ANALYSIS OF CHEMICAL COMPOUNDS DISTINGUISHER FOR AGARWOOD QUALITIES

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Received: 23 October 2013, Revised: 14 October 2014, Accepted: 16 October 2014

ANALYSIS OF CHEMICAL COMPOUNDS DISTINGUISHER FOR AGARWOOD QUALITIES. Gaharu (Agarwood) is described as a fragrant-smelling wood that is usually derived from the trunk of the genus Aquilaria and Gyrinops (both of the family Thymelaeaceae), which have been infected by a particular disease. Based on Indonesian National Standard, agarwood can be classified into various grades, i.e. *gubal gaharu*, *kemedangan* and *serbuk gaharu*. The grading system is based on the color, weight and odor. It seems that such a grading is too subjective for agarwood classification. Therefore, to minimize the subjectivity, more objective agarwood grading is required, which incorporates its chemical composition and resin content. This research was conducted focusing on the analysis of the particular grade of agarwood originating from West Sumatra. The different types of agarwood qualities are: *kemedangan C*, t*eri C*, *kacangan C* and s*uper AB*. Initially, the obtained agarwood samples were grounded to powder, extracted on a Soxhlet extractor using various organic solvents (i.e. n-hexane, acetone, and methanol). The agarwood-acetone extracts were analyzed using GC-MS to determine its chemical composition. The results showed a positive, linier relationship in which the resin yield increased with the increase in agarwood quality grades. GC-MS analysis revealed that several sesquiterpene groups can be found in *kemedangan C*, *teri C*, *kacangan C* and *super AB* qualities. It is interesting that aromadendrene could be identified or found in all agarwood quality grades. Therefore, it is presumed that the aromadendrene compounds can act as an effective chemical distinguisher for agarwood, whereby the greater the aromadendrene content, the better is the agarwood grade.

Keywords: Agarwood, extraction, resin yield, chemical component, gaharu qualities

ANALISIS SENYAWA KIMIA PENANDA KUALITAS GAHARU. Gaharu merupakan produk kayu penghasil resin beraroma wangi dari kayu genus Aquilaria dan Gyrinops (Famili: Thymelaeaceae). Pembentukan gaharu merupakan mekanisme pertahanan pohon terhadap suatu gangguan lingkungan atau penyakit. Berdasarkan Standar Nasional Indonesia, gaharu dapat diklasifikasikan menjadi beberapa tingkatan antara lain gubal gaharu, kemedangan, dan serbuk gaharu. Sistem pengkelasan yang ada didasarkan pada warna, berat, dan aroma. Hal ini menunjukkan bahwa sistem pengkelasan kualitas gaharu saat ini masih subyektif. Oleh karena itu dibutuhkan pengkelasan yang lebih obyektif yang berhubungan dengan komposisi kimia dan kadar resin. Tulisan ini menganalisa kualitas gaharu yang berasal dari Provinsi Sumatera Barat meliputi kemedangan C, teri C, kacangan C, dan super AB. Penelitian dimulai dengan pembuatan serbuk gaharu, kemudian diekstraksi dengan teknik soxhlet menggunakan beberapa pelarut organik (n-heksana, aseton, dan methanol). Ekstrak aseton gaharu dianalisa menggunakan GC-MS untuk menentukan komposisi kimia. Hasil penelitian menunjukkan hubungan linear antara peningkatan kadar resin dengan peningkatan kualitas gaharu. Hasil pengujian GC-MS menunjukkan adanya kelompok sesquiterpena pada gaharu kualitas kemedangan C, teri C, kacangan C, dan super AB. Keberadaan senyawa aromadendrene dijumpai pada semua kualitas gaharu; senyawa ini diduga kuat berperan sebagai senyawa kimia penanda gaharu. Semakin tinggi kadar aromadendrene, kualitas gaharunya semakin baik.

Kata kunci: Gaharu, ekstraksi, kadar resin, komponen kimia, kualitas gaharu

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I. INTRODUCTION

Agarwood plant consists of Thymelaeaceae, Leguminosae, and Euphorbiaceae families. The Thymelaeaceae has two genera that is categorized by producing high quality agarwood, i.e. *Aquilaria* and *Gyrinops genera* (Sidiyasa & Suharti, 1986; Sumarna, 2002). The species are *Aquilaria malaccensis*, *A. microcarpa*, *A. filaria*, *A. beccariana* and *A. Gyrinops versteegii*. Agarwood is one of the non timber forest products (NTFPs) commodities in Indonesia, which has a high economic value.

The quality of agarwood is determined by its resin content. The higher resin content, the higher class (Mashur, 2009). In general, agarwood is clasified into three groups, i.e. *gubal*, *kemedangan* and *abu* (Mashur, 2009; Salampessy, 2009; Santosa, 2009). The gubal quality consists of double super, *super* A, *super* B, *kacang teri* A, *kacang teri* B and *sabah tenggelam*. The *kemedangan* group consists of *kemedangan* quality A to C, BC quality, kemedang putih and *teri* terapung. The abu group is originating from the cleaning process of the *gubal* and *kemedangan* quality. It is divided into four qualities, i.e *abu gaharu* super, *abu gaharu kemedangan* A, abu gaharu kemedangan and TGC (Mashur, 2009; Salampessy, 2009; Santosa, 2009).

Yoneda et al. (1984) identified the sesquiterpenoids in *Aquilaria agallocha* and *Aquilaria malaccensis* using combination of GLC and GC/MS. The sesquiterpenoids are: β-agarofuran, α-agarofuran, nor-ketoagarofuran, (-)-lO-epi-y-eudesmol, agarospirol, jinkohol, jinkoh-eremol, kusunol, dihydrokaranone, karanone, jinkohol II and oxo-agarospirol. Identification of sesquiterpene compounds in the four grades of agarwood have been done on *Kacangan* B, *teri* B, *kemedangan* A and *kamedangan* B quality. The presence of sesquiterpene and chromone with particular portion and characteristics in each of those four agarwood grades have their roles in explaining their grades from the best to the lowest (Waluyo & Anwar, 2012). Furthermore, Pasaribu, Waluyo and Pari (2013) mentioned that the extracts yield of various solvent of agarwood is decreasing from super AB toward *kacangan* C, *teri* C and *kemedangan* C. The agarwood samples contain furan compounds and ester aromatic groups that is responsible for the agarwood's nice scent.

Balfas (2009) studied the resin content of low-grade agarwood. Raw ma*teri*als of similar grades were collected from Irian Jaya, Jambi (Sumatra) and Banjarmasin (Kalimantan). Extraction results were significantly influenced by the source of the wood samples and the kind of solvent. The use of ethanol gave greater resin yields than the use of methanol or distilled water. However, the use of methanol instead of ethanol is more recommendable for future works.

Determination of agarwood class is related to its price. Based on Indonesian National Standard (SNI, 2011), agarwood can be classified into various grades, i.e. gubal gaharu, kemedangan and serbuk gaharu. The grading system is made according to the color, weight and odor. It seems that such grading is too subjective for agarwood classification. Therefore, to minimize the subjectivity, it is required that more objective agarwood grading is being introduced, such as incorporating the chemical composition and resin content of agarwood.

II. MATERIAL AND METHOD

A. Plant Materials

The material used in this study is natural agarwood (*Aquilaria malaccensis*) which was collected from West Sumatra. Samples were obtained from traders. Agarwood class consisted of *kemedangan C*, *teri C*, *kacangan C* and *super AB*. The chemicals used were methanol, acetone and n-hexane.

B. Extraction

The first step, the obtained agarwood samples were grounded to wood powder, to obtain sizes of 40 to 60 mesh. Then, the wood powder was extracted in soxhlet apparatus using, extracted on a soxhlet apparatus using various organic solvents (i.e. n-hexane, acetone

and methanol). Extraction process was done during 3 hours or until the extract in a soxhlet became colorless. The apparatus was heated in water bath with temperature ± 100°C. The extraction was further concentrated by rotary vacuum evaporator. Concentrated extract was agarwood resin, which was blackish brown. Concentrated extracts were then weighted to determine the yield of the agarwood resin.

Extract yield was calculated by formula:

$$\text{Yield (\%)} = \frac{A}{B} \text{ X } 100$$

where :
A = resin weight after extraction
B = powder weight before extraction

C. Chemical Compound Analysis

Acetone extracts of agarwood qualities i.e. *kemedangan C*, *teri C*, *kacangan C* and super AB were used for the analysis. The analysis used Gas Chromatography Mass Spectra (GCMS) at Forensic Laboratory Center (Puslabfor POLRI), Indonesian Police Headquarters. The GCMS specification is electron ionization detector attack (EI) on GC-17A gas chromatograph (Shimadzu) which combined with MS QP 5050A mass spectrometer, and with the Wiley 7N 2008 data base. GC/MS instrument (Shimadzu QP 2010) running time was 39.67 minutes, with the initial GC oven temperature of 70°C, and final temperature of 290°C, using DB5 MS detector.

III. RESULT AND DISCUSSION

A. General Condition

The specific site of agarwood source is Nagari Lubuk Basung, Sub-district Lubuk Basung, West Sumatra Province. The collection of natural agarwood has decreased because of the limited availability in the forest. Some people have started to cultivate the agarwood. The other Nagari (village) who is looking for agarwood is the Batu Kambing and Nagari Sitanang villages, sub-district Ampe Nagari, district Agam. One of the businessmen in agarwood (Hasan Basri) told about the existing agarwood business specifically in West Sumatra and the island of Sumatra in general.

He has started agarwood business 20 years ago. His target market is the Middle East by going directly to the buyers in Kuwait, Bahrain, Qatar and Saudi Arabia. In the Middle East, the most favorite agarwood species is *Aquilaria malaccensis*. In West Sumatra, agarwood comes from Mentawai, Agam, Pasaman and Pesisir Selatan districts. According to his experience, agarwood is used by people in the Middle East for relaxation and stamina (sexuality).

The grading classification used in West Sumatra is different from the Indonesian National Standard (SNI). The trader's classificaton is ranging from double Super, Super A, Super B, Super AB, Super BC, *Kacangan*, *Teri* (three levels) to *kemedangan* (three levels). Some level classes and prices are presented in Table 1. The collector in Nagari usually sells

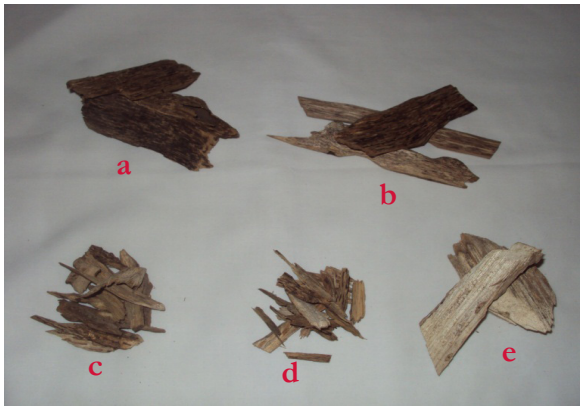

Figure 1. Some of agarwood grades from West Sumatra
Remarks: a. *Super AB*, b. *Super BC*, c. *Kacangan C*, d. *Teri C*, e. *Kemedangan C*

Table 1. The prices of some of agarwood qualities in West Sumatra

No	Quality class	Price (IDR) / kg
1.	*Super AB*	8,750,000 - 10,000,000
2.	*Super BC*	1,500,000 - 2,000,000
3.	*Kacangan*	1,100,000 - 1,500,000
4.	*Teri*	350,000 - 500,000
5.	*Kemedangan bagus*	300,000 - 400,000
6.	*Kemedangan biasa*	75,000 - 150,000

directly to the province collectors. Further, the businessman in the province is selling to a big businesman or exports directly to the Middle East.

B. Extraction and Yield

The Soxhlet extraction results of various solvents from West Sumatra are presented in Table 2. The use of Soxhlet extraction is proper for compounds that are not affected by heat, and also it is more economical.

The methanol resin yield was higher than acetone and n-hexane yields. The study of Pasaribu et al. (2013) showed differences in the yield of the extract of agarwood with methanol, acetone and hexane solvent. Balfas (2009) said that the use of ethanol gave greater yields of resin than the use of methanol or distilled water.

There was no difference in the yield of resin between methanol and acetone solvents, but by using methanol solvent the yield tended to increase. In case of aceton extract of Super AB, the yield looks higher than methanol extract. The methanol solvent has a property that can dissolve almost all of the components in polar, semi-polar and non-polar solvent.

The agarwood resin yield indicates generally that the super AB has the highest level in resin level, followed by *kacangan* C, t*eri* C and *kemedangan* C. In general, the higher quality of agarwood, the higher is the resin yield. The consistency of the resin content can be used as a valid measure to classify agarwood grade.

C. Chemical Component Analysis

The results of the analysis of chemical components of four agarwood resin grades from West Sumatra are presented in Table 3. Extracts analyzed were from acetone extracts; based on the literature which suggested that sesquiterpene compound isolation is better than using acetone solvent. The acetone solvent is better to dissolve the resin which is an agarwood extract as resinous product. Ishara, Tsuneya and Uneyama (1993) used acetone solvent to extract sesquiterpene compound from *Aquilaria agallocha* agarwood. In order to isolate resin from rubber wood acetone solvent was also used that has a good property in isolating resin groups (American Society for Testing and Materials [ASTM], 1997). Agarwood as resinous group is more suitable to be extracted by semi-polar solvent. The *Like Dissolve Like Theory* explains that solvents will dissolve the compounds according to their solubility properties. The polar solvents will dissolve polar compounds easier and non-polar solvents will be easier to dissolve by non-polar compounds (Harborne, 1987). Chemical components with high percentage peaks at retention time, namely 7.57, 8.76, 8.9, 9.0 and 10.6 are not included in sesquiterpene compounds groups. The compounds are 2,5-bis(2,2-dimethylpropylidene) cyclopentanone; beta.-Maaliene; Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethylidene)-, (4aR-trans)-; Tricyclo[3.2.1.02,7]oct-3-ene, 2,3,4,5-tetramethyl-; and valerenol. This compounds group is commonly found in healthy

Table 2. Agarwood resin yield

No	Quality	Moisture content (%)	Yield (%)		
			Methanol	Acetone	n-hexane
1.	*Kemedangan C*	7.39	9.53	9.07	4.57
2.	*Teri C*	11.48	20.91	19.25	1.42
3.	*Kacangan C*	10.30	24.95	21.04	0.81
4.	*Super AB*	8.11	27.34	30.71	3.50

agarwood (not infected) (Chen, Yeh, Chao, & Chen, 2013). The GCMS chromatogram of *super* AB is presented in Figure 2.

The results of testing the chemical composition refers to the chemical composition of agarwood reviewed by Chen et al. 2013. From Table 3 it can be explained that the aromadendrene compound group (Figure 3) is present in all grade tested. Aromadendrene is one of the sesquiterpene derivatives. It was presumed that its compound is one of the distinguisher compound (chemical marker) of agarwood. The increasing aromadendrene chemical content indicated increasing agarwood level. On the other hand, this research showed that there are some sesquiterpenene chemical compound with the same compound was isolated before by Yoneda et al. (1984). For example the β-agarofuran and α-agarofuran compounds.

However, Waluyo and Anwar (2012) research showed that there is no consistency in sesquiterpene compounds type for each quality of agarwood. The chromone and sesquiterpene compounds are found in kacangan B, teri B, kemedangan A and kemedangan B qualities. Likewise Pasaribu et al. (2013), stated that agarwood grade (super AB, kacangan C, teri C, and kemedangan C) showed that the agarwood contain furan compounds and ester aromatic groups that are responsible for agarwood's nice scent. There are many causes which can make the differences in the results of agarwood resin spectroscopy. The causes can be the type of

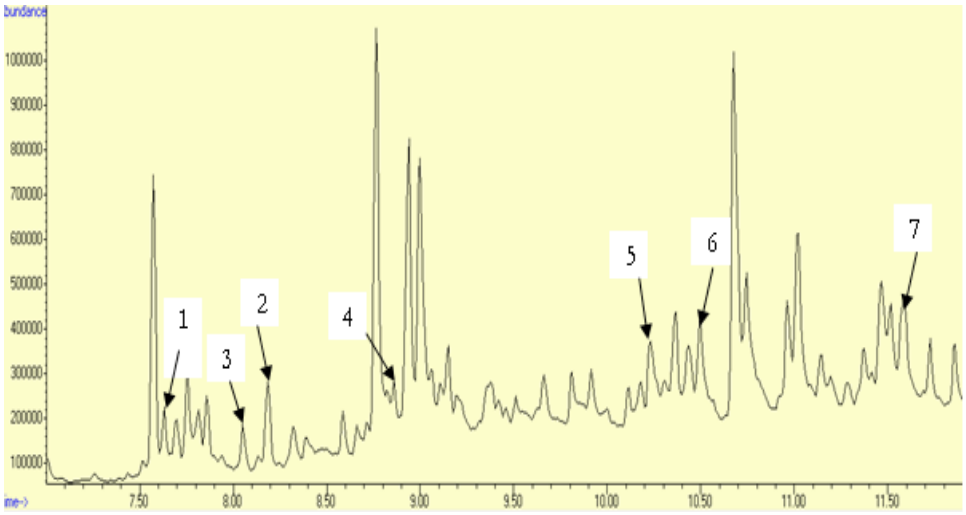

Figure 2. GCMS chromatogram of Super AB extract

Remarks:1. β-agarofuran, 2. α-agarofuran, 3. α-gurjunene, 4. Agarospirol, 5. Chromone, 6. Aromadendrene epoxide, 7. Aromadendrene

Table 3. Chemical components of agarwood

No	Quality	Chemical component	%
1.	*Kemedangan C*	Alloaromadendrene	0.77
2.	*Teri C*	Aromadendrene	0.66
		Aromadendrene epoxide	0.77
		Isoaromadendrene epoxide	2.10
		Alloaromadendrene	0.81
3.	*Kacangan C*	β-agarofuran	0.47
		α-gurjunene	0.20
		Agarospirol	0.67
		Aromadendrene	1.65
		Isoaromadendrene epoxide	0.53
4.	*Super AB*	Aromadendrene	2.57
		β-agarofuran	0.74
		α-gurjunene	0.46
		α-agarofuran	0.77
		Agarospirol	0.74
		Chromone	1.58
		Aromadendrene epoxide	1.55

raw material, the source of raw material of the different species.

Similarly, the different locations of plant growing of the same species can produce different chemical content. The method of analysis can also produce different outputs of the chemical content, due to differences in the condition of GCMS column and databases used in the tool. Nakanishi et al. (1984) said that the main fragrant compounds of agarwood are sesquiterpenes and phenylethyl chromone derivatives, and a great variety of sesquiterpenes are contained in high-level agarwood.

IV. CONCLUSION

The agarwood resin yield is influenced by the quality of the agarwood. A positive linier relationship has been found in which the resin yield increased with the increase in agarwood class grades.

The aromadendrene compound could be identified or found in all agarwood quality grades. Therefore, it is presumed that the aromadendrene compounds can act as an effective chemical distinguisher (chemical markers) for agarwood, whereby the greater the aromadendrene contents the better the agarwood grade.

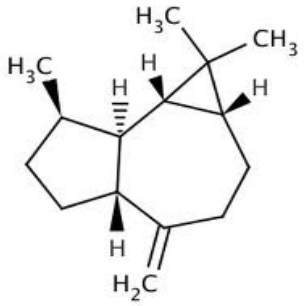

Figure 3. Aromadendrene structure

ACKNOWLEDGEMENT

The authors are very grateful to the Center for Forest Product Research and Development for financial support to conduct this research. Thanks also due to Pudji Hastuti and Umi Kulsum for their help on the laboratorium.

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