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Prediction of the rhodinol content in Java citronella oil using NIR spectroscopy in the initial stage of developing a spectral smart sensor system – Case report

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Abstract: The rhodinol content is an essential component in determining the citronella oil qualities. This study aimed to develop a model calibrated to predict the rhodinol content in citronella oil using near-infrared (NIR) spectroscopy. This research is the initial stage in developing a spectral smart sensor system that predicts the rhodinol content of citronella oil in the distillation and fractionating process. Citronella oil samples were scanned by NIRFlex liquid N-500 with a wavelength of 1 000–2 500 nm having an absorbance value (log 1/T). The accuracy of the prediction was achieved using the partial least square (PLS) model. Based on the NIR spectrum at a peak of around 1 620 nm, the rhodinol content in the citronella oil was estimated. The finest model to predict the rhodinol content was $y = 0.9874x + 15.6439$ with a standard error of the calibration set (SEC) = 2.78%, a standard error of the prediction set (SEP) = 2.88%, a ratio of the performance to the deviation (RPD) = 9.23, a coefficient of variation (CV) = 16.81%, and the correlation coefficient (r) = 0.99. The NIR and PLS models are possible to use for the initial stage in developing a spectral smart sensor system to determine the rhodinol content of citronella oils.

Keywords: calibration; fractional distillation; partial least square; process control; spectra

Citronella oil is an essential liquid fat obtained from the leaves and stems of *Cymbopogon* spp. The major terpenoids found in this oil are citronellal, citronellol, and geraniol (Eden et al. 2018). It is a major raw material for industries due to its application as fragrances in perfumes, as flavour additives in food or pharmaceutical products, a mosquito repellent, even as an additive in fuel oil (Tsimogiannis and Oreopoulou 2018; Setyaningsih et al. 2020). In Indonesia, there are two types of citronella oils, namely the Ceylon type (*Cymbopogon nardus* L. Rendle) commonly known as the Lenabatu variety, and the Java species (*Cymbopogon winterianus* Jowit ex Bor) widely known as the Mahapengiri derivative (Verma et al. 2020). The cultivation of the Java type is higher than that of the Ceylon one as it is superior in terms of its citronellal and geraniol contents (Sulaswatty et al. 2019). Moreover, its oil offers twice the yield of the Ceylon type (Avizienis 2019).

Indonesia is the second largest citronella oil producer in the world, and almost all the oils are exported in the form of crude from distilleries. The

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extraction of crude citronella oil is carried out by water-steam distillation techniques. To increase its added value, a small fractionation distillation column is built. One of the separating techniques for isolating the citronella oil component is by fractional distillation. Its vacuum fractionating column is used for the fractionation of Java citronella oil in batch systems (Beneti et al. 2011; Almeida et al. 2018).

The distillate product consists of two groups; the first is the light fraction rich in citronellal. The second is the heavy fraction consisting of citronellol and geraniol, widely known as rhodinol (Wany et al. 2014). Therefore, rhodinol is a determining factor in the fractionation which the content in citronella oil needs to be detected in the fractionation process system.

The technology of modern vacuum fractionating distillation continues to develop and even works automatically. However, its setting process is still conventional because it depends on the laboratory analysis results of the citronella oil feed, using gas chromatography-mass spectrometry (GC-MS) (Agustian et al. 2007). The oil composition from the GC is used to evaluate the volume for each fraction. The parameters for controlling the separation are not based on the concentration of the component. However, depending only on its volume fractions. Consequently, the time processing it is inefficient and costly.

Developing a modern agro-industry requires process technologies to work more quickly, practically, and effectively to increase the productivity and quality. It is necessary to innovate technology to control the fractionation distillation. A technological innovation is the process control based on a smart sensor system. In applying smart sensor systems, digital methods related to computing and programming can ensure the acquisition and processing of data in real-time to assist in designing control systems and monitoring the production process conditions (Chandra et al. 2019; Jumaah and Xue 2019).

In data acquisition, the activities include sensing units, signal conditioning, and signal processing to obtain the appropriate data. The sensing unit is the main factor that must be explored to match the characteristics of the detected chemical components (Hutchins 1997; Popescu et al. 2017; Chandra et al. 2019). One of the sensing unit developments is the adoption of the principle of spectrometry, which has been used to analyse the components of the citronella oil fraction using near-infrared (NIR) spectroscopy,

Spectrometric techniques have been utilised for the characterisation analysis of citronella products using near-infrared (NIR) spectroscopy. Also, the NIR spectrum measurement technique is accepted to rapidly assess the essential oil products' authenticity, not damage the material and due to its low cost. The NIR spectrum measurement at a wavenumber of about 4540 cm^{-1} combined with the GC-MS result is used in predicting the citronella oil products' content (Bota et al. 2015). The vibrations of C-H, N-H, and O-H bonds in almost all substances containing a hydrogen covalent force, are absorbed in the near-infrared region. NIR spectroscopy allows the measurement of the concentration of the constituents in a solution as the intensity of the O-H overtone vibration mode decreases significantly compared to the fundamental one in the infrared (IR) region (Rondonuwu and Setiawan 2020). The molecular structure and O-H and C-H bonds of rhodinol compounds absorb energy from the infrared electromagnetic radiation, and are recorded as spectral data. The development of NIR spectroscopy calibration statistics is used not only for fast quality control, but also it is successfully applied in monitoring the rectification of essential oil components during the distillation process (Pfeffer et al. 2001).

The gap in this research is the control of the fractionating distillation citronella oil process based on a smart sensor system. With the development of this technology, it is hoped that the fractional distillation process can be carried out online because it is integrated into the column and provides real-time quality data to make process improvements quickly. This study aims to develop a calibration model based on the NIR spectroscopy approach for the initial stage of developing a spectral *smart sensor system* to predict the rhodinol content in citronella oil.

MATERIAL AND METHODS

Preparation of the samples. Forty-eight samples which were obtained from one of the citronella oil refining industries in West Java, Indonesia, were divided based on the variation of the rhodinol concentration, i.e., 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, and 95% v/v. The calibration model used two groups of the sample and one group for predicting the rhodinol content and model validation intent.

Instruments and equipment. A liquid BUCHI NIRFlex N-500 spectrometer (BUCHI, Switzerland),

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a measuring cylinder, a volumetric pipette, a dropper, a magnetic stirrer, a GC-MS, a CAMO Unscrambler X Prediction Engine (CAMO Software, Norway), and MS Excel office software (Ver. 16.0, 2019) were used in this study.

NIR spectra measurements. The transmittance of the NIR spectral data was obtained from eighteen citronella oil samplers using fibre-optic liquid NIR-Flex N-500. The samples were placed into cuvettes with a thickness of 2 mm, each filled with 0.5 mL. The NIR spectra was acquired with the spectral area wavelength ranging from 1 000 to 2 500 nm (4 000 to10 000 cm^{-1} wavenumber). The scanning interval was set to 4 cm^{-1} with a speed of 1 scans/s for 10 s. During the spectra measurements, the sample temperature was maintained at 26 °C. The spectra of the samples were acquired from a mean of sixty-fourth scans.

NIR data processing and analysis. The derivative technique (first and second derivatives) can clarify the peaks and valleys of the absorbance spectra of the NIR spectroscopy data. This technique removes the background and increases the resolution of the spectra. The first derivative corrected the baseline spectral absorbance. Meanwhile, implementing the second derivative improved the inseparability. Each derivative step starts with a spectrum using the Savitzky-Golay smoothing (SGs) technique of the 3rd order polynomial with eleven frames (Bota et al. 2015). It is usually used to eliminate noise. Smoothing is used in the signal-to-noise rate optimisation so that the overlapping spectra can be decomposed and easily observed.

Furthermore, the calibration and validation of the logarithmic absorbance spectra (log 1/T) analysis of the NIR used the partial least squares (PLS) method (Novianty et al. 2020). The method to evaluate the predicted model used several statistical parameters including the correlation coefficient (*r*), standard error of calibration set (SEC), standard error of prediction set (SEP), coefficient of variation (*CV*), the ratio of the performance to deviation (RPD), and the consistency. The model had high accuracy when the SEC and SEP scores were small, while the *r* and RPD scores were significant (Bec et al. 2020; Novianty et al. 2020). Moreover, the models had minor differences in the SEC scores. The spectra data pre-treatment technique and the PLS method calibration used the Unscrambler X software (Ver. 10.4, 2016).

RESULT AND DISCUSSION

NIR spectra and rhodinol content of citronella oil. The absorbance value of the citronella oil's spectra increased from the range of 1 000 to 2 500 nm, as shown in Figure 1. The physical characteristics of the functional groups and the substance in the material will affect the shape of the spectra. When a molecule is emitted by IR electromagnetic wave radiation with the appropriate frequency, the molecular bonds in the material carry out a vibrational motion, both in stretching and bending. These molecular bonds respond, such as C-C, C-H, C-O, and O-H, and absorb this energy (Singh and Jayas 2012). Therefore, the NIR spectroscopy recorded the absorption intensity,

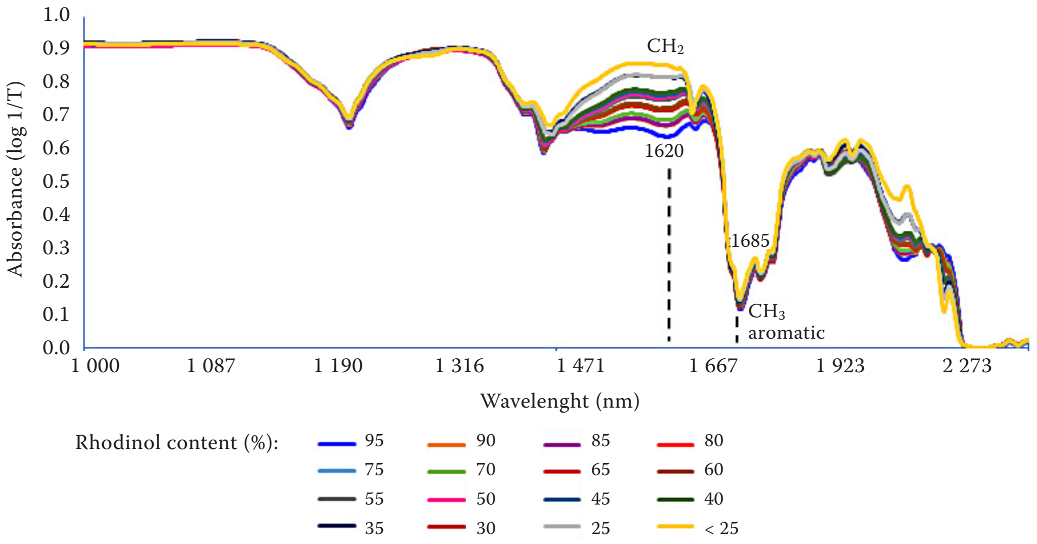

Figure 1. Near-infrared spectroscopy (NIR) absorbance spectra of the various rhodinol contents in the citronella oils

represented as a valley on the spectrum (Purwanto et al. 2013; Kurniawan et al. 2019).

Based on Figure 1, a distinctive rhodinol concentration was observed in the NIR spectra region at the wavelength of 1 620 nm. The higher the rhodinol content in the citronella oil, the higher the absorbance spectra value. Furthermore, the deepest absorption intensity at the wavelength of 1 685 nm indicated the citronellol and geraniol compound (the main component of rhodinol). This study matches the absorbent characteristics based on the C-H stretching in the first overtone (Cen and He 2007). The selected characteristics are absorbent, based on the distribution of the C-H stretching the first overtone of the organic bonds in the electromagnetic wave, as shown in Table 1.

Different spectra peaks were marked about 1 620 nm considering the C-H bond in the first stretching overtones while featuring some of the functional groups in the molecular structure of the rhodinol compound. The peak absorption at the wavelength of 1 685–1 695 nm was probably from the geraniol content due to the stretching vibration from CH_3 and the aromatic bond. It is known that aromatic terpene alcohol compounds, including geraniol and citronellol, are the main components of rhodinol having a CH_3 bond (Tisserand and Young 2014; Bota et al. 2015). Meanwhile, about 55–65% of the rhodinol consists of a mixture of citronellal-L and geraniol. This high content causes the photon energy absorption in the transmittance spectrum.

The rhodinol content was measured using the GC-MS method. Its value was obtained from the total percentage of the citronellol and geraniol. Furthermore, the absorbance spectrum that was sensitive to the changes in the rhodinol content in the citronella oil was created in a calibration curve. The rhodinol content of the citronella oil in this research was around 11.07–95%, as shown in Table 2.

Table 1. Selected characteristics of the absorbent based on the C-H stretching first overtone

Wavelength (nm)	Product example
1 620	CH_2
1 645	R-CH-CH
1 660	cis-RCH=CHR
1 685	aromatic
1 695–1 699	CH_3
1 705	CH_3
1 725	CH_2
1 740, 1 742, 1 765	SH, CH_2
1 780	cellulose

Bota et al. (2015) described combining the measurements of the crude Java citronella oil spectrum in the NIR wavelength region of 2 200 nm with a GC-MS analysis could build the predictors of the pure citronella oil content from distinguishing it with the adulterants. However, the results of this study showed that the difference in the rhodinol concentration in the citronella oil can be seen from the absorbance spectrum value in the NIR wavelength region of 1 620 nm. The distinct wavelength point was due to the differences in the main constituent in the citronella oil samples. The rhodinol product obtained from fractional distillation is rich in two components, citronellol and geraniol, according to Eden et al. (2018). Meanwhile, the main component of crude Java citronella oil is citronellal, citronellol, and geraniol.

The study written by Pfeffer et al. (2001) mentioned the principle of NIR spectroscopy is applicable for the characterisation of various essential oils by applying an identical prediction quality. This study developed the prediction model using data referenced from the rhodinol content data and band assignment spectrum. The correlation between the NIR spectroscopy band spectrum changes the obtained prediction model that is sensitive to the citronella oil. Therefore, the reference data determined the success in predicting the value of the rhodinol compound in the citronella oil using NIR spectroscopy.

Calibration and prediction model. A calibration model can be created by first building a calibration database. Commonly, a reliable calibration model is necessary for quantitative and qualitative analysis purposes using the NIR spectroscopy application. This model is combined with chemometric techniques, which is a multivariate data analysis using the partial least square (PLS) regression method. PLS is a quantitative analysis method widely used in developing ideal qualities for linear analysis (Iqbal et al. 2019). It also reduces the dimensions of the data

Table 2. Rhodinol content in the citronella oils (in %)

Process	Range	Mean	SD
Calibration	11.07–95.00	56.60	25.00
Validation	10.75–92.93	54.22	23.86

SD – standard deviation

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Table 3. Calibration and validation of the near-infrared spectroscopy (NIR) data process using the partial least square (PLS) regression

Data process	Factors	Calibration			Validation		Consistency (%)
		r	SEC	SEP	RPD	*CV* (%)	
			(%)				
No pre-treatment							
	F4	0.99	2.78	2.88	9.23	16.81	96.53
Pre-treatment							
SGs	F4	0.99	3.18	3.32	8.06	19.25	95.78
DT	F4	0.84	3.13	3.28	8.19	22.63	95.43

SGs – Savitzky-Golay smoothing technique; DT – De-trending; *r* – correlation coefficient; SEC – standard error of calibration set; SEP – standard error of prediction set; RPD – ratio of performance to deviation; *CV* – coefficient of variation

to obtain relevant factors to predict and interpret information and provides a better method of calibration than polymerase chain reaction (PCR).

The NIR transfectant spectrum data are used to develop the rhodinol levels prediction model with the GC-MS results of the chemical content information. The mathematical model of the calibration database is used to predict the chemical components of a constituent (Windawati et al. 2019).

To perform the calibration and model validation, the pre-treatment and non-pre-treatment (original spectrum) data are applied to refine the data and reduce the complexity of the overlapping data spectrum. Thus, the gradations of the spectrum graphics will be readily observed clearly with each other. The NIR data treatment processing and PLS regression method for calibrating and validating the rhodinol content prediction model are shown in Table 3.

Table 3 shows the results of the calibration and validation using the PLS regression. The RPD value of 9.23 indicated that the model performed well. The RPD value is inversely proportional to the *CV* score. Therefore, the bigger the RPD, the smaller the *CV* score (Bec et al. 2020). The chemical content prediction accuracy was determined by the correlation coefficient ($r > 0.9$), low predictive standard error, low coefficient of variation (*CV*), high RPD (> 2), and in the range of showing 80% to 110% consistency (Windawati et al. 2019; Novianty et al. 2020). The original spectrum and PLS-R calibration gave the best predictions for the rhodinol content ($r = 0.99$, SEC = 2.78%, $CV = 16.81\%$, RPD = 9.23, and consistency 96.53%). The Savitzky-Golay smoothing (SGs) first derivative data processing methods and De-trending (DT) were used for the data prediction, even though their accuracies were lower than the original spectrum.

The finest model to predict the rhodinol content was $y = 0.9874x + 15.6439$, left out the application of the pre-treatment data ($r = 0.99$, SEC = 2.78%, SEP = 2.88%, $CV = 16.81\%$, RPD = 9.23). Figure 2 shows the finest calibration model result plot for the

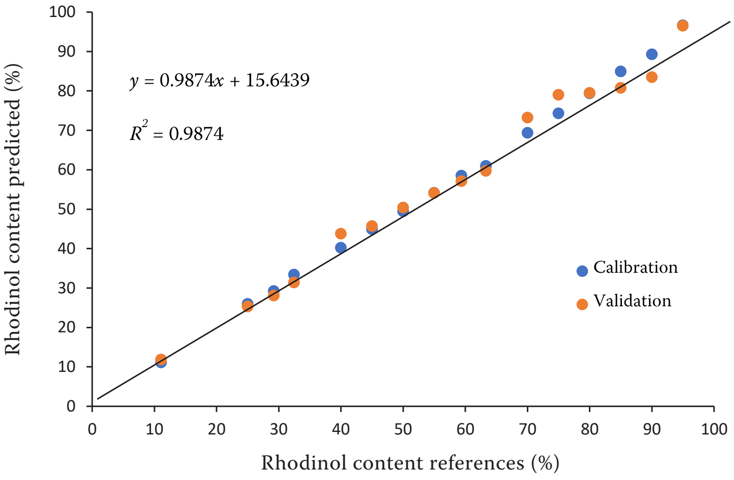

Figure 2. Rhodinol content references (%) and rhodinol content prediction (%) plot

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NIR spectrum of the rhodinol content references and the rhodinol prediction in the citronella oil. NIR spectroscopy can be used to analyse the components in the citronella oil fraction. These results are in agreement with (Iqbal et al. 2019; Windawati et al. 2019; Novianty et al. 2020), which confirm that the PLS method can improve the accuracy of the NIR spectroscopy analysis to predict the various chemical compounds in materials, such as the main components in oil. This study indicated that the model to predict the rhodinol content using the PLS method could be reliable in the initial stage of the spectral smart sensor development. According to Pfeffer et al. (2001), developed NIR spectroscopy calibrated statistics can be used not only for rapid quality control purposes, but also to monitor the enrichment of the valuable essential oil components during fractionation distillation.

CONCLUSION

This study reported the utilisation of NIR spectroscopy for developing a calibration model to predict the rhodinol content in citronella oil. The NIR spectrum at a wavelength peak of 1 620 nm estimated the rhodinol content in the citronella oil. Moreover, the absorption peak at 1 685 nm attracted more attention because of the geraniol and citronellol content as the bonds of aromatic compounds. The optimum calibration model for predicting the rhodinol content was successfully acquired using a four-factor PLS method. At the same time, the absorbance of the spectral data was analysed without the pre-treatment information. To predict the rhodinol content, it was represented by a mathematical model $y = 0.9874x + 15.6439$ with SEC = 2.78%, SEP = 2.88%, $CV = 16.81\%$, RPD = 9.23, $r = 0.99$. The spectrum band assignment of the rhodinol content prediction is acceptable and robustly improved the accuracy of the PLS model. Finally, this research shows that NIR spectroscopy and PLS models were possible to use for the initial stage in developing a spectral smart sensor system to determine the rhodinol content of citronella oils.

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REFERENCES

Agustian E., Sulaswatty A., Tasrif, Laksmono J.A., Adilina I.B. (2007): Isolation of citronellal from citronella oil using bench scale fractionation unit. Journal of Agroindustrial Technology, 17: 49–53.

Almeida R.N., Soares R.P., Cassel E. (2018): Fractionation process of essential oils by batch distillation. Brazilian Journal of Chemical Engineering, 35: 1129–1140.

Avizienis A. (2019): Essential Oils. San Diego, Thunder Bay Press.

Bec K.B., Grabska J., Huck C.W. (2020): Near-infrared spectroscopy in bio-applications. Molecules, 25: 2948.

Beneti S.C., Rosset E., Corazza M.L., Frizzo C.D., Luccio M.D., Oliveira J.V. (2011): Fractionation of citronella (*Cymbopogon winterianus*) essential oil and concentrated orange oil phase by batch vacuum distillation. Journal of Food Engineering, 102: 348–354.

Bota W., Martosupono M., Rondonuwu F.S. (2015): Characterization of citronella oil products using near infrared spectroscopy (NIRs). Journal Faculty of Engineering Muhammadiyah University of Jakarta, 2: 1–7.

Cen H., He Y. (2007): Theory and application of near infrared reflectance spectroscopy in determination of food quality. Trends in Food Science and Technology, 18: 72–83.

Chandra S., Krishanthi M., Octavian P.J., Postolache A. (2019): Smart Sensors, Measurement and Instrumentation: Modern Sensing Technologies. Sidney, Springer.

Eden W.T., Alighiri D., Cahyono E., Supardi K.I., Wijayati N. (2018): Fractionation of Java citronella oil and citronellal purification by batch vacuum fractional distillation. IOP Conference Series: Materials Science and Engineering, 349: 012067.

Hutchins D.A. (1997): Data Acquisition for Sensor Systems. London, Springer Science + Business Media.

Iqbal Z., Herodian S., Widodo S. (2019): Development of partial least square (PLS) prediction model to measure the ripeness of oil palm fresh fruit bunch (FFB) by using NIR Spectroscopy. IOP Conference Series: Earth and Environmental Science, 347: 012079.

Jumaah A.M.S., Xue J. (2019): Developing intelligent machines with smart sensors for a smart factory. International Journal of Scientific and Research Publications, 9: 221–230.

Kurniawan F., Budiastra I.W., Sutrisno, Widyotomo S. (2019): Classification of arabica Java coffee beans based on their origin using nir spectroscopy. IOP Conference Series: Earth and Environmental Science, 309: 012006.

Novianty I., Seminar K.B., Irzaman, Budiastra I.W. (2020): Improving the accuracy of near-infrared (NIR) spectroscopy method to predict the oil content of oil palm fresh fruits. IOP Conference Series: Earth and Environmental Science, 460: 012004.

https://doi.org/10.17221/87/2021-RAE

Pfeffer S., Schulz H., Kruger H. (2001): Potential of near infrared spectroscopy (NIRS) for rapid quality evaluation of essential oils. ISEO Journal, 32: 93–94.

Popescu D., Gharbi A., Stefanoiu D., Borne P. (2017): Process Control Design for Industrial Applications. Hoboken, John Wiley & Sons, Inc.

Purwanto Y.A., Zainal P.W., Ahmad U., Sutrisno M., Makino Y., Oshita S., Kawagoe Y., Kuroki S. (2013): Non destructive prediction of pH in mango fruit cv. Gedong Gincu using NIR spectroscopy. International Journal of Engineering and Technology, 13: 70–73.

Rondonuwu F.S., Setiawan A. (2020): Determination of glucose content with a concentration within the physiological range by FT-NIR spectroscopy in a trans-reflectance mode. AIP Conference Proceedings, 2237: 020013.

Setyaningsih D., Roselly F., Muna N. (2020): Formulation of essential oils as mosquito repellent. Journal of Tropical Pharmacy and Chemistry, 5: 71–79.

Singh C.B., Jayas D.S. (2012): 5 - Optical sensors and online spectroscopy for automated quality and safety inspection of food products. Robotics and Automation in the Food Industry: Current and Future Technologies, 2013: 111–129.

Sulaswatty A., Rusli M.S., Abimanyu H., Tursiloadi S. (2019): Quo Vadis Citronella Oil and Its Derivative Products. Jakarta, LIPI Press.

Tisserand R., Young R. (2014): Essential Oil Composition. In: Williamson E.M. (ed.): Essential Oil Safety. London, Elsevier: 5–22.

Tsimogiannis D., Oreopoulou V. (2018): A kinetic study of essential oil components distillation for the recovery of carvacrol rich fractions. Journal of Applied Research on Medicinal and Aromatic Plants, 9: 117–123.

Verma R.S., Verma S.K., Tandon S., Padalia R.C., Darokar M.P. (2020): Chemical composition and antimicrobial activity of Java citronella (*Cymbopogon winterianus* Jowitt ex Bor) essential oil extracted by different methods. Journal of Essential Oil Research, 32: 449–455.

Wany A., Kumar A., Nallapeta S., Jha S., Nigam V.K., Pandey D.M. (2014): Extraction and characterization of essential oil components based on geraniol and citronellol from Java citronella (*Cymbopogon winterianus* Jowitt). Plant Growth Regulation, 73: 133–145.

Windawati V., Purwanto Y.A., Budiastra I.W., Widodo S., Kuroki S. (2019): Prediction of chemical content in patchouli oil (*Pogostemon cablin* Benth) by portable NIR spectroscopy. IOP Conference Series: Materials Science and Engineering, 557: 012087.

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