet, it is not only slowing down the extraction process but also can turn down the beaker glass so it would complicate the determining the constant weight of the beaker glass.

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\text{Resin yield} (\%) = \frac{A}{\text{Weight of Sample}} \times 100\% 
\]

(1)

2.5 Water content
Water content is the difference between material weight before and after drying/heating. Every material will come to the balance with surrounding humidity if being put in the open air. This water content is named balanced water content. Every certain relative humidity can produce certain balanced water content, too. Therefore, it can relate the balanced water content and relative humidity. Principally, it steams the water contained in the material by heating/drying, then weights the material until it reaches the constant weight, and it means that all the water has been steamed.

\[
\text{Water content} = \frac{A-B}{\text{gram sample}} \times 100\% 
\]

(2)

2.6 Determining ashes content
Ashes are the rest of complete burning from organic material (unsteamed residue if burned in a certain way). Chemically, ashes can be defined as metal oxide and other unburned materials it is an indicator of a clean level where the higher level of the ashes means the higher impurity is. Naturally, there are metals in dragon blood resin. These metals are the nutrient of the plant, which plays the important role in biochemical reaction. The metals are physiologic ashes. In the preparation stage, the rattan fruit can be contaminated with sand, soil, etc. Sand is unburned silicate compound and not dissolved in acid thus it acid undissolved composer compound of ashes. For this reason, the waste of dragon blood needs to
be determined to observe the impurity content that contains the waste. If the ashes content is beyond the requirement, the resulted resin is unable to be used.

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\text{Ashes Content} = \frac{B-A}{\text{gram sample}} \times 100\%
\]  

(3)

2.7 Determining the melting point

The melting point is the observed temperature when the solid material (dragon blood) started to melt until the whole particles changed into liquid, where the solid temperature changes into liquid in atmospheric pressure. To determine the melting point, a one-gram sample that needs to be inserted into a tube of capillary glass. The tube contained the dragon blood was set in a determiner tool of melting point. After the tool being operated, the temperature when the sample changed from solid to liquid was noted as the melting point of dragon blood.

3. Results and discussion

In this study, the quality of the sample is determined based on SNI parameters and matched with the produced quality according to the research that has been conducted. The resin is produced by extracting the jernang with the water's sub-critical method by using water and methanol with the difference of the jernang ratio, which is carried out by heating; the purpose of heating (boiling) is to melt the resin contained in the fruit of the jernang. Based on the obtained data after heating using different solvents, the one that using water contender more than the one using a methanol solvent. This is because the solvent water is more soluble with the resin than the methanol solvent. Based on the obtained information from the SNI quality table standard, the quality class for samples using water solvents and methanol can be classified by the following tests:

3.1 Resin

The resin content is determined by heat extraction using soxhlet and diethyl ether solvent. The level testing of resin is using to notice the purity of jernang. Figure 2 illustrates the comparison of resin content to the ratio of jernang. In that figure, it can be analysed and compared that the water solvent and produced resin methanol of jernang quality requirements (SNI 1671: 2010), is B-quality ranging from 40% -41%. The produced resin content between the water solvent and the methanol solvent is almost adjacent, but the water solvent produces the highest resin content. This shows that many of the polar compounds contained in the jernang recall that only polar compounds are soluble in a polar solvent. Based on the ratio of the raw material to the solvent, obtained by more resin with a ratio of 1: 3 this can cause more solvent that penetrates the fruit cell membrane of the vein for the occurrence of diffusion. Consequently, more extracts have come out from the jernang cell membrane.
3.2 Water

Water content is determined to notice the results of the product, whether it has a good quality and it also depends on the results of the analysis, by testing the quality of the jernang in accordance with the SNI. Figure 3 illustrates the comparison of water content to the ratio of jernang whereas the produced water content by the water solvent and methanol is very significantly different. However, the comparison produced based on SNI shows that the quality in the methanol solvent ranges from 8.8%, then the water levels in this test achieves the AB-quality. Furthermore, in the resulting quality water solvent the reached quality is B-quality. This indicates that the methanol solvent does not contain much water so that the water content that measured by the produced resin using the methanol solvent is significantly different from the resin obtained by using a water solvent.
3.3 Dirt (impurity)

The impurity content indicates the amount of impurity mixture present in the jernang resin. In Figure 4 we can see the ratio of the impurity content to the ratio of jernang, where the resulting ratio between the two solvents is significantly adjacent. In the water solvent, the resulting impurity content from 42-43.5% and in the water solvent the resulting impurity content from 41-42%. Requirements generated based on the quality of SNI resulting impurity reaches the B-quality.

![Figure 4. Comparison of dirt content toward jernang ratio.](image1)

3.4 Ashes

The determination of ash content aims to measure the level of organic material that presents in jernang. Ash content is a physical parameter that can indicate the number of other compounds that are considered as impurities contained in the jernang resin.

![Figure 5. Comparison of ash content toward jernang ratio.](image2)
Figure 5 illustrates the highest percentage of ash obtained in water solvents; this is due to the large amount of organic material present in jernang. The percentage of ash content generated by the water solvent ranged from 7.3 to 16.8%. It means that the greater the ratio jernang, the greater it is resulting ash content. This is due to the existence of other polar compounds, which are not the compound of jernang resin that participate in dissolving into the water (polar solvent). Based on the specification of quality requirements in accordance to SNI, in the analysis of ash content obtained is A-B quality.

4. Conclusion
The quality of the produced resin by using methanol solvent is classified into B quality in accordance the quality of jernang resin in SNI 1671: 2010. Additionally, the quality of the produced resin by using water solvent is classified into B quality in accordance with the quality requirements of jernang resin in SNI 1671: 2010. However, the produced resin used more water solvents, instead of water momendipol (water engineering), the produced resin is better than the results from previous studies, which is concluded with methanol solvent that obtained more resin.

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