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Non Destructive Measurement of Catechin Content in Gambir (*Uncaria gambir Roxb.*) Using NIR Spectroscopy

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Abstract

Gambir is one of Indonesian export commodities. Catechin content is main determinant of gambir quality. In traditional market, determining of the gambir catechin content is conductedqualitatively based onexperience ofthe assessor which led to subjectivemeasurement. Chemical method to determine catechin content of gambir quantitatively. Thismethodis notefficient since it requires expensivechemical reagents,takes a long time, and destructive. Near infrared (NIR) spectroscopy is one of the non destructive techniques which can inform gambir quality. The objective of this study was to demonstrate of NIR spectroscopy to measure of catechin content in gambir. Partial Least Square (PLS) method by combination pre-treatment between normalization between 0 and 1 (n01), and first derivative Savitzky-Golay 9 points (dg1) was used to develop calibration model. Value of consistency and V-Set PRESS was used to determine the optimum number of PLS factors. The result showed that calibration model with 6 PLS factors was the best predictive models for catechin content since it provided a high accuracy as well as precise models. Model for catechin content showed the bias value = 0.10 %, SEC = 3.56 %, SEP = 3.27 %, correlation coefficient (r) = 0.95, CV = 4.86 %, and RPD = 3.60. The result demonstrated that NIR spectroscopy might be applied to measure catechin content in gambir accurately.

Keywords: gambir, catechin, NIR spectroscopy, non destructive measurement, PLS.

Introduction

Gambir is an extracted product from the leaves andyoungtwigsof gambir(*Uncaria gambier*Roxb.) plant. Gambir is one of the Indonesian export commodities. It contributes to around 80% of the gambir trading in the world (Gumbira-Sa'id, 2009).Some studies related the presence of catechin in gambir revealed that it is usually the most abundant bioactive compound (Taniguchi et al., 2007a; Apea-Bah et al., 2009; Anggraini et al., 2011). It is potential as araw material in various industries, particularly pharmaceutical andcosmetic industries. Catechin content in gambir is used as one of the quality parameters of gambir in accordance with the Indonesia gambir trading standard, SNI01-3391-2000. Traditionally, determining of the gambir catechin content is conducted qualitatively based on experience of the assessor which led to subjective measurement. Meanwhile, there is chemical method to determine catechin content of gambir quantitatively. However, this method is not efficient since it requires expensive chemical reagents and takes a long time. In addition, this method

is destructive. Therefore, an efficient and non-destructive method is needed to determine gambir catechin content.

In recent years,Near Infra Red (NIR) spectroscopy isone of non-destructive techniques for measuring qualityparameters of different commodities. NIR spectroscopy is particularly sensitive to the presence of molecules containing the C-H,O-H, and N-H groups (Abu-Khalaf, 2002). NIR spectroscopy has decisive advantages compared to traditional methods, whereby it analyse sample rapidly (a few seconds per sample) and no need sample preparation (Guggenbitchler et al., 2006; Pissard et al., 2012; Saleh, 2012). In addition, it is a chemical-free (limited to the reagents required for reference analyses) and no waste is produced (Yan et al., 2009; Pissard et al., 2012) and can be carried out on-line (Saleh, 2012) and can be applied quickly, accurately and non destructive which has grown rapidly and can replacethe old chemical analysis (Chen *et al.*, 2009). NIR spectroscopy has been applied to determine bioactive compound such as carotenoids, glucosinolates, phenolics, fatty acids (McGoverin et al., 2010).The objective of this study was to demonstrate of NIR spectroscopy to measure of catechin content in gambir.

Materials and methods

SamplePreparation

The 162 raw gambir used in this study were randomly divided into two groups of samples: the first group was used to develop the calibration models (108 samples) and the other for predicting quality and model validation purposes (54 samples). The samples wereobtainedfromSigunturvillage, Koto 11Tarusan subdistrict, Pesisir Selatan District, West Sumatera, Indonesia.

Methods

Chemical Analysis

Determining catechin content of gambir was conductedby referring to Indonesia National standard namely was SNI 01-3391-2000. Instrument of SpectrophotometerU-2010, Hitachi was used to measure gambircatechincontent.

Spectra acquisition

This study used instrument Buchi NIRFlex N-500 Fiber optics solids which had resolution of 4 cm^{-1} and 8 scans, to collect sample spectra. The instrument was operated using software NIRWare 1.2 (Büchi Labortechnik AG, Flawil, Switzerland). Spectra data was collected from 10000 to4000cm^{-1} (1000 to 2500 nm) with interval of 4 cm^{-1}. Measurements of each sample were conducted three times at different positions in a room temperature of 25 ^{0}C. Spectrum which was produced by each samples, was averaged prior to build a calibration model.

Chemometrics

Chemometricsanalysis in this study used NIRCal5.2(Büchi LabortechnikAG, Flawil, Switzerland) byusing Partial LeastSquare(PLS) algorithm. This study did not only use the originalspectra(original), but also combination of normalization between 0 and 1 (n01)withfirst derivative Savitzky-Golay 9 points (dg1). Selection the number ofoptimumPLS factors was done basedon value ofconsistency(80-110%) andas smallest as

possible value of PredictedResidualSumSquareError(PRESS) of thevalidationset(V-set-PRESS). The number ofPLSfactorswas 1to 15.

Data analysis

Statisticalparametersusedtoevaluatethe resulted model were bias, standard errorofcalibrationset (SEC), standard errorofvalidationset (SEP), coefficient correlation (r),ccoefficientofvariation(CV) and ratio of prediction to deviation (RPD).

$$\text{Bias (\%)} = \frac{1}{N}\sum (x_n - y_n)$$

$$\text{SEC (\%)} = \sqrt{\frac{1}{N-1}\sum (x_n - y_n)^2}$$

$$\text{SEP (\%)} = \sqrt{\frac{1}{N-1}\sum (x_n - y_n - \text{Bias})^2}$$

$$r = \frac{\sum (x_n - \bar{x}_n)(y_n - \bar{y}_n)}{\sqrt{\sum (x_n - \bar{x}_n)^2 \sum (y_n - \bar{y}_n)^2}}$$

$$\text{CV (\%)} = \frac{\text{SEP}}{\bar{x}} \text{ x } 100$$

$$\text{RPD} = \frac{\text{SD}}{\text{SEP}}$$

$$\text{PRESS} = \sum (x_n - y_n)^2$$

$$\text{Consistency (\%)} = \frac{\text{SEC}}{\text{SEP}} \text{x } 100$$

WhereNisthe number of samples; x_n is value of reference catechin; y_n isthe value ofNIRprediction catechin.

Results and discussion

Data of Gambir Catechin and Spectra

Table1 shows the statistics summary for all samples catechin content in the calibration set and validation set. Standard deviation between the calibration set and validation set showed insignificant differences. Therefore, the variance of data in the set calibration and validation set are equal.

Table 1. Statistical of value of gambir catechincontent (% w/w)

Sample Set	Number of sample	Minimum	Maximum	Average	Standard deviation
Calibration Set	108	40.71	84.79	65.65	11.88
Validation Set	54	41.54	83.91	67.21	11.76

The original reflectance spectra of some gambir samples reveal some valleys in the region of 1000-2500 nm (Figure 1). These valleys exist because molecule structures of catechin contain has many hydric groups. However, as NIR spectra in the region of 2222.22

– 2500 nm showed high noise, it was eliminated for analysis. Therefore spectra in the region 1000 - 2222.22 nm were used to develop the model.

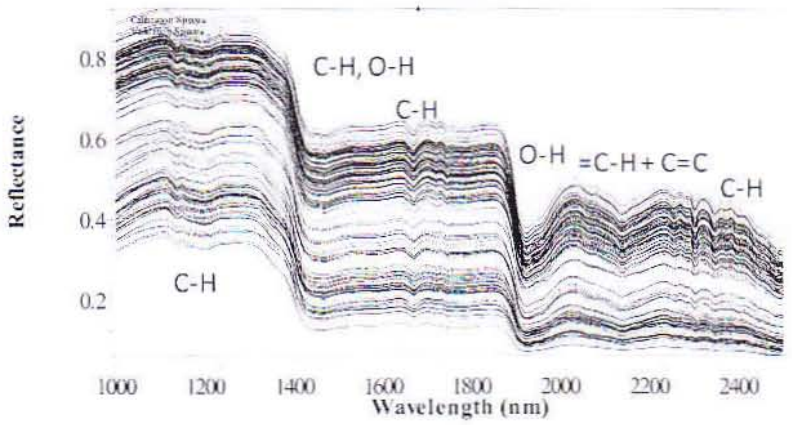

Figure 1. The original reflectance spectra of some gambir samples

The influence of differentpre-processing methodsand number offactorsto accuracy of PLS Model

PLS is an effective dimension reduction method in near-infrared spectroscopy analysis. The spectrum information of sample components are showed the latent variables. Furthermore, the selection of number of PLS factors was very essential to reduce noise and use of spectral information fully (Chen et al., 2013).Figure2shows influence of the number of PLS factors to consistency and V-set PRESS value. If spectra pre-processing treatment was not applied, a minimum of validation error was observed in the 15 PLS factors.It provided consistency value 98.69 % and V-set PRESS value 948.51. Optimal number of factor obtained while using n01 in combination with dg1 pre-treatment method was 6. This number of factor provided consistency 108.96 % value and V-set PRESS value 566.226.It was found that if spectra pre-processing method was applied, the number of PLS-factors could be reduced.It could be explained that spectra pre-processing method of the derivative could overcome the overlapping spectra and throw other components except catechin which left factors that inform about catechin only.

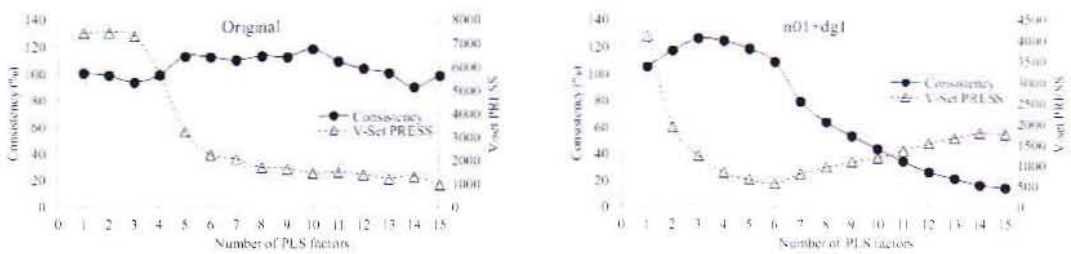

Figure 2. The influence ofthe number ofPLSfactorstoconsistency and V-Set-PRESS

Performance of parameters of the model using different pre-processing methods to predict catechin content of gambir are given in Table2. Spectra pre-processing method ofn01 in combination with dg1 increased correlation coefficient between catechin references and predicted from 0.94 to 0.95 whilst SEP value decreased from 4.14 % to 3.27 % and number

of PLS factors decreased from 15 to 6. It could be concluded that spectra pre-processing methodand number of factor had effects on the prediction performance of model PLS.

Table 2. The result ofcalibrationandvalidation ofgambircatechin content

Pre-processing	PLS Factor	Consistency (%)	Calibration Set		Validation Set				
			SEC (%)	r	SEP (%)	r	CV (%)	Bias (%)	RPD
Original	15	98.70	4.09	0.94	4.14	0.94	6.16	-0.86	2.84
n01, dg1	6	108.96	3.56	0.95	3.27	0.96	4.86	0.10	3.60

Prediction of Catechin Content in Gambir

Figure 3 shows calibration model forpredicting catechin content. It was y = 0.91 x + 5.90.The model provided low value of SEC (3.56 %) and SEP (3.27 %). In addition, the SEP value was not greater than two times of SEC prevented over fitting (Hruschka, 1990). The values of SEC and SEP which were generated by the model indicated that the model has high precision. Bias values closed to zero indicated that the model has high accuracy (Williams and Norris, 1990). It means that the model will be maintained for the prediction of catechin content in gambir. Furthermore, the modelalsoshoweda goodcorrelationbetween thereference catechin content withNIRprediction catechin, as indicated by thehighvalue ofthecorrelationcoefficient(r>0.90) (Williams andNorris, 1990).

The model obtained CVvalue<5%, which indicatedthatthe resulted modelwas appropriate to predict catechin content of gambir in the newdata set. RPD was measurement ability of NIR model topredicta component tefficiently (Williams and Norris, 1990). Based onobtained RPDvalues (3.6),then theresulted modelwas excellenttopredict the gambir catechin content.RPD value above 3.0 is very good for predicting (Mouazen etal., 2005).It could be concluded that model withapplication of pre-processing method of n01 in combination with dg1 showed higher accuracyandprecisionthan the originalmodel. It indicated that pre-processing methodwas important prior to modelingas itwould improve the accuracy and precision of calibration model (Schulz etal., 1999; Udelhovenetal., 2002; and Ouyangetal., 2012).

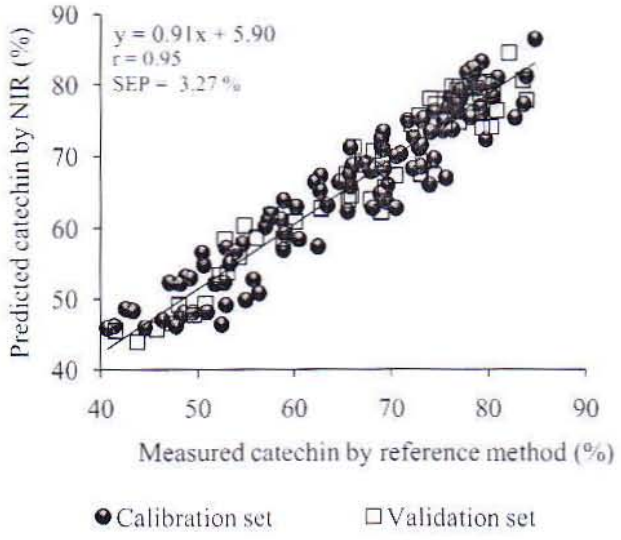

Figure 3. Scatter plot of measured versus predicted catechin content using n01 in combination with dg1 and 6 PLSfactors

Conclusion

The prediction modelwas developed using thePLSalgorithm to explain relationship between NIR spectra data and catechin content.The model hada lowSECandSEP, a high rand aslightly difference between SEC and SEP values. These result were achieved when n01 in combination with dg1pre-processing method and 6 PLS factors was applied.This study demonstrated capability of NIR spectroscopy as a method which could replace traditional as well as chemical method to determine catechin content of gambir. It is also showed that there is possibility to develop non-destructive method to measure gambir catechin content.

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