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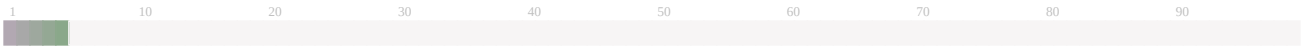

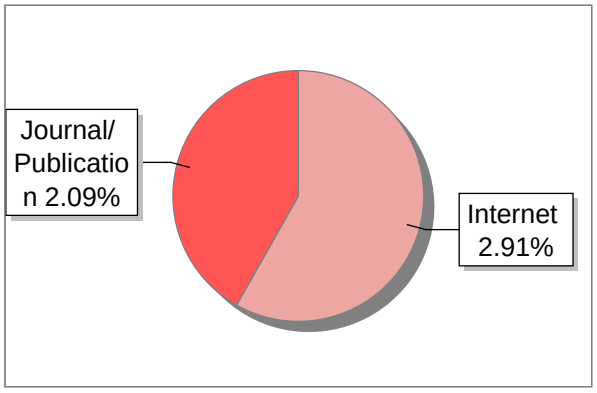

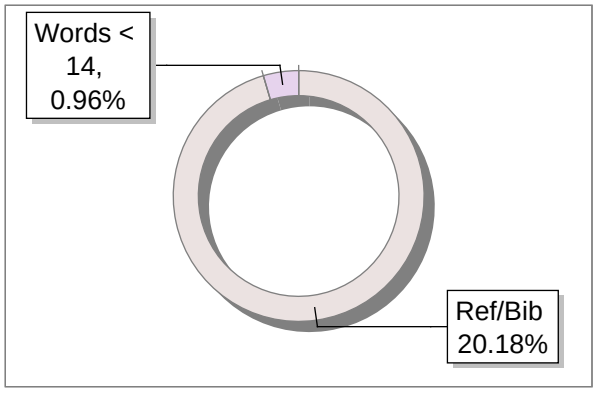

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AUTHENTICATION OF PATCHOULI OIL FROM VARIOUS GROWING REGIONS USING GC-MS METHOD WITH CHEMOMETRIC COMBINATION ON THE PRODUCTS IN THE MARKET

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ABSTRACT

Adulteration in patchouli oil trade is an ancient practice, where additional substances like turpentine oil are added to increase volume and odor. Therefore, this research aimed to determine the composition of patchouli oil, considering variations in growing regions and potential adulteration in the products available in the market. The analysis was carried out using the Gas Chromatography-Mass Spectrormetry (GC-MS) method with a Principal Component Analysis (PCA) chemometric combination for authentication. The sample obtained from Bantul, Kulon Progo, and Purworejo was isolated through steam and water distillation. Subsequently, it was tested in accordance with SNI standard 06-2385-2006 and analyzed using GC-MS. The results were compared to the products on the market and processed using multivariate chemometric, namely PCA with Minitab 19 software. GC-MS analysis showed the presence of various compounds contained in the oil, including alcohol, alpha-guaiene, beta-humulene, seychellene, trans-caryophyllene, neoalloocimene, and beta-patchoulene. The combination of GC-MS and PCA chemometrics was able to distinguish patchouli oil from others and the products available on the market. PCA chemometric analysis showed that the patchouli oil from various growing regions had the same chemical components as essential oil. Furthermore, PCA chemometric analysis of market products also showed similar results but varied significantly from turpentine oil. This showed that the patchouli oil product available on the market did not contain turpentine oil.

Keywords: Authentication; Essential oil; GC-MS; Patchouli oil; PCA chemometrics

1. INTRODUCTION

The market demand for patchouli oil in Indonesia is significantly increasing every year, with a stable price, contributing approximately 50% of total exports in the country. Patchouli oil is fixative (binding) in nature, presenting a good opportunity for application in several sectors due to unavailable substitutes (Hariyani et al., 2015). However, this product is still sold in its crude form (Manurung, 2003), affecting the quality, as defined by the Indonesian National Standard (SNI) 06-2385-2006.

The export of essential oil is mainly influenced by the decrease in quality due to adulteration. Moreover, adulteration is the incorporation of additional substances to increase the volume or weight, meet quality standards, and enhance the oil properties. Adulterants that are commonly used include fats, kerosene, turpentine oil, specific organic solvents, and keruing oil (Ma'mun, 2003). This makes authentication an essential process to detect and prevent exposure to adulterated products using a combination of physical and chemical methods (Rohman, 2017).

The differences in growing regions, as well as the regional variations in the source of extraction, can affect the quality and quantity of essential oil. The primary components of patchouli oil that contribute to the distinctive aroma include alcohol and norpatchoulenol. In theory, the concentration of patchouli alcohol is relatively higher (30-40%) compared to norpatchoulenol (0.3-0.4%) (Manalu et al., 2019). It is necessary to authenticate patichouli oil obtained from different growing locations because the growing location has a significant impact on the chemical content. Climate, soil, sunlight, and elevation above sea level are all factors in this (Sufriadi et al., 2021).

In previous research, gas chromatography (GC) has been applied using the principle of separating mixtures based on differences in migration speed and boiling points (or vapor pressure) of the constituent components (Gandjar & Rohman, 2007). As technology develops, this method is combined with mass spectrometry (MS) to identify compounds, and determine molecular weight, and molecular formula (David, 2005). The combination of gas chromatography and mass spectrometry (GC-MS) allows rapid and sensitive identification of essential oil components, which is commonly used in quantitative analysis to assess PA levels and other chemical components (Ramayanti et al., 2021). Chemical methods are analytical techniques used to monitor the quality of essential oil.

This research aimed to analyze the chemical component profile of patchouli oil using GC-MS combined with PCA chemometric. The analysis was carried out to group the chemical components of patchouli and turpentine oils for product authentication.

2. METHODS

2.1. Materials

The main materials used included oil obtained from patchouli plant harvested in Bantul, Kulon Progo, and Purworejo on August 29, 2021. In addition, turpentine oil was obtained from CV Multi Kimia, and patchouli oil with a brand that has received 4.9 out of 5 customer evaluations in the online market, so brand A, B, and C were chosen. Other chemicals used included anhydrous sodium sulfate (Merck) and 90% ethanol (Merck). The main instruments were refractometer (Atago Abbe) and a GC-MS (Shimadzu QP2010SE).

2.2. Patchouli Plant Preparation

Patchouli leaves and stems were collected from Bantul, Kulon Progo, and Purworejo. Subsequently, the samples collected were washed, and dried in the sun covered with a black cloth for 9 days (Ardianto & Humaida, 2020).

2.3. Water Steam Distillation Process

A total of 3 kg of patchouli plants from Bantul, Kulon Progo, and Purworejo was distilled using steam and water distillation. The oil obtained was collected and weighed, followed by drying with anhydrous sodium (Wu et al., 2019).

2.4. Oil Quality Test

The test requirements were determined based on Indonesian National Standards (SNI) (Standar Nasional Indonesia, 2006), which included:

a) Color test: observed with the eye directly.
b) The refractive index is determined using a refractometer irrigated with water, ensuring the tool reaches a stable temperature required for reading.
c) Solubility test in ethanol: 90% ethanol is dropped into a measuring cup, and the solution is shaken to obtain a clear sample at a temperature of 20 °C.

2.5. Analysis by GC-MS

Patchouli oil obtained from various growing regions, turpentine oil, and three samples of market products were placed into a 2 mL vial. This process was repeated three times, depending

on the growing regions, and placed sequentially in the sample container of the GC-MS tool. Hexane was also put into a 2 mL vial and placed in the last container. Subsequently, 0.2 µL of oil samples were injected into GC-MS, and data analysis was carried out in the form of the relative region.

2.6. Chemometric

The relative region data was analyzed by grouping patchouli oil with market products using PCA, followed by a biplot generated with MINITAB 19 software. This grouping was based on the diversity of the data, resulting in a scree, score, loading, and bi-plot (Akbar, 2020; Anggraeni et al., 2020).

3. RESULTS AND DISCUSSION

3.1. Results of Characteristics and Quality Requirements of Patchouli Oil

Dark green patchouli leaves were harvested, washed with running water, dried in the air, and distilled. The distillation process was carried out based on growing regions using water and steam methods (Tauhana, 2008). The results of patchouli oil characterization are presented in **Table 1** and **Table 2**.

Table 1. Results of steam-water distillation of patchouli oil from various growing regions

Origin of Growing Regions	Rendement (%)
Bantul	0.29
Kulon Progo	0.30
Purworejo	0.28

Table 2. Comparison of the characteristics and quality requirements of patchouli oil SNI 06-2385-2006 and research

Parameter	Indonesian National Standards (SNI 06-2385-2006)	Results		
		Bantul	Kulon Progo	Purworejo
Color	Light yellow-reddish brown	Light yellow	Light yellow	Light yellow
Refractive index	1.507 – 1.515	1.510	1.508	1.509
Solubility in ethanol	Clear or lightly opalescent solution in a volume ratio of 1:10	Clear solution 1:8	Clear solution 1 :4	Clear solution 1:7
Patchouli alcohol ($C_{15}H_{26}O$)	Min 30%	26.11 %	26.14 %	26.93 %
Alpha copaene ($C_{15}H_{24}$)	Max 0.5 %	0.09 %	0.09 %	0.07 %

In this research, the yield produced was small because patchouli oil was obtained from Javanese patchouli (Pogostemon heyneatus Benth), consisting of approximately 0.5% - 1.5% oil content (Zhao et al., 2005). This variation in yield was also attributed to differences in time and temperature in the distillation process.

The differences in the physical properties of patchouli oil obtained in this research with the quality requirements were attributed to several factors. These included climate, soil conditions, growing regions, cultivation, and harvesting processes, which resulted in decreased quality compared to standard requirements (Schaduw et al., 2012).

3.2. Profile of Patchouli Essential Oil Components Using GC-MS

Analysis of the chromatogram profile for essential oil compounds was carried out using GC-MS. The Area Under the Curve (AUC) shown in the chromatogram was directly proportional to the concentration of each component contained in the sample. The use of GC-MS allowed the determination of a potential number of essential oil components and their concentrations.

Meanwhile, the type of essential oil component is determined using Mass Spectrometry, followed by identification through spectra from NIST and WILEY.

Based on the result, out of the 25 chromatogram peaks produced by patchouli oil component profile in Bantul, 7 were selected as the main peaks. Each selected peak was estimated to contain Patchouli alcohol (26.13%), Alpha-Guaiene (14.85%), Beta-Humulene (14.41%), Seychellene (11.47%), Trans-Caryophyllene (7.02%), Neoalloocimene (5.23%), and Beta-Patchoulene (4.53%). Similarly, among the 25 chromatogram peaks produced by patchouli oil component profile in Kulon Progo, 7 were selected as the main peaks, each containing Patchouli alcohol (26.20%), Alpha-Guaiene (14.90%), Beta-Humulene (13.74%), Seychellene (11.50%), Trans-Caryophyllene (7.03%), Neoalloocimene (5.19%), and Beta-Patchoulene (4.54%). Patchouli oil component profile in Purworejo produced 25 chromatogram peaks, with 7 main peaks. Based on estimation, each main peak contained Patchouli alcohol (26.99%), Alpha-Guaiene (14.74%), Beta-Humulene (14.07%), Seychellene (11.36%), Trans-Caryophyllene (6.69%), Neoalloocimene (5.46%), and Beta-Patchoulene (4.44%).

3.3. Comparison of Essential Oil Component Profiles in Patchouli Oil, Turpentine Oil, Products A, B, and C

In this research, turpentine oil was used as a counterfeit oil, and 3 samples of essential oil products (A, B, and C) were 100% pure. The results of the component analysis of patchouli oil, turpentine oil, products A, B, and C are presented in **Table 3**.

Table 3. Results of analysis of the main components of patchouli oil, turpentine oil, products A, B, and C

Patchouli oil components	Percentage (%) of GC results						
	Bantul	Kulonprogo	Purworejo	Product A	Product B	Product C	Turpentine
Patchouli alcohol	26.11	26.14	26.93	26.53	31.30	21.53	N/A
Alpha -Guaiene.	14.74	14.85	14.87	14.63	12.86	14.73	N/A
Beta-Humulene	14.26	14.21	14.48	15.10	N/A	14.02	N/A
Seychellene	11.85	11.88	11.60	10.68	10.36	0.68	N/A
Trans-Caryophyllene	6.98	7.03	6.71	6.58	4.79	8.26	N/A
Neoalloocimene	5.35	5.3	5.34	N/A	N/A	4.83	N/A
Beta-Patchoulene	4.49	4.52	4.47	4.58	3.81	5.95	N/A
Alpha Pinene	N/A	N/A	N/A	0.97	0.067	0.06	53.59
Delta Carene	N/A	N/A	N/A	N/A	N/A	N/A	14.10
Beta Pinene	N/A	N/A	N/A	0.18	0.123	0.15	7.03
Camphene	N/A	N/A	N/A	N/A	N/A	N/A	3.01
Limonene	N/A	N/A	N/A	N/A	N/A	N/A	1.48

Note: N/A = not detected

Based on **Table 3**, the largest patchouli alcohol component was found in product B, followed by Purworejo, product A, Kulon Progo, Bantul, and product C, with proportions of 31.30%, 26.93%, 26.53, 26.14%, 26.11%, 21.53%, respectively. Alcohol is the compound that determines the smell of patchouli oil, constituting the largest component (Trifilieff, 1980). As presented in **Table 4**, the essential oil content in products A, B, and C was similar to pure patchouli oil.

3.4. Principal Component Analysis (PCA) of Patchouli Oil with Turpentine Oil and Market Products

The results of PCA analysis were evaluated using Minitab 19 software and expressed the form of principal components (PC). This showed the magnitude of variation in the initial data, where PC1 contained the largest variance. **Table 4** shows the results from the eigenanalysis score plot.

Based on **Table 4**, PC1 has an eigenvalue of 9.8822, showing 82.4% of the total original data variables, while PC 2 has 10.2% with an eigenvalue of 1.2209. The results of PCA analysis are good when a small number of main components describes a large total variation

(Purwakusumah et al., 2014). In this research, the use of two PC resulted in a cumulative value of 99.8% (Rohman, 2014).

Table 4. Eigenanalysis of the correlation matrix

Eigenvalue	9.8822	1.2209	0.5897	0.2891	0.0094	0.0035	0.0031	0.0012	0.0008	0.0001
Proportion	0.824	0.102	0.049	0.024	0.001	0.000	0.000	0.000	0.000	0.000
Cumulative	0.824	0.925	0.974	0.998	0.999	1.000	1.000	1.000	1.000	1.000
Eigenvalue	0.0000	0.0000								
Proportion	0.000	0.000								
Cumulative	1.000	1.000								

Based on **Figure 1**, the main component of turpentine oil is completely separated in a different quadrant from patchouli oil in various growing regions and market products A, B, and C. This showed that PCA chemometrics could be used to analyze or group patchouli with fakes and products available in the market.

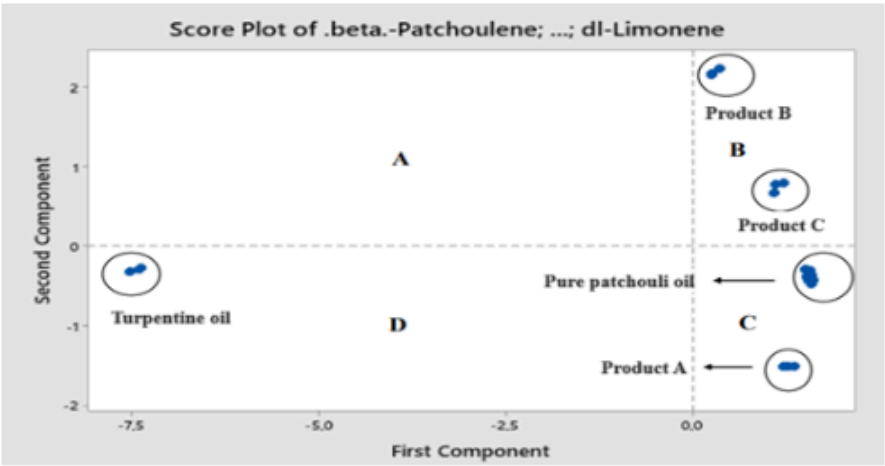

Figure 1. PCA score plot of patchouli oil, turpentine, product A, product B, and product C with type of essential oil as variable

PCA scoring between product A and others was close to pure patchouli oil but significantly varied from turpentine oil, resulting in the categorization of the score plots in different quadrants. This showed that the selected market products did not use turpentine oil as a mixture. However, products B and C are close to pure patchouli oil but are in different quadrants due to the presence of impurities (Sim et al., 2004). GC-MS can effectively analyze patchouli oil with key essential oil components, including patchouli alcohol, alpha-guaiene, beta-humulene, seychellene, trans-caryophyllene, neoalloocimene, and beta-patchoulene. When combined with PCA chemometrics, GC-MS proves useful in categorizing patchouli oil alongside other oils and various patchouli oil products available on the market. PCA chemometric analysis shows that patchouli oil from various growing regions shares common essential oil chemical components. It also confirms that patchouli oil products on the market do not contain turpentine oil.

4. CONCLUSION

GC-MS combined with PCA chemometrics successfully grouped patchouli essential oil with others and samples of products available on the market. PCA chemometric analysis showed that patchouli oil from various growing regions had the same essential oil chemical components, and market products did not contain turpentine oil.

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6. CONFLICT OF INTEREST

All authors declare no conflict of interest.

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