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Discrimination of cassava, taro, and wheat flour using near-infrared spectroscopy and chemometrics

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Abstract

There is a difference in the selling price for cassava, taro, and wheat flour, with taro flour having a higher price. It could be a reason for adulterating the taro flour from the other two flours and reducing quality. This study aims to distinguish the three types of flour using the near-infrared (NIR) spectra combined with chemometrics. The NIR spectra of all samples were measured at a wavelength of 1000-2500 nm. The multivariate analysis used was principal component analysis (PCA), and PCA followed with discriminant analysis (DA). The preliminary process of the signal using area normalization was carried out before the multivariate analysis. The PCA results showed that most of the samples were grouped in their respective groups except for two samples, namely 1 sample of taro flour and 1 sample of cassava flour. Meanwhile, the PCA-DA results using seven main components showed that the three samples were grouped well. DA validation was carried out using the cross-validation method, showing that the samples could be identified into their respective groups. Therefore, a combination of NIR spectrum and chemometric analysis can be used to differentiate cassava, taro, and wheat flour

1. Introduction

Many flour-based foods products have been produced to meet people's daily needs, such as bread, cakes, noodles, pasta, so forth. One type of flour that has been widely used as a raw material for making cakes is taro flour. Taro flour is obtained from the taro tubers containing high starch, protein, and fiber [1]. The taro tubers can also be used as other food products, such as chips, getuk, and so forth.

Taro production in Indonesia is still not much compared to other commodities that can also be used as flour, such as cassava and wheat. The price of taro flour in the Indonesian market is higher than that of cassava and wheat flour. These price differences can lead to substitution or counterfeiting of one another to obtain high profits. This substitution/counterfeiting will undoubtedly reduce the quality of flour and its processed products. Therefore, an analytical method to identify taro flour from the other two flours needs to be developed.

Spectroscopic-based analytical techniques such as near-infrared spectroscopy (NIR) is commonly used to identify, discriminate, and authenticate raw materials and food products. The NIR spectrum has high complexity because the signal output represents the overall signal from the compounds in the sample. If used directly to distinguish types of samples similar in chemical content, it will not be easy. To facilitate the interpretation, a chemometric method such as principal component analysis is needed. The combination of NIR and chemometric spectroscopy has been reported in various research results such as estimation of water content and total carotene in fresh oil palm fruit bunches [2], prediction of the chemical content of *arumanis* mango during storage [3], classification of alcoholic beverages from the fruit [4], rapid quantification cholesterol in powdered milk [5], adulteration detection in bilberry extract [6], and identification and quantification of adulterated egg paste by turmeric [7]. The two can be combined with a relatively short time, easy sample preparation, non-polluting, and non-destructive [8].

Rachmawati *et al.* [9] have used NIR spectroscopy and chemometrics to identify and authenticate taro flour from sago starch and wheat flour. In this study, we continue to use a combination of NIR spectroscopy and chemometric analysis to identify and differentiate between cassava, taro, and wheat flour. The developed analytical method could be used to identify and differentiate the three types of flour.

2. Methodology

2.1. Instrumentation and materials

In this study, we used NIR spectrophotometer type NIRFlex Solids Petri N-500 (Buchi, Flawil, Switzerland) with a diffuse reflection system, The Unscrambler X version 10.1 (CAMO, Oslo, Norway), and XLSTAT version 2019.4.1 (Addinsoft, New York, United States). The materials used are taro from various regions such as Muntilan (Magelang, Central Java), Cipanas (Cianjur, West Java), Cicurug (Sukabumi, West Java), and Cigombong, Cihideung, Bubulak, Ciapus (Bogor, West Java). Cassava was collected from Bojongsari (Depok, West Java), Central Singkawang (Singkawang, Kalimantan Barat), Muntilan (Magelang, Central Java), and Ciampea, Dramaga, Kemang (Bogor, West Java) as well as five commercial wheat flour purchased from local supermarkets in Bogor (West Java).

2.2. Preparation of flours

The taro tubers obtained are cleaned first from the soil attached to the tubers, washed with water, drained, peeled, rewashed, soaked with water, and sliced about 0.2 cm in size. The taro tuber slices' results are then air-dried at ± 65 °C for 5 hours in the oven. The dried sample was ground and sieved about 100 mesh. A similar treatment was used for the preparation of cassava flour without soaking it in water. For wheat flour, we purchased from several local supermarkets in Bogor, West Java.

2.3. Measurement of NIR spectrum

The near-infrared spectrum for all samples was made by preparing flour in a petri dish with 3/4 cups filled with flour. Measurement of the NIR spectrum was made three times, with each replication measured three times in the near-infrared (1000-2500 nm) with a resolution of 4 cm^{-1} and a pay speed of 32 scans/minute. The NIR absorbance spectrum of the samples was stored as a Microsoft Excel file.

2.4. Chemometrics analysis

Before chemometrics analysis, the NIR spectra were pretreated using area normalization to minimize problems due to baseline shear and increase the coincided spectrum's resolution using The Unscrambler X version 10.1 software (CAMO, Oslo, Norway). The absorbance data from the preprocessed NIR spectrum were then analyzed using XLSTAT version 2019.4.1 software (Addinsoft, New York, United States) to create a three-flour discrimination model used.

3. Results and Discussions

3.1. Near-infrared spectra of the samples

Taro, cassava, and wheat flour showed identical NIR spectral patterns but different in the absorbance intensities (Figure 1). This shows that the three flour have relatively identical chemical components. The difference in the absorbance intensity of the three flour is due to the variation in the growing places for cassava and taro flour and the production process for wheat flour.

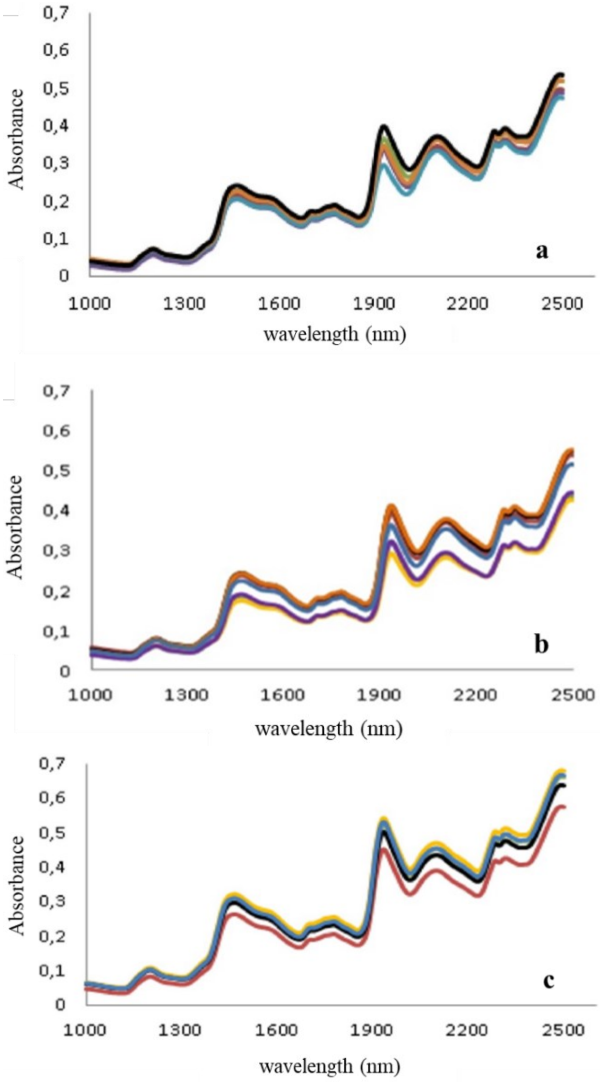

Figure 1. Representative NIR spectra of cassava (a), taro (b), and wheat (c) flour for several locations.

The NIR spectrum of the three flour produces eight absorption bands, as shown in Figure 1. The absorption band at 1450 and 1540 nm indicates OH the first overtone stretching vibrations. The absorption band at 1930 nm is the stretching vibration of OH or HOH deformation. The absorption band at 1960 nm is a representation of the bending vibration combination of OH. The absorption band at 2100 nm indicates the O-H bending vibration or the C-O stretching combination. For the absorption band at 2280 nm and 2322-2330 nm, it is the region of the C-H stretching vibration of CH_2 deformation. The absorption band at 2500 nm indicates C-H stretching vibrations or C-C and C-O stretching vibrations [10]. These absorption bands (Table 1) indicate the presence of starch, which is the main constituent of the three flours used in this study. This is also consistent with the absorption bands reported by Aenugu *et al.* [11]. The absorption bands obtained from the three flour samples' measurement results correspond to the absorption bands of commercially pure starch of various brands and commercial corn flour in the near-infrared [12].

Table 1. Peak absorbance in NIR spectra of samples

Wavelength (nm)	Vibration mode	Structure
1450 and 1540	O-H stretching vibration (*first overtone*)	starch
1930	O-H stretching vibration or HOH deformation	
1960	O-H stretching vibration or O-H bending vibration	
2100	O-H bending vibration or a combination of C-O stretching vibration	
2280	C-H stretching vibration or CH_2 deformation	
2322-2330	C-H stretching vibration or CH_2 deformation	
2500	C-H stretching vibration or C-C and C-O-C stretching vibration	

3.2. Discrimination of cassava, taro, and wheat flour

The NIR spectrum's direct use in distinguishing the three flour cannot be carried out because the different information is only on the absorbance value in certain areas. After all, the signals come from relatively the same components. However, this difference in absorbance value can describe the characteristics of a sample. Information in the form of absorbance values combined with chemometric analysis allows us to distinguish the three samples.

Combining the NIR spectrum and chemometric analysis has been widely used in food quality control and herbal medicine. The chemometric analysis used in this study is a principal component analysis and discriminant analysis. Before the analysis is carried out, the spectrum data is pretreated first. This pretreatment is intended to improve data information, reducing random noise in the spectrum, and avoiding baseline shear. The pretreatment used is normalization, which can reduce unwanted systematic bias in the measurement to better the data.

3.2.1. Principal component analysis

Principal component analysis (PCA) is a data exploration method used to reduce data while at the same time, classifying samples into the same class [13]. This multivariate analysis will reduce the original variable to a new variable called the main component (KU). These principal components are not correlated but store some information from the original variables. Principal component 1 (PC-1) has the largest variance in the data set and followed by principal component 2 (PC-2) [14]. The original data in PCA will be converted into two matrices, namely scores and loading. The score provides sample information while loading focuses on the variable that significantly influences the differences in the sample groups.

The principal component analysis applied to the NIR spectrum of the three types of flour with the data matrix obtained was 1501 columns of absorbance values as variables and 162 sample rows. Figure 2 shows the three flour's PCA score plot, and based on the score plot, cassava, taro, and wheat flour have almost the same characteristics. This is indicated by the distance between class points, which are relatively close together. The closer the distance between each point, the similarity level of the sample was high. This similarity occurs because the chemical composition of the three is not too different. In the PCA score plot, there are groups of taro flour originating from Cihideung, Bogor, and cassava flour from Central Singkawang, Singkawang City, which are not grouped into their respective groups. This is because taro and cassava characteristics from the two regions are more like the other groups.

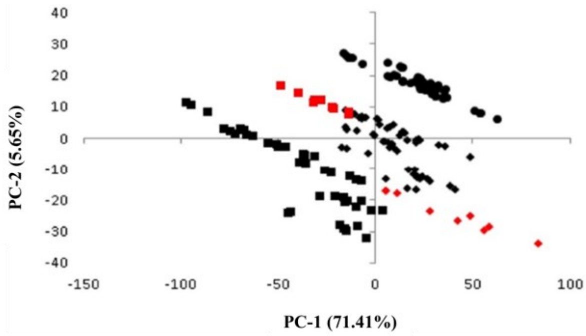

Figure 2. PCA score plot of cassava (■), taro (♦), and wheat (•) flour, taro flour from Cihideung, Bogor (♦), and cassava flour Singkawang Tengah, Singkawang (■).

The resulting PCA score plot was able to explain 87.07% of the total variance (PC-1 = 71.42% and PC-2 = 15.56%). According to Varmuza [15], principal component score plots will show good dimensional data visualization if the total variance of PC-1 and PC-2 is greater than 70%. The PCA result can be stated as good if the small number of main component variances could describe the data's total variance. Therefore, the PCA sample's grouping pattern can distinguish cassava, taro, and wheat flour, even though the three are still close together.

3.2.2. Discriminant analysis

Discriminant analysis (AD) is one of the supervised pattern recognition methods commonly used to discriminate two or more observations using a set of independent variables to find linear combinations of variables between observations [14]. To construct a discrimination model, AD will calculate the centroid for each observation, expressed as a linear combination of the independent variables. The sample will be classified into one of two observation groups depending on the centroid score's value. The model's predictive ability is evaluated by cross-validation by dividing the sample into samples to create a discriminant analysis model and then the rest as samples included in the model. If the sample is included in its class, the developed discriminant model has good accuracy.

Table 2. Cross-validation of discriminant analysis for discrimination of cassava, taro, and wheat flour

Initial group	Prediction by DA			Total	% correct
	Wheat	Cassava	Taro		
Cassava	0	13	0	13	100%
Taro	0	0	16	16	100%
Wheat	9	0	0	9	100%
Total	9	13	16	38	100%

Discriminant analysis was carried out using seven PC obtained from the PCA and showed two values of the discriminant function (DF), which were DF-1 with a diversity of 94.67% and DF-2 with a diversity of 5.33% so that this analysis was able to explain the diversity of data by 100%. Based on these results, the three flour samples can be separated into their respective groups (Figure 3a). Validation of a model is a step in testing the success of placing data in a group. The total sample measurements for cassava flour, taro, and flour were 162 samples. Of the total measurements, 54 samples were randomly selected to be observed. The modeling was carried out on 38 samples (13 cassavas, 16 taros, and nine flours), and 16 samples (5 cassavas, nine taros, and two flours) were used for model validation. Figure 4 shows that all samples can be separated into their respective groups. The results of cross-validation on model testing showed that as many as 100% of the samples were identified as belonging to their respective groups (Table 2). These results indicate that the prediction accuracy of the discrimination models of cassava, taro, and flour is good. Therefore, combining the NIR spectrum with discriminant analysis using 7 PC values can discriminate between cassava, taro, and wheat flour.

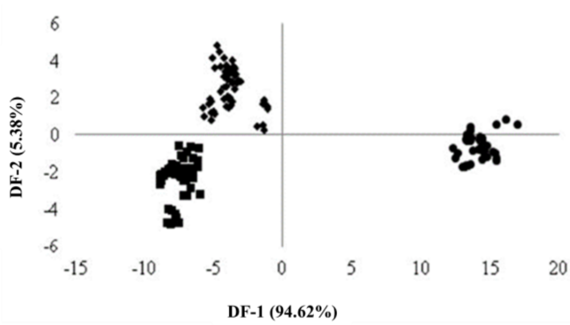

Figure 3. DA plot of cassava (■), taro (♦), and wheat (•) flour.

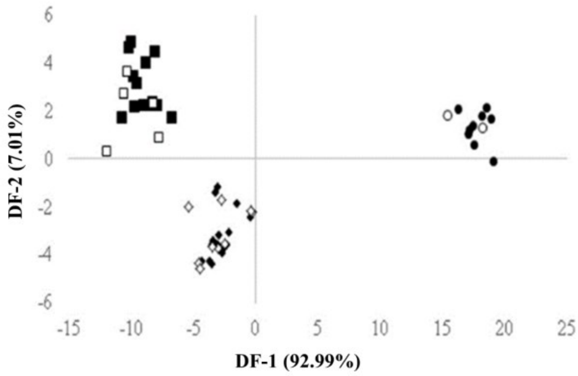

Figure 4. DA validation plot of cassava (■), validation sample of cassava (□), taro (♦), validation sample of taro (◊), wheat (•), and validation sample of wheat (○) flour.

4. Conclusions

A combination of NIR spectra and chemometrics have been developed to differentiate cassava, taro, and wheat flour. The three flour can be adequately distinguished using principal component analysis followed by discriminant analysis. The obtained model provides an adequate level of accuracy in distinguishing the three flour samples using the cross-validation method.

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