Yield and Physicochemical Properties of Candlenut Oil by Microwave Assisted Extraction

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ABSTRACT

Candlenut (Aleurites moluccana L) is one of the native plants of Indonesia, used as a spice and in the cosmetic industry. Candlenut seeds contain high oil content with unstable properties at high temperatures. Generally, candlenut oil production is carried out by direct heating and on a laboratory scale using Soxhlet extraction with chemical solvents. Microwave heating has been widely used to extract the active compounds in plant materials. The study of candlenut oil extraction with microwaves is still limited. This study aims to identify the physicochemical properties and yield of candlenut oil extracted using the Microwave Assisted Extraction (MAE) method and compare it with solvent extraction. This research was conducted by varying the extraction time to 35 minutes, 70 minutes, and 105 minutes. The results showed that candlenut oil produced by the MAE method had a density, refractive index, free fatty acid content, and saponification value of 0.867 g/ml, 1.477, 2.8085%, and 212.9764 mgKOH/g samples with a yield of 38.50%.

1. Introduction

Candlenut is a plant widely distributed in Asia, known by different local names, namely hard fruit (Malaysia), Candlenut, Candleberry, Varnish tree, Belgaum walnut (England); Kukui Nuts (Hawaii). Lichtnussbaum (Germany); Noisette, Noix, Noyer, Noyer des Indes (France); Calumbàn, Noz da India (Portuguese); Lumbang Bato (Philippines); Kekuna (Sri Lanka); Kyainthee (Burma); Kemiri (Indonesia). The candlenut fruit consists of an outer skin that is green or dark brown at harvest. The skin of the candlenut seeds is blackish brown and the candlenut seeds are pale yellow. Candlenut (*Aleurites moluccana L*) is commonly used as a cooking spice and is believed to be able to nourish and repair damaged hair. Candlenut contains tocopherol and tocotrienol compounds which are isomers of vitamin E and amyronine which function as a pain reliever and anti-inflammatory [1,2]. The content of saponins, flavonoids, and polyphenols in candlenut seeds is thought to have benefits in healing burns [3]. The content of omega-3 unsaturated fatty acids in candlenut can strengthen and repair hair that is exposed to radiation. Candlenut is also rich in antioxidant content in the form of vitamins A and E which causes candlenut to be applied for skincare so that it looks young and radiant [4].

Traditional communities produce candlenut oil through both pressing and cooking methods. Constraints faced in producing candlenut oil are the length of time of candlenut oil extraction and the low quality of the oil which is marked by a brownish color in the oil due to oxidation of unsaturated bonds. Candlenut oil is thermostable, so the high temperature and length of cooking time will affect the quality of the candlenut oil produced. Candlenut seeds are high in oil content, up to 60%, making the pressing method a common method used to obtain candlenut oil [5-7]. The extraction process by pressing takes a long time which results in increased oxidation of unsaturated fat so that the product is dark in color and has a rancid smell.

The extraction of candlenut oil using Supercritical Fluid Extraction (SFE) obtained a 52.58% w/w yield of candlenut oil. The SFE method is more environmentally friendly because it does not use organic solvents and the product has high purity and quality. The SFE method has a weakness, using high operating pressure requires special skills to operate SFE and requires good safety [6]. Extraction of candlenut oil using methanol as a solvent, for 80 minutes produces a yield of 35.67%, the advantage of the solvent extraction method is the clear color of the oil [5]. Another factor affecting the extraction is the operating temperature. Arlene et. al (2015) stated that the highest yield of candlenut oil by solvent extraction method was achieved at a temperature of 50 ºC. Microwave Assisted Extraction (MAE) is an extraction method that utilizes electromagnetic waves to heat samples and solvents. The MAE method will increase the kinetic energy of polar compounds so that the extraction process is faster. Heat transfer that occurs during the extraction process using microwave waves with water solvent will be more stable because water is a solvent that is able to significantly withstand the rate of heat transfer [8]. Lipid extraction using a microwave at a temperature of 120 ºC increases the yield and extraction rate by 10 to 15 times compared to solvent extraction [9]. Extraction of antioxidant compounds from the fruit of Gordonia axillaris using the MAE method provides an extract that is able to retain the active ingredients in it where the antioxidant properties of the extract are stronger than the soxhletation and maceration methods [10]. Mango seed kernel oil extraction gave the highest yield by using ethanol rather than hexane. The yield of mango seed kernel oil by using MAE and solvent extraction was 18% and 6.69% respectively [11].

The purpose of this study was to identify the yield and physico-chemical properties such as density, refractive index, saponification number, and free fatty acids from candlenut oil extracted using the MAE method and ethanol solvent extraction.

2. Research Methodology

2.1.Material and Equipments

The materials used in this study were candlenut seeds from The Protected Forest of Register 21 Perentian Baru, Pringsewu Regency, Lampung Province, 96% ethanol, aquadest, NaOH > 99.0% (Merck), KOH > 85.0% (Merck), HCl 38% (Merck), hexane, selene, and phenolphthalein. The candlenut seeds to be used were first carried out with a proximate analysis including water content, ash content, carbohydrates, protein, and fat. The equipment used include a Sharp microwave oven, rotary evaporator, blender, buchner funnel, porcelain dish, vacuum filtration, mortar, filter paper, boiling flask, hotplate, pycnometer, desiccator, and upright cooler. This research is experimental research, by varying the extraction time and method. Extraction times were varied from 35 minutes, 70 minutes, and 105 minutes for the MAE extraction and solvent extraction methods.

2.2.Procedure

1) Extraction of Candlenut Oil by MAE Method

The 125 grams of candlenut seeds were pounded with a mortar then together with 250 ml of distilled water were blended to form a candlenut slurry then separated the solid phase and the filtrate using a vacuum filter. The filtrate was placed in a boiling flask and then heated in a 1200 watt microwave oven at a temperature of 105 ºC for 35 minutes, 70 minutes, and 105 minutes, respectively. After completing the extraction, the candlenut oil was separated from the sediment using a vacuum filter.

2) Candlenut Oil Solvent Extraction Method

The 125 grams of candlenut seeds were ground with a mortar and then dissolved in 250 ml of ethanol in a boiling flask for extraction using an upright cooler for 35 minutes, 70 minutes, and 105 minutes, respectively. After extracting the candlenut oil, it was separated using a vacuum filter, then the filtrate was evaporated using a rotary evaporator at a temperature of 50 ºC until all the solvent was evaporated.

Candlenut oil from each experiment were analyzed for density, and refractive index and calculated the yield using the following equation:

$$Yields = \frac{ml\ of\ candlenut\ oil}{gram\ of\ candlenut\ seed} \times 100\% \quad (1)$$

The highest yield of each extraction method was analyzed for saponification number and free fatty acid content.

2.3. Proximate and Physicochemical Properties Analysis of Candlenut Oil

A proximate test was carried out on candlenut seeds with test parameters including water content, ash content, protein content, fat content, crude fiber content, and carbohydrate content according to SNI 01-2891-1992.

1) Proximate Analysis

a) Moisture Test

A total of 2 g of candlenut oil was weighed in a glass cup whose empty weight was known, then dried in a drying oven at 105 ºC for 3 hours. The cup with its contents was then cooled in a desiccator and weighed. Moisture content is calculated based on weight loss, namely the difference in the initial weight of the sample before drying with the final weight after drying.

$$Moisture\ content(\%) = \frac{(initial\ weight - final\ weight)}{final\ weight} \times 100\% \quad (2)$$

b) Ash Content

A total of 2 g of candlenut seed was put in a porcelain dish and weighed, then burned until it no longer smoked and ashed in a furnace at 550 ºC until it turned white (all samples turned to ash). After that, it was cooled in a desiccators and weighed.

$$Ash\ content(\%) = \frac{ash\ weight}{candlenut\ seed\ weight} \times 100\% \quad (3)$$

c) Protein Content

A total of 0.51 g of candlenut seed was put in a 100 ml Kjeldahl flask. Add 2 g of selen and 25 ml of concentrated H_2SO_4. Heat the mixture on an electric heater until the mixture is greenish, for 2 hours. After cooling, dilute the mixture in a 100 ml volumetric flask with distilled water to the mark. Then pipette 5 ml of the mixture, add 5 ml of 30% NaOH and 3 drops of phenolphthalein. Distill the mixture for 10 minutes by placing an Erlenmeyer containing 10 ml of H_3BO_3 solution and a few drops of methyl red indicator. The distillate was titrated with 0.01 N HCl. The same procedure was carried out on the blank (without the sample). The amount of titration (a ml) and titration blank (b ml) is expressed in ml of 0.01 N HCl.

$$Protein\ content(\%) = \frac{(a-b)\times 0.01\times 6.25\times 0.014}{candlenut\ seed\ weight} \times 100\% \quad (4)$$

d) Fat Content

The candlenut seed was weighed as much as 2 g, put in a round flask and wrapped in filter paper and covered with fat-free cotton, placed in a soxhlet extractor with a condenser. The extraction was carried out for 6 hours using hexane. Then hexane is separated from fat by distillation. Residual hexane was removed by drying the flask in an oven at 105 ºC for 2 hours.

$$Fat\ content(\%) = \frac{(weight\ of\ flask\ after\ oven - weight\ of\ empty\ flask)}{candlenut\ seed\ weight} \times 100\% \quad (5)$$

e) Crude Fiber Content

The 1 g of candlenut seed was put into a 500 ml Erlenmeyer flask then added 50 ml of 1.25% H_2SO_4 and boiled for 30 minutes under an upright cooler. Then add 50 ml of 3.25% NaOH and boil again for 30 minutes. In hot conditions, the mixture is filtered using filter paper whose weight is known. The residue obtained was washed successively with 50 ml of hot 1.25% H_2SO_4, boiling water until it is no longer acidic (tested with lakmus paper), and washed with 15 ml of 96% ethanol. Then the filter paper was dried at 105 ºC for 2 hours and then weighed.

$$Crude\ fiber\ content(\%) = \frac{weight\ of\ sample\ after\ drying}{candlenut\ seed\ weight} \times 100\% \quad (6)$$

f) Carbohydrate Content

The carbohydrate content in the sample was calculated by difference. Subtracting 100% from the total value of the water content, ash content, protein content, fat content, and crude fiber content.

$$Carbohydrate\ content(\%) = 100\% - (water + ash + protein + fat + crude\ fiber) \quad (7)$$

2) Psychochemical Properties Test of Candlenut Oil

a) Density Test (SNI 01-2891-1992).

Density testing using a pycnometer by pouring candlenut oil into the pycnometer and weighing the weight of the candlenut oil in the pycnometer. The density of the pycnometer is calculated using the formula:

$$The\ density\ of\ candlenut\ oil(g/ml) = \frac{weight\ of\ candlenut\ oil}{pycnometer\ volume} \times 100\% \quad (8)$$

b) Refractive Index Test (ASTM D – 1218 - 02)

2 drops of candlenut oil were dripped on the cleaned surface of the Abbe refractometer. Take a reading against the scale indicated by the refractometer.

c) Free Fatty Acid Test [12].

28 g of candlenut oil was weighed and put into a 250 ml Erlenmeyer flask. 50 ml of hot neutral alcohol and 2 ml of phenolphthalein (PP) indicator were added to the sample and immediately titrated with 0.100 N NaOH until a color change from colorless to pink did not disappear for 30 seconds. Free fatty acids are expressed in the percent of free fatty acids which are calculated using the following equation:

$$Free\ Fatty\ Acid\ Content(\%) = \frac{NaOH\ Volume\ (ml) \times N\ NaOH \times Mr\ NaOH}{candlenut\ oil\ weight} \times 100\% \quad (9)$$

d) Saponification Number Test [13].

Candlenut oil as much as 2 grams of the sample was weighed into a 500 ml Erlenmeyer. Added 25 ml of 0.5 N alcohol-KOH. Then the Erlenmeyer was connected to an air cooler (upright cooler) and boiled over a water bath for half an hour. Then cooled and titrated with 0.5 N HCL and p.p as an indicator (a ml is required). Blanks (without samples) were also carried out as above (b ml of 0.5 N HCL was required).

$$Saponification\ Number = \frac{28.05(a-b)}{candlenut\ oil\ weight} \times 100\% \quad (10)$$

3. Result and Discussion

The candlenut seeds used in this study were first tested for their chemical content with the results as shown in Table 1.

Table 1. Proximate Analysis of Candlenut Seeds

Parameters	Results (%)
Moisture Content	11.72
Ash Content	2.81
Fat Content	49.40
Protein Content	17.29
Carbohydrate Content	6.89
Crude Fiber Content	11.88

The results of the analysis in Table 1 show that the raw material for candlenut seeds used has the potential to produce quite high oil as indicated by the high-fat content of 49.40%. The value of the fat content of the candlenut seeds used is close to the value of the oil content of the candlenut seeds from the previous study, namely 57.12% [14].

3.1. Effect of Extraction Time on Candlenut Oil Yield

Traditional candlenut oil extraction uses water as a solvent by a direct heating method. The direct heating method takes a long time and the resulting candlenut oil is brown in color. On a laboratory scale, oil extraction from plants is carried out by extraction using chemical solvents [3]. The effect of extraction time on the yield of candlenut oil using ethanol as solvent and the MAE method in this study is shown in Table 2.

Table 2. Yield of Candlenut Oil

Extraction Time	Candlenut Oil Yield (%)	
(Minutes)	*Solvent*	*MAE*
35	6.87	9.47
70	11.13	38.50
105	15.10	25.17

Table 1 shows the extraction using the MAE method and the solvent extraction method producing candlenut oil yields ranging from 9.47-38.50% and 6.87-15.10%, respectively. Compared to the solvent extraction method, the MAE method produced the highest yield of 38.50% with a shorter extraction time of 70 minutes. Meanwhile, the smallest yield of the solvent extraction method was 15.10% with an extraction time of 105 minutes. The MAE extraction method is influenced by the type of solvent, the higher the dielectric constant or the more polar solvent that was used, the higher the solvent capacity to absorb microwaves, this causes the extraction rate and the amount of oil released to the solvent to increase. Increasing the extraction rate shortens the extraction time. The results showed that the extraction time of 105 minutes resulted in a lower yield than the extraction time of 70 minutes, with values of 25.17% and 38.50%, respectively. The decrease in oil yield is thought to be due to the evaporation of the solvent along with the formed oil.

The result of ethanol solvent extraction in this study is lower than the results of previous research, which is 42%, this is because the ethanol used in this study is technical ethanol, where there is the water content in it. And the previous research stated that oil extraction is easy to do with non-polar solvents, the presence of polar water results in the minimal transfer of oil mass to the solvent.

3.2. Effect of Extraction Time and Method on Physical Properties of Candlenut Oil.

The physical properties of the candlenut oil produced were tested for density using a pycnometer with the results as shown in Table 3.

Table 3. Density of Candlenut Oil

Extraction Time	Oil Density (g/ml)	
(Minutes)	*Solvent*	*MAE*
35	0.841	0.851
70	0.869	0.861
105	0.893	0.867

The density of candlenut oil produced by the solvent extraction method and MAE were in the range of 0.841-0.893 g/ml and 0.851-0.867 g/ml, respectively. Table 3 shows that as the extraction time increases, the density of candlenut oil increases, both the oil from the solvent extraction method and the result of MAE. Oil density is influenced by the relative molecular weight (Mr) of the compounds that make up the oil and the oxidation process of saturated bonds in the oil [15]. Low density oils have low molecular weights. The oxidation of unsaturated bonds in the oil causes an increase in free fatty acid levels and will result in an increase in the density of the oil [16]. The refractive index is one of the parameters that can be used to determine the purity of hydrocarbon compounds [17]. The refractive index of candlenut oil produced from the two methods is presented in Table 4. Table 4 shows the refractive index value of candlenut oil from both solvent extraction and the MAE method to produce candlenut oil with refractive indexes of 1.477 and 1.477-1.478, respectively.

Table 4. Refractive Index of Candlenut Oil

Extraction Time	Refractive Index	
(Minutes)	*Solvent*	*MAE*
35	1.477	1.478
70	1.477	1.477
105	1.477	1.477

The results showed that the extraction method and time did not affect the value of the resulting refractive index. The bias index generated from this study is close to the value index bias generated by the previous researcher, namely 1.476-1.477 [15].

3.3. Effect of Time and Extraction Method on Chemical Properties of Candlenut Oil.

Candlenut oil with the highest yield from the solvent extraction method and MAE was tested for chemical properties parameters including saponification number and free fatty acid content. The saponification number stated the amount of alkali metal needed to saponify a certain amount of oil. The saponification number values from the solvent extraction method and MAE were 198.8093 and 212.9764 mgKOH/g sample, respectively, as shown in Figure 1.

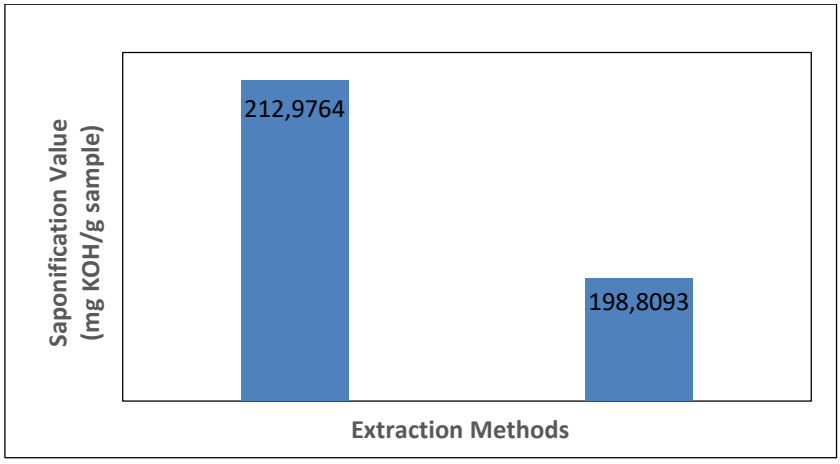

Fig. 1. Effect of Extraction Method on Saponification Number

The value of the saponification number shows the average molecular weight of the triglycerides that make up the oil component [16]. A large saponification number indicates the constituent compound has a relatively small molecular weight. Figure 1 shows the MAE method produces a higher saponification value than solvent extraction, it is suspected that the relative molecular weight of the MAE extracted oil is smaller than the molecular weight of the solvent extracted oil and this corresponds to the density value as shown in Table 3. Table 3 shows the density of the MAE extracted oil lower than the density of the solvent extraction oil, this indicates the relative molecular weight of the oil from the MAE method is lower than the solvent extraction method.

The free fatty acid content of candlenut oil from the MAE method and solvent extraction were 2.8085% and 1.0636%, respectively, as shown in Figure 2.

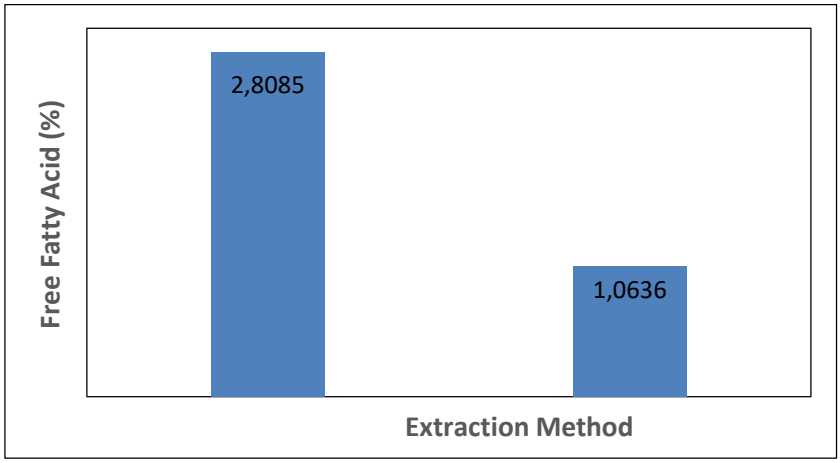

Fig. 2. Effect of Extraction Method on Free Fatty Acid Content

Figure 2 shows the oil extracted from MAE is higher than the oil extracted from the solvent. Free fatty acids showed degradation due to the oxidation process on unsaturated bonds in the oil. A high

free acid content indicates a higher level of oxidation towards the unsaturated bond. The free fatty acid content of the MAE extracted oil was higher than that of the solvent extracted oil due to the relatively high operating conditions of the microwave heating at a temperature of 105 ºC.

4. Conclusion

Candlenut oil extraction using the MAE method resulted in a higher yield than the solvent extraction method, namely 38.50% with density, refractive index, free fatty acid content, and saponification value of 0.867 g/ml, 1.477, 2.8085%, and 212.9764 respectively. Mg KOH/g sample, this condition was achieved with an extraction time of 70 minutes. Candlenut oil produced from the MAE method has the potential to be developed as raw material for pharmaceuticals and cosmetics.

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