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Analysis of Agarwood Smoke Chemical Compounds using Solvent Trap, GC-FID and GC-MS

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ABSTRACT

Agarwood or gaharu, due to its unique scent and quality is considered one of the most expensive wood in the world. This paper uses solvent trap, Gas Chromatography-Flame Ionization Detector (GC-FID) and Gas Chromatography-Mass Spectrometry (GC-MS) to establish agarwood quality, and is part of ongoing research. The result showed that monoterpenes hydrocarbon, sesquiterpenes hydrocarbon and oxygenated sesquiterpene contribute to agarwood smoke. Among many compounds extracted, 2-hydrdoxy-benzaldehyde, β-selinene and guaia-1(10),11-dien-15,2-olide were found dominant in monoterpenes hydrocarbon, sesquiterpenes hydrocarbon and oxygenated sesquiterpenes respectively. This finding pointed to the utility of solvent trap in extracting chemical compounds of agarwood smoke. This study is also useful for further research on establishing the grade of agarwood.

Keywords: Agarwood, GC-FID, GC-MS, Quality, solvent trap

INTRODUCTION

Agarwood or Gaharu is known as Woods of God due to its unique scent (Hamid, 2011). Agarwood has been widely used as incense, and as an ingredient in perfumes, during religious ceremony and in traditional medical preparation. In the Middle East, agarwood is burnt during weddings and as a symbol of wealth. Due to that, agarwood is in high demand and one of the most expensive woods in the world. Agarwood and its essential oil are considered premium and prices are based

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on their quality (Hamid, 2011; Naef, 2011). The price for top grade oil ranges between USD126 and USD633 per tola or 12 cm^3 and for high quality wood, it is approximately USD30000 per kg (Jayachandran, Sekar, Parthiban, Amirtham, & Suresh, 2014; Lias, Ali, Jamil, Zainal, & Ab Ghani, 2015).

Traditionally, agarwood is graded based on its physical appearance such as colour and odour (Nor Azah et al., 2008). An agarwood which is dark and black, as well as having strong and lasting odour is considered high quality. This is based on human perception through visual observation and smell; in short, based on human experiences. This method has limitations as highlighted by Hidayat, Shakaff, Ahmad, and Adom (2010) in which the sense of smell weakens when dealing with many samples at the same time, resulting in grades being inconsistent (Hidayat et al., 2010).

The solvent trap is one of the extraction methods where hexane and ethyl acetate solvent are used to dissolve agarwood smoke (Ishihara, Tsuneya, & Uneyama, 1993). A previous study discovered the volatile compounds from smoke using TENAX TA sampling tube with solvent hexane to dissolve smoke (Ishihara, Tsuneya, & Uneyama, 1993). In the study, cluster of sesquiterpene group and aromatic compounds were detected. This technique was applied to determine the active volatile compounds in the smoke and headspace volatiles from Cryptomeria species Japonica (Yamada & Yatagai, 2007).

Researchers from Japan revealed that agarwood is a mixture of monoterpenes, sesquiterpenes and its chromone derivatives (Ishihara, Tsuneya, & Uneyama, 1993; Espinoza et al., 2014). In their studies, Gas Chromatography – Mass Spectrometry (GC-MS) technique was used to characterise the chemical composition of agarwood high (Kanankoh) and low (Jinkoh) quality. Some of the compounds were guaia-1(10),11-dien-15-al, benzaldehyde, β-agarofuran, and epoxybulnese (Ishihara, Tsuneya, & Uneyama, 1993; Yamada & Yatagai, 2007). Furthermore, methods used to extract the agarwood and its oil also affect the results of extraction. In 2013, Espinanoza et al. found 2-(2-phenylethyl) chromones using direct analysis in real time and time of-flight mass spectrometry (DART-TOFMS). On the other hand, dry Gas – Chromatography (GC) and preparative Thin Layer Chromatograph (TLC) were performed by Yoshii et al. and found out that agarospirol, agarol and agarofurans in their agarwood samples (Espinoza et al., 2014). Several researchers agreed that Gas Chromatography – Flame Ionization Detector (GC-FID) and GC-MS are the most common analytical methods to identify the agarwood compounds (Marriott, Shellie, & Cornwell, 2001; Pripdeevech, Khummueng, & Park, 2011; Tajuddin & Yusoff, 2010). The analysis was conducted especially in 12 tabulated guaia-1(10),11-dien-15-ol, karanone, jinkoheremol and isoamyldodecanoate as major compounds. Generally, it can be said that the compounds are varied accordingly to extraction, identification as well as quality of the agarwood.

MATERIALS AND METHOD

Agarwood chipwood used in this study was obtained from Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang (UMP), Pahang. Low and high-quality samples were

purchased from an authorised agarwood dealer in Kelantan and commercial samples were purchased from a local supplier, Konsesi Utama Sdn. Bhd. All samples were prepared in dry conditions. They were then ground and baked in an o oven at a temperature of 40°C until a constant weight was achieved.

Solvent trap extraction: Each sample was burnt under inverted glass funnel and which allows the smoke to stream through a passage. Later, using an electric pump, the smoke was extracted and eventually dissolved as shown in Figure 1. The duration of the extraction was 30 minutes and hexane was used as solvent.

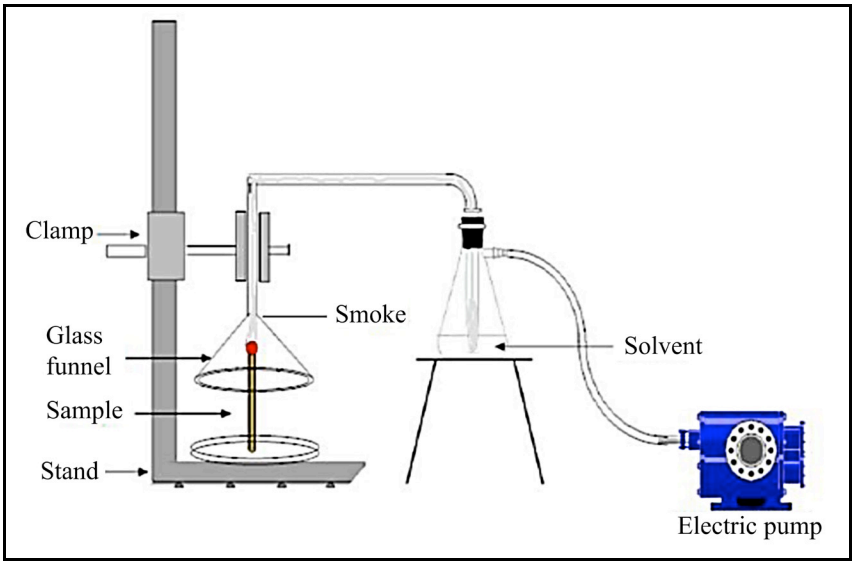


Figure 1. Schematic diagram of solvent trap (Mastura, 2014)

All samples in this study were analysed using the GC-MS and GF-FID. The analysis was completed using the experiment parameters of DM-1MS for column with 30 m length, 0.25 mm diameter and 0.25 µm film thicknesses. After that, 1 µL was injected into sample with the split ratio of 1:5.

The compounds were identified by comparing their retention indices (RI) with published data. Retention Indices or Kovats Index were calculated using a linear hydrocarbon (C8 – C22) as stated in study by Joulian and Konig, 1998.

RESULTS AND DISCUSSION

Table 1 shows the chemical composition of high, low and commercial types of agarwood in hexane solvent trap. The table lists a total of 27 volatile compounds that was identified by GC-FID and GC-MS. It shows that monoterpenes hydrocarbon, sesquiterpenes hydrocarbon and oxygenated sesquiterpenes were major groups in agarwood smoke. This finding is

consistent with those of earlier studies which showed agarwood is a mixture of monoterpene, sesquiterpenes and its chromone derivatives (Ishihara, Tsuneya, & Uneyama, 1993). It is also observed that compounds from the sesquiterpene group were absent in low quality agarwood. In addition, high quality agarwood produced a high percentage of peak area, 29.12%, whereas 17.31% of peak area for low quality agarwood. Meanwhile, commercial agarwood afforded 27.55%. The monoterpene hydrocarbon group produced a high percentage of peak area for all types of samples and less percentage in the oxygenated sesquiterpene group. Eleven compounds (from monoterpenes hydrocarbon and sesquiterpenes hydrocarbon) were detected in high quality and commercial samples. However, no compounds from group sesquiterpenes hydrocarbon were detected in low quality samples. Furthermore, in low quality samples, only two compounds - pentadecanoic acid (0.38%) and guaia-1(10),11-dien-15,2-olide (8.96%) - were detected. This finding revealed that for low quality agarwood, there were not many compounds from sesquiterpenes hydrocarbon and oxygenated sesquiterpenes groups. It is interesting to note the presences of all 27 compounds in commercial samples. It is believed that there were compounds from other substances which were added into agarwood during the manufacturing process.

Table 1
Chemical compound (% relative peak area) of three types of agarwood in hexane solvent trap

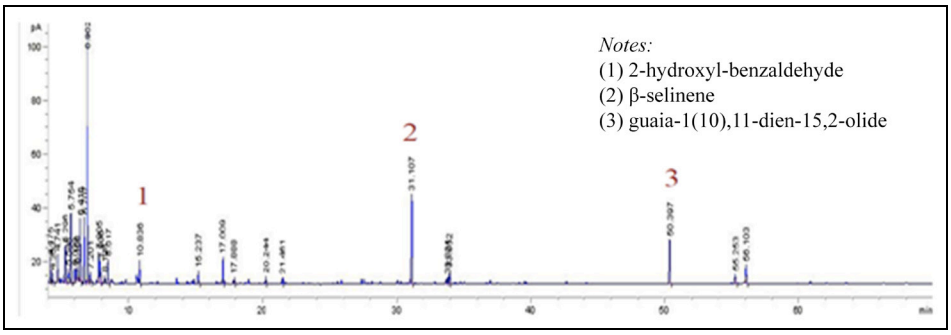
Compound	[1]KI	Types of agarwood			Identification
		High	Low	Commercial	
Monoterpene Hydrocarbon					
furfuryl alcohol	830	3.99	0.29	6.12	[3]RI
benzaldehyde	935	3.52	0.43	1.71	RI, [4]MS
phenol	956	2.02	2-	1.67	RI
p-methylanisol	1002	1.12	1.04	0.31	RI
2-hydroxy-benzaldehyde	1003	2.01	4.04	3.50	RI, MS
guaiacol	1062	-	-	1.74	RI
acetophenone	1066	0.38	0.41	0.19	RI, MS
p-methoxyphenol	1198	0.50	1.30	0.37	RI
4-phenyl-2-butanone	1210	-	-	0.10	RI, MS
p-vinylguaiacol	1286	-	0.46	0.40	RI
vanillin	1367	-	-	0.11	RI
Sesquiterpenes Hydrocarbon					
β-maaliene	1414	-	-	0.11	RI, MS
aromadendrane	1443	-	-	0.39	RI, MS
β-selinene	1486	8.79	-	1.01	RI, MS
α-murolene	1496	-	-	0.16	RI

Table 1 *(continue)*

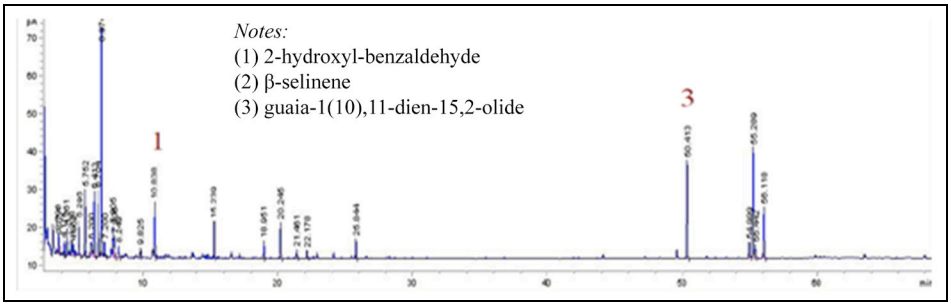
Oxygenated Sesquiterpenes					
α-elemol	1530	-	-	0.25	RI
nor-ketoagarofuran	1555	0.62	-	0.09	RI, MS
tridecanol	1561	1.30	-	0.20	RI
epoxybulnesene	1572	-	-	0.22	RI
caryophyllene oxide	1600	-	-	0.24	RI
epi-α-cadinol	1640	-	-	0.07	
selina-4, 11-dien-14-al	1758	-	-	0.09	RI
oxo-agarospirol	1822	-	-	0.17	RI
pentadecanoic acid	1842	-	0.38	2.02	RI
hexadecanol	1865	-	-	0.65	RI
guaia-1(10),11-dien-15,2-olide	2019	4.87	8.96	5.14	RI
Others					
2-(2-phenylethyl) chromone	2296	-	-	0.52	RI
Sesquiterpene Hydrocarbons		3.28	13.28	2.99	
Oxygenated Sesquiterpenes		70.46	62.02	73.58	
Others		74.34	77.83	78.18	

[1]KI: Kovats retention indices on DB-1 column, [2]-: not identified [3]RI: linear retention indices relative to the retention time on DB-1 column of a homologous series of n-alkanes (C8-C22), [4]MS: identification by comparison of MS with those of the NIST library

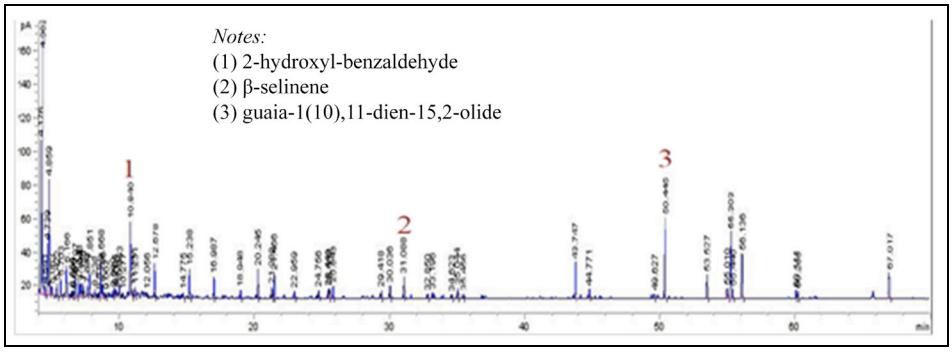
Figure 2 shows the GC-FID chromatogram of those three types of samples. The pattern was slightly different for high quality sample. It appeared that a cluster of monoterpene group at retention time ranges from 4.00 to 12.00 for all types of samples. The compounds of sesquiterpene group was barely noticed in all types of samples. Specifically, 2-hydrdoxy-benzaldehyde, β-selinene and guaia-1(10),11-dien-15,2-olide exist in high and commercial groups. On the other note, β- selinene was absent in the low-quality sample.



(a)



(b)



(c)

Figure 2. GC-FID chromatogram of: (a) high quality; (b) low quality; and (c) commercial agarwood in hexane solvent trap

CONCLUSION

This study has shown that the proposed solvent trap, GC-FID and GC-MS, was successful in characterising agarwood smoke from high, low and commercial types. Three major groups were found: monoterpenes hydrocarbon, sesquiterpenes hydrocarbon and oxygenated sesquiterpenes. Among all the compounds, three were most significant. They were 2-hydrdoxy-benzaldehyde, β-selinene and guaia-1(10),11-dien-15,2-olide. This finding confirms that of earlier studies

which pointed to agarwood being a combination of monoterpenes, sesquiterpenes and chromone derivatives (Ishihara, Tsuneya, & Uneyama, 1993). Thus, further study is useful to establish the grade of agarwood.

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