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Chemical Components of Agarwood (*Aquilaria crassna*) Essential Oils Grown in Various Regions of Asia

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This study presents a chemometric study on agarwood (*Aquilaria crassna*) essential oils extracted from selected agarwood samples grown in various regions of Asia. Adopting gas chromatography-mass spectrometry (GC-MS) technique, it was revealed that essential oils, produced by hydrodistillation,constitutes mainly volatile aromatic compounds. Several major components are shared in all samples including dihydro-agarofuran-15-al, jinkoeremol, 10-epi-γ-eudesmol, agarospirol, valerianol, *n*-hexadecanoic acid, neopetasane and dihydrokaranone. Despite differences in composition, extraction yield and detected constituents found in analyzed samples, characteristic aromatic compounds were abundantly found in the Agarwood essential oil. These discrepancies could be due to cultivation season, climatic conditions and extraction methods. Unambiguous identification of components in agarwood essential oils thereby opens new potential in the application of high-value aromatic compounds in agarwood essential oil in cosmetic products, perfumes, and pharmaceuticals.

Keywords: Essential oil, Agarwood, *Aquilaria crassna*, Chemical Components, GC-MS.

INTRODUCTION

Essential oils are mixtures consisting aromatic substances secreted in some parts of plants (seeds, roots, bark, leaves, and sap) or animals (essential oil bags) [1-5]. Essential oils are found in these sources with very different concentrations and are relatively volatile [6-10]. The concentration of essential oils depends on many factors such as seed, genetics, soil, fertilizer, weather, light, harvest time, *etc*. The main components of essential oils could be classified into four main groups including terpenoid, monoterpenoid, sesquiterpenoid and diterpenoid.

Agarwood is the resinous heartwood of aquilaria (*Aquilaria crassna*) tree, produced as a result infection or injury-induced defense. The plant is taxonomically classified in the Thymelaeaceae family. Other names for agarwood from Aquilaria spp. are gaharu, eaglewood, oudh, oud, kanankoh, kyara, jinkoh and kalambak. There are 19 species of aquilaria found in the Asian region [11-14]. Agarwood is a highly valued product in oriental cultures due to its special aroma and exclusive use in incense and perfumes. Chemically, the complex composition of agarwood oils is characterized by sesquiterpene hydrocarbons, oxygenated sesquiterpenes and their chromone derivatives [15-17]. Prominent compounds detected in agarwood include α-agarofuran, β-agarofuran, 10-epi-γ-eudesmol, agarospirol, jinkohol, jinkohol II and valerianol. The colour of oil extracted from agarwood may vary from yellowish to deep brownish, making it difficult to identify.

Compositional differences between chemical profiles of regionally different agarwood essential oils have been rarely examined. Therefore, the research objective of this study is to compare chemical compositions of different agarwood oil samples extracted from agarwoods in Asian regions. Gas chromatography with mass spectrometry (GC-MS) was selected as the method of analysis. The results will provide a basis for selecting the best quality agarwood grown in various regions of Asian and a foundation for the quality evaluation study of agarwood.

EXPERIMENTAL

Vietnamese agarwood (*Aquilaria crassna*) was collected in Phu Quoc Island and essential oil extracted by hydrodistillation method, resulting in the content yield of 0.13 %. The agarwood essential oil samplesfrom India, Indonesia, Laos, Taiwan and Thailand are provided by the Vietnam Agarwood Association.

GC-MS analysis of essential oils: An Agilent Technologies HP7890A GC instrument, coupled with a mass spectrum detector (MSD) Agilent Technologies HP5975C and a DB-XLB column (60 m × 0.25 mm, film thickness 0.25 µm, Agilent Technologies) was used to perform GC-MS analysis. Injector and detector temperature was set at 250 and 280 ºC, respectively. Thermal progress of the column temperature was initiated at 40 ºC, followed by an increase to 140 ºC at 20 ºC/min and a subsequent increase to 270 ºC at 4 ºC/min. The carrier gas was helium at a flow rate of 1 mL/min. A 1 µL of essential oils was injected by splitting with the split ratio of 100:1. The MSD conditions were as follows: ionization voltage 70 eV, emission current 40 mA, acquisitions scan mass range 35-450 amu under full scan. To determine retention time indices (RI), a homologous *n*-alkane series was used as a standard. The relative amounts of individual components were calculated based on the GC peak area (MSD response) without correction.

RESULTS AND DISCUSSION

Frankincense essential oil products originating from different Asian regions were analyzed by GC-MS. In this study, peaks whose retention time indices ranged from from 1100 to 2200 are studied. Fig. 1 and Table-1 displays GC-MS spectra and summarizes component content in the oils, respectively. Visually, small peaks could be observed in large quantities. These correspond to compounds that could not be determined. Overall, primary compounds detected in the samples are sesquiterpenes and 2-(2-phenylethyl) chromones [15], which are largely responsible for the pleasant and desirable odour of the materials. In addition, other minor volatile components could augment the oil and create other odours that could be described as balsamic, spicy, woody and sweet.

Analysis of the essential oil derived from Vietnamese agarwood showed a total of 26 components,accounting for 78.74% of the total content. The abundant compound identified in the oil was neopetasone (14.43 %), followed by dihydroagarofuran-15-al (9.20 %), jinkoeremol (5.02 %), valerianol (4.94 %), β-agarofuran (8.02 %), valenca-1(10),8-dien-11-ol (5.95%), dihydrokaranone (3.25 %) and selina-4,11-dien-14-al (2.73 %). Among them, neopetasane, β-agarofuran, agarospirol, dihydrokaranone and selina-3,11-dien-14-al are very valuable fragrant compounds.

A total of 23 components representing 70.1 % of total content were found in the agarwood essential oil from Thailand. Abundant compounds were β-agarofuran (8.32 %), 10-epi-γ-eudesmol (5.2 %), agarospirol (5.76 %), jinkoeremol (5.31 %), valerianol (6.86%) and dihydroagarofuran-15-al (4.94 %).

Components found in Laos agarwood essential oil represent only 59.57 % of the total volatiles. Thirty components were detected and the most abundant compound was *n*-hexadecanoic acid (15.04 %). This content far exceeded that of valerianol (6.15 %), jinkoeremol (4.81 %), agarospirol (3.53 %), oleic acid (3.87 %) and dihydrokaranone (4.58 %). In general, Laos agarwood essential oil is characterized by the high percentage of fatty acids and fatty acid derivatives, which could be detrimental to the quality of oil.

Indian agarwood essential oil is similar to the oil from Thailand in terms of major constituents. Among 34 components accounting for 62.30 % of the total oil content, β-agarofuran had the highest content at 7.03 %. Other constituent with moderate content were valerianol (4.01 %), β-eudesmol (4.07 %), valenca-1(10),8-dien-11-ol (4.45 %), dihydroagarofuran-15-al (3.12 %) and dihydrokaranone (6.03 %).

In the agarwood essential oil obtained from Indonesia, 31 components representing 68.74 % of the total volatiles were found. Dihydrokaranone was identified as the most abundant compound (6.18 %), followed by valerianol (5.95 %), β-agarofuran (5.74 %), valenca-1(10),8-dien-11-ol (5.04 %), jinkoeremol (4.48 %), dihydroagarofuran-15-al (4.42 %), β-eudesmol (3.45%) and neopetasone (3.14 %).The compounds that make up the aroma for essential oils have a relatively high content in the essential oil sample.

Taiwanese Agarwood essential oil shows 34 detectable components representing 84.59 % of the total oil contents. The identified compound occupying the largest content was valerianol (9.07%), followed by *n*-hexadecanoic acid (7.77 %), jinkoeremol (7.04 %), valenca-1(10),8-dien-11-ol (6.39 %), neopetasone (6.2 %), agarospirol (5.36 %), dihydroagarofuran-15-al (5.14 %) and oleic acid (4.14 %). The composition in this sample is characterized by the higher content of sesquiterpene compounds and fatty acids in comparison with those originating from the surrounding areas.

Sesquiterpenes species including agarofurans, eudesmanes, guaienesas well as their oxidized formswere found in agarwood and their use have been the long-established in the literature [18]. To date, approximately 70 sesquiterpene compounds have been identified and structurally elucidated [15]. In addition, chromone is also one characteristic compound in agarwood which has been extensively reported in terms of identification of structures and oxygenated derivatives since 1978 [19]. However, no chromone compounds as well as its derivatives were detected. This is contrast with previous studies which indicated the exclusivity of 2-(2-phenylethyl)chromone derivatives in agarwood oil from the aquilaria species [20-26]. These components are mainly responsible for the special fragrance of agarwood, but they are rarely detected by GC-MS.

Table-1 shown that fatty acid components (*n*-dodecanoic acid, *n*-tetradecanoic acid, pentadecanoic acid, octadecanoic

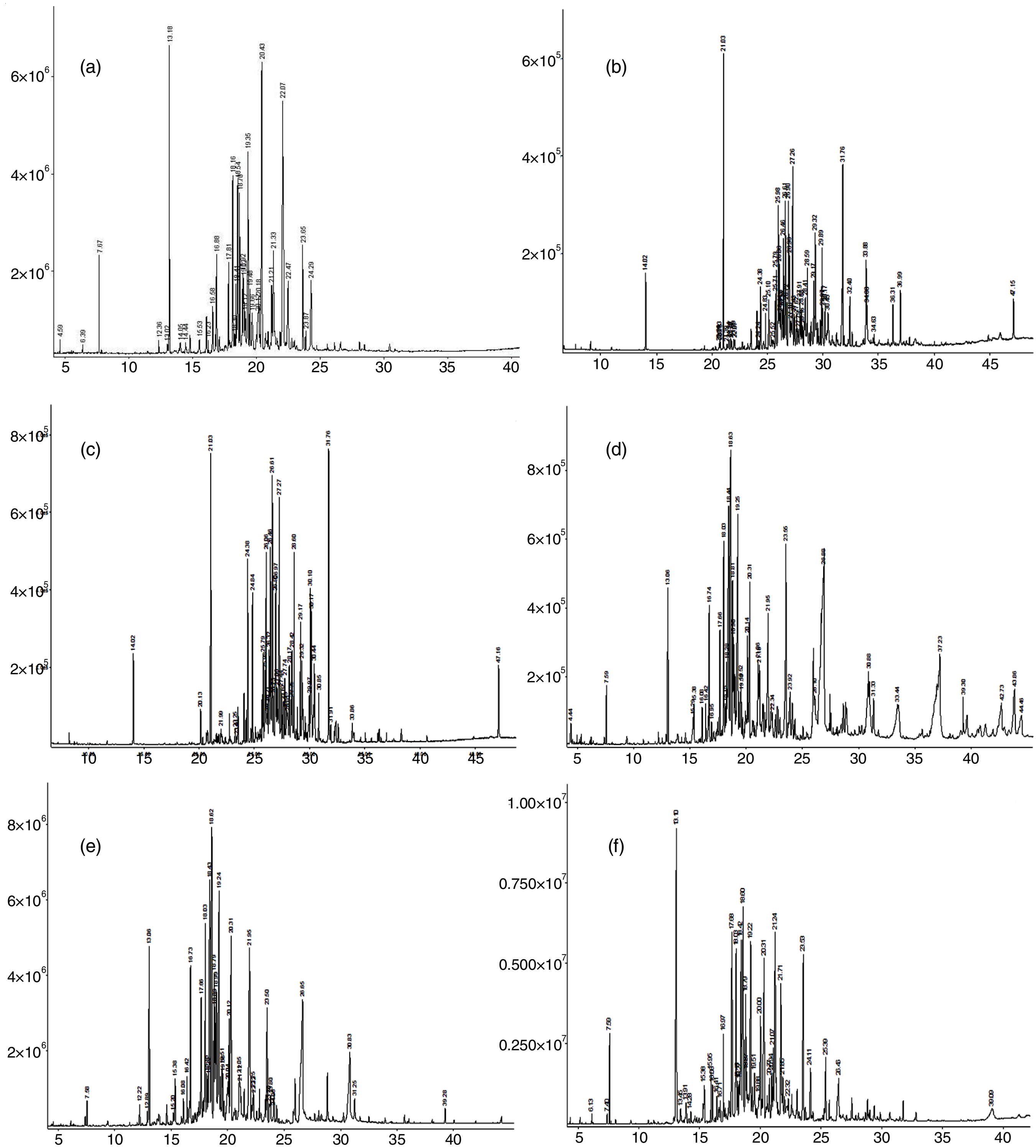

Fig. 1. GC-MS analysis results of volatile compounds present in the Agarwood essential oils in (a) Vietnam, (b) India, (c) Indonesia, (d) Laos, (e) Taiwan, (f) Thailand

acid and oleic acid) are mainly found in agarwood oils in Laos and Taiwan. In Vietnamese essential oils, fatty acid components are almost non-existent. According to Yoneda *et al*. [27], agarospirol and jinkoheremol were found in all types of agarwood. However, further investigations showed that such chromone derivatives absent in agarwood, which are key components of the resin formed in aquilaria species [15].

More than 150 compounds have been detected in various agarwood samples from various species and regions [1], confirming diverse organoleptic properties of the materials. Fig. 2 shows that the main component of agarwood oil differs according to the country in which the material is originated. Most of the essential oils contain a large amount of agarospirol, jinkoerenol, β-agarofuran, valerianol and dihydroagarofiran-15-al. While neopetasone was found with the highest content in the Vietnamese sample, essential oil samples in Laos and Thailand did not find neopetasone in their compositions. A study conducted on agarwood oil by Takemoto *et al*. [28] also proved

TABLE-1
CHEMICAL COMPOSITION OF AGARWOOD ESSENTIAL OIL IS EXTRACTED FROM *Aquilaria crassna* IN DIFFERENT AREAS

RI	Chemical name	India	Indonesia	Laos	Taiwan	Thailand	Vietnam
1288	Benzylacetone	1.61	1.62	0.41	0.26	1.07	1.53
1490	2,6-Di-*tert*-butyl-4-methylphenol	nd	0.62	nd	0.36	nd	0.35
1507	ar-Curcumene	0.19	nd	nd	nd	nd	nd
1509	β-Chamigrene	0.26	nd	nd	nd	nd	nd
1511	4,5-di-epi-Aristolochene	0.15	nd	nd	0.31	nd	0.31
1519	β-Agarofuran	7.03	5.74	2.04	3.45	8.32	8.02
1530	β-Vetispirene	0.18	nd	nd	nd	0.44	nd
1539	α-Bulnesene (d-Guaiene)	0.30	nd	nd	nd	nd	nd
1543	α-Selinene	0.21	nd	nd	nd	nd	nd
1550	β-Dihydroagarofuran	0.25	0.19	nd	nd	0.56	0.40
1552	Anisylacetone	0.26	nd	nd	nd	0.19	0.21
1578	*n*-Dodecanoic acid	nd	nd	0.5	0.24	nd	nd
1581	α-Agarofuran	nd	0.45	0.62	1.08	0.93	0.49
1624	nor-Ketoagarofuran	0.22	0.77	0.44	0.52	0.75	0.36
1628	Epoxybulnesene	1.58	3.6	0.5	0.93	0.61	1.27
1644	7-epi-Eremophila-1(10),8,11-triene	0.85	2.96	1.83	3.27	0.49	nd
1676	10-epi-γ-Eudesmol	1.99	1.75	1.65	2.77	5.2	2.44
1682	γ-Eudesmol	3.66	1.51	nd	nd	nd	nd
1685	Agarospirol	2.41	4.12	3.53	5.36	5.76	5.64
1688	Guaiol (=Champacol)	0.92	0.6	nd	nd	nd	nd
1690	Hinesol	1.09	0.79	0.54	1.11	0.87	0.54
1699	Jinko-eremol	2.98	4.48	4.81	7.04	5.31	5.02
1704	Valerianol	4.01	5.95	6.15	9.07	6.86	4.94
1714	β-Eudesmol	4.07	3.45	2.42	3.31	3.09	nd
1716	α-Eudesmol	2.40	3.26	1.41	2.48	1.07	2.17
1721	Dihydro-eudesmol	1.37	nd	nd	nd	nd	nd
1727	Valenca-1(10),8-dien-11-ol	4.45	5.04	4.16	6.39	4.86	5.95
1739	Dehydrojinko-eremol	0.99	1.01	0.77	1.1	1.53	1.65
1744	(Z)-α-Santalol	nd	1.46	nd	nd	nd	nd
1746	Eudesma-3,11-dien-8-one	0.49	0.49	0.6	1.02	nd	nd
1750	4,15-Epoxy-dihydroagarofuran	nd	nd	nd	1	nd	1.72
1759	Cadina-1(10),4-dien-8a-ol	0.59	0.57	1.62	2.1	nd	0.95
1774	Dihydroagarofuran-15-al	3.12	4.42	2.6	5.14	4.94	9.20
1776	Selina-3,11-dien-9-ol	1.83	2.58		1.42		1.97
1780	*n*-Tetradecanoic acid	nd	nd	1.7	0.47	nd	nd
1808	Neopetasone	nd	3.14	3.24	6.2	nd	14.43
1824	α-Costol	1.23	1.24	nd	0.75	nd	nd
1842	Selina-4,11-dien-14-al	1.54		0.32	0.52	0.45	2.73
1891	Dihydrokaranone	6.03	6.18	4.58	2.55	4.59	3.25
1898	Nootkatone	nd	0.34	nd	0.39	nd	0.61
1902	Pentadecanoic acid	nd	nd	1.13	0.68	nd	nd
1913	oxo-agarospirol	1.42	nd	nd	0.79	nd	2.59
1962	Cyclohexadecanolide	nd	nd	3.09	nd	nd	nd
1994	*n*-Hexadecanoic acid	2.62	0.41	15.04	7.77	1.68	nd
2164	Oleic acid	nd	nd	3.87	4.14	nd	nd
2181	Octadecanoic acid	nd	nd	0.69	0.6	nd	nd
	Total	**62.30**	**68.74**	**70.1**	**84.59**	**59.57**	**78.74**

that the constituents of agarwood oil vary between trees and the variation occurs naturally due to the biological characteristics of trees. Since the quality of agarwood essential oil is characterized by the number and quantities of volatile compounds, it is suggested that agarwood oil which is rich in resin is of high quality due to the presence of oxygenated sesquiterpenes and chromone derivatives [29].

Conclusion

From the study, it is suggested that the quality of agarwood (*Aquilaria crassna*) essential oil is determined by the abundance of important chemical compounds. The chemical compositions of agarwood oil comprise sesquiterpene, oxygenated sesquiterpenes and its chromone derivation. In addition, no striking differences were found between compositions of agarwood samples from various countries in the region. Agarospirol, β-agarofuran, jinkoeremol and valeriano were among abundant volatiles in the oil and it is suggested that contents of such components could determine quality of agarwood essential oil.

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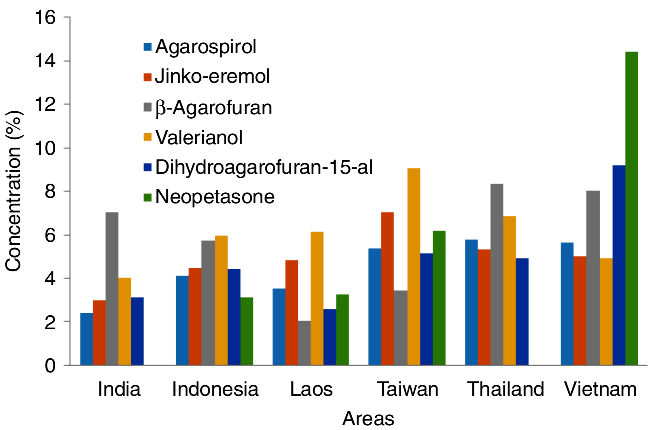

Fig. 2. Main ingredients in agarwood essential oils in Asian Countries

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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