Quality and Chemical Composition of Cajuput Oil from Moluccas and Papua

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Abstract. Melaleuca leucadendron Linn is a type of cajuput oil producer was found in the Moluccas are mostly on the Buru Island and West Seram, while Asteromyrtus brasii is a type that is found in Wasur National Park, Merauke, Papua. This study aims to decide on the chemical content and physical properties of cajuput oil that distilled from Melaleuca leucadendron leaves from Moluccas and A. brasii which grow in meet Wasur National Park. Analysis of the chemical content of essential oils was carried out using the Gas Chromatography and Mass Spectrometer method. Physical properties analysis was carried out using the method according to SNI 06-3954-2006. The test results showed that the quality of cajuput oil from Melaleuca leucadendron the SNI 06-3954-2006 standard, while type A. brasii did not meet the quality requirements based on SNI 06-3954-2006. The results obtained from the test using the GCMS method showed that there were 26 peaks with the highest peak being 1.8 cineole. The content of 1.8 cineole from Buru Island at 61.69%, West Barat at 70.22% and Wasur National Park at 34.88%.

1. Introduction
The distribution and potential of cajuput plants in Indonesia is quite large, starting from the regions of Moluccas, East Nusa Tenggara, Southeast Sulawesi, Bali and Papua which grow in the form of cajuput natural forests. Meanwhile, trees located in East Java, Central Java and West Java in the form of cajuput plantations [1]. The Moluccas has a huge potential of cajuput trees that grow in several regions, Buru district about ± 120,000 ha, West Seram district about ± 50,000 ha, West Southeast Moluccas Regency about ± 20,000 ha, and Central Moluccas district about 60,000 ha [2], while the area of cajuput trees in Papua about 120,000 ha [3].

The main market for cajuput oil include The United States, Japan, Singapore, France and the Netherlands. According to Rimbawanto and Susanto [4], the annual supply of cajuput oil that Indonesia needs as much as 1500 tons, whereas Indonesia itself is only able to supply 400 tons and the gap is filled with imports from China. In the Moluccas Island, the annual production of cajuput oil reached 21.98 tons in 2014 and increased to 26.65 tons in 2015 [5] with raw materials from natural stands. In Papua, data on cajuput oil production is not yet known, only estimated to produce 2 tons/ha [3].

The genus Melaleuca also contains hundreds of individual species with a myriad of oil constituents present in the leaf [6]. Asteromyrtus brasii is a member Asteromyrtus genus (previously classified as
Cajuput oil quality depends on the content of 1,8-cineole, a pharmaceutically active component of aromatic oil. Good quality of cajuput oil that contains cineol levels between 65-75%. In general, the chemical components contained in cajuput oil include: β-pinene 1.2%; cineol 60.03%; terpinolene 0.47%; 4, 11, 11, -tetramethyl - 8 methane 1.44%; β linalool 1.59%; α terpineol 14.96%, caryophyline 1.26%; α caryophyline 0.52%; iso-cariophylline 0.87%; and dehydro - 1,1,4,7, - tetramethyl elemol 5.32% [8]. The European Pharmacopoeia monograph for Eucalyptus oil specifies a chromatographic profile: 1,8-cineole (=eucalyptol; not less than 70%), limonene (4-12%), α-pinene (2-8%), α-phellandrene (less than 1.5%), β-pinene (less than 0.5%), camphor (less than 0.1%) [9].

In addition, factors such as location, tree age, leaf age and harvest season also influence quality of oil [10,11,12]. The oil quality from Melaleuca and Eucalyptus trees in Australia have been well documented in their native range of the distribution [10], but less information is available for the quality from M. leucadendron and Asteromyrtus in Indonesia.

In this research, we compared cineole content among three cajuput plantations in Moluccas and Papua, Indonesia. It is expected that with the information on the chemical composition and physical properties of cajuput oil can be utilized for the development and production of cajuput oil type M. leucadendron from the Moluccas and Asteromyrtus types from Papua.

2. Experimental

2.1 Materials

Fresh leaves of M. leucadendron cajuput the national park were collected from 2 sites of Moluccas, in Lahnbatang beach, Namlea, Buru Islands and Kotania West Seram and Asteromyrtus leaves from Wasur National Park in the administrative regions of Sota District, Merauke Regency, Papua Province.

2.2 Methods

2.2.1 Distillation of the volatile oil

Cajuput oil are extracted using an water and steam distillation, then quality standards are tested using SNI cajuputs oil (SNI 06-3954-2006) to determine its quality.

2.2.2 Determination of physical properties and chemical analysis of the oil components

Cajuput oil is tested using SNI 06-3954-2001 which includes specific gravity at 15 °, odor, optical rotation, solubility in alcohol, fat oil and cineole content. The content of the oil chemical compound was analyzed using GCMS-QP2010 Ultra SHIMADZU Rtx-5MS column with a length of 30 meters with a diameter of 0.25 mm. Oven temperature 30 ° C, interface temperature 35 ° C, and ion source temperature 200 ° C. The time for each sample is 23 minutes with a start time of 1 minute.

3. Results and Discussion

3.1 Quality of cajuput oil

The results of distillation of Cajuputs oil leaves using stainless kettle with a capacity of 250 kg kettle gives a yield of 1.25%, this is far greater than wood kettle of 0.8% with the same capacity. The fuel in the form of wood is 75% more efficient compared to wood-based refineries commonly used by craftsmen. The refining time of 4 hours, much faster than what is needed by a wood kettle of 8 hours.
Table 1. Physical properties of the oils from cajuput leaves collected.

| Physical properties of the oils | Melaleuca leucadendron L | Asteromyrtus brasii |
|--------------------------------|--------------------------|---------------------|
|                               | Lahnbatang Beach Namlea City Buru Island Moluccas Indonesia | Kotania Piru City Seram Bagian Barat Moluccas Indonesia | Taman Nasional (TN)Wasur Merauke Papua Indonesia [7] |
| Oil Yield (%)                 | 1.25                     | 0.90                | 0.33                |
| Cineol content (%)            | 61.69                    | 70.22               | 34.88.              |
| Oil Color                     | Clear Pale yellow        | Clear Pale yellow   | Clear Pale yellow   |
| Density (g/mL) at 25°C        | 0.930                    | 0.920               | 0.898               |
| Refractive index at 20°C      | 1.460                    | 1.462               | 1.467               |
| Optical rotation              | -1.90                    | -2.20               | 9.80                |
| Solubility in 70% ethanol     | 1:1 to 1:10 clear        | 1:1 to 1:10 clear   | 1:1 clear           |

Cajuput oil production is influenced by several factors including leaf filling in kettle, cajuput tree varieties, leaf storage, distillation techniques, and leafage. In Java, the distillation yield is still low, only having a yield of 0.6% - 1.0%. Whereas Arnita [13] with steam and water distillation method produces eucalyptus oil yield between 0, 84% to 1.21%. In previous studies [14] produced cajuput oil refining yields in Moluccas ranging from 0.80 to 1.25%. From the results of cajuput oil test produced, it can be seen that there are differences in optical rotation, density, cineol content and oil yield. The yield was one factor that is important in a cajuput oil refinery, because the value is very useful if a type of cajuput will be developed for the industry. The greater the yield value, the more potential a type of cajuput will be produced. The main factors that influence the differences in yield of cajuput oil produced include the time of refining and origin of cajuput leaf raw materials. The optical rotation and solubility in alcohol are strongly influenced by the chemical content present in oil. Optical rotation of A. brasii is greatly influenced by natural conditions and refining conditions including the water used.

The color of cajuput oil produced is strongly influenced by heat and pressure during refining. Observation of pressure during the distillation process shows that as the temperature rises, the boiler pressure will increase, at the beginning of the start of the cajuput oil droplets mixed with water, the pressure rises to 0.5 bar with a clear color. Yields will increase when the pressure rises to 1 bar to 1.5 bar with the resulting drop being cajuput oil with a slightly yellowish-green color, this condition is maintained until the end of refining. To stabilize the temperature the flame is maintained by reducing and increasing the combustion flame. The same thing has also been reported by Setyaningsih et al [15], at an increase of 0.5 bar obtained cajuput oil with a clearer color and at an increase of 1 bar obtained a slightly greener yield color which indicates the start of the process of extracting terpenoids from leaves.

3.2 Chemical content of cajuput oil

The results of measurements using GC-MS (Table 2), showed that there were 26 chemical components detected, with the greatest abundance of 1.8 cineole, with an abundance of 61.69% for the Buru island, 70,22% for the West Seram and 34.88% for the Papua Wasur Park.
Tabel 2. Chemical compositions in the cajuput oils of *M. leucadendron* and *A. brasii*.

| Chemical Composition (%) | Melaleuca leucadendron L | Asteromyrtus brasii |
|-------------------------|---------------------------|------------------|
|                         | Lahnbatang Beach Namlea City | Kotania Piru City Seram Bagian Barat Moluccas Indonesia |
|                         | Buru Island Moluccas Indonesia | Taman Nasional (TN) Wasur Merauke Papua [7] |
| β-Ocimene | 4.06 | 1.52 | - |
| trans-beta-ionon-5,6-epoxide | - | - | 21.26 |
| Acetic acid (CAS) Ethylic acid (CAS) Methanamide | - | - | 8.14 |
| 2-Propanone (CAS) Acetone | - | - | 2.36 |
| β-pinene | 2.20 | 0.87 | - |
| α-pinene | - | - | 4.39 |
| β- Myrcene | 0.88 | - | - |
| Limonene | 5.96 | 3.42 | 1.23 |
| 1.8-Cineole | 61.69 | 70.22 | 34.88 |
| Phenol. 2-methoxy- Guaiacol | - | - | 2.14 |
| γ-Terpinene | 1.98 | 2.77 | - |
| α-Terpipolene | 0.85 | 1.26 | - |
| Terpinen-4-ol | 0.74 | 0.93 | 5.17 |
| α-Terpineol | 10.03 | 10.32 | 2.34 |
| 2.3-Dihydro-Benzofuran | - | - | 3.04 |
| α-Terpinyl Acetate | 2.01 | 1.75 | - |
| l-Caryophyllene | 6.05 | 3.69 | 0.83 |
| Junipene | 0.25 | - | - |
| α-Humulene | 0.64 | 0.48 | 1.40 |
| β-Selinene | 1.28 | 0.96 | - |
| Germacrene A | 0.50 | 0.68 | 0.60 |
| Aromadendrene | - | 0.34 | - |
| β-elemene | - | 0.80 | - |
| Farnesol | - | - | 1.15 |
| solvanol | 0.88 | - | - |

Other content found in Wasur Park Papua and not found in Moluccas with a large abundance, namely Trans-Beta-Ionon-5,6-Epoxide (21.26% abundance), Formamide (CAS) Methanamide (11.20%) and Acetic acid (CAS) Ethylic acid (8.14%). γ-Terpinene and α-Terpipolene with an abundance of 0.85-2.77% were found in Moluccas but were not found in Wasur Park. 2-methoxy-(CAS) Guaiacol, and 2,3-Dihydro-Benzofuran are only found on Wasur Park Papua. Cineole is also known by various synonyms: 1,8-cineole, eucalyptol, cajeputol, 1,8-epoxy-p-mentana, 1,8-oxido-p-mentana, eucalyptol, eucalyptole, 1, 3,3-trimethyl-2-oxabicyclo [2,2,2] octane, cineol, cineole. 1,8-cineole is a natural cyclic ether and a member of monoterpenoids or monoterpene ether. Cineole with a purity of 99.6-99.8% can be obtained in large quantities by fractional distillation of eucalyptus oil. Although it can be used as food flavoring and ingredients, cineole can cause poisoning if ingested exceeds normal doses [16].

From phytochemical laboratory [17] data (Papua, β- myrcene, solvanol and jupinene are only found on Buru Island. Aromadendrene and β-elemene are only found on West Seram. Phenol. 2-methoxy-
(CAS) Guaiacol, Farnesol, α-pinene, 2-Propanone (CAS) Acetone, Phenol2015), 36 compounds were identified with a total identified of 98%. Cineole has the highest concentration of 63%. It is very much different from the results of identification carried out only about 26 compounds. It is still very dependent on the identification tool used. The location factor of the growth of cajuput leaves also influences the number of compounds in the oil.

4. Conclusions
The quality of cajuput oil of Melaleuca type meets SNI 06-3954-2006 standards and Asteromyrtus brasii does not meet the requirements of the cajuput oil quality according to SNI 06-3954-2006 because it has less specific gravity from 0.900. The results of analysis with GC-MS showed 26 peaks, with the highest intensity identified as 1.8 cineole compounds.

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