Measurement of quality properties of honey by reflectance spectra

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Introduction

Honey is the nectar and saccharine exudations of plants that have been gathered, modified and stored in the comb by honeybees. It is the only sweetening material that can be stored and used as it is produced in nature.[1] Honey consists essentially of different sugars, predominantly glucose and fructose. Besides these, honey also contains protein, ash, amino acids, enzymes, organic acids, mineral substances, pollen and oligosaccharides.[2]

There has been a considerable lack of information concerning nutritional aspects of honey. Consumer groups are demanding an accurate description of the nutrient content and its quality. The composition of honey depends upon the floral sources, the composition of the nectar, the climate and the differences in processing.[3] The quality of honey is determined by the composition of sugar, moisture, ash, protein, hydroxymethyl furfural (HMF), proline, PH, diastase activity etc.[4]

The objectives of this study were to develop models to predict quality properties of Korean honeys by visible and near infared (NIR) spectroscopic techniques.

Materials and methods

Two kinds of honey from acacia and polyfloral sources were tested in this study. The honeys were harvested in the spring of 2000 and stored in the storage facility at 20°C during experiments. A total of 394 samples of honey were collected from the Korean Bee Product's Research Institute, Suwon, Korea. Reflectance spectra, moisture content, ash, invert sugar, sucrose, fructose/glucose (F/G) ratio, hydroxymethyl furfural (HMF) and carbon isotope (C12/C13) ratio of honey were measured. Honey samples were left at room temperature when their measurements were made. Temperatures of honey samples were not measured or controlled during measurements.

A digital refractormeter (Atago Co, Japan) was used to measure the moisture content of honey. Ash in honey was determined by the AOAC method.[5] Invert sugar, sucrose, and HMF in honey were measured by high performance liquid chromatography (HPLC) following the Korean Food Code methods.[6] Isotope Mass (Integra-CN, Europa, UK) was used to measure C12/C13 ratio of honey and Pee Dee Belemnite (PDB) was used as the reference.

An NIR spectrophotometer, equipped with a single-beam scanning monochromator (NIRSystems, Model 6500, USA) and a horizontal set-up module, was used to collect reflectance data from the honey. The reflectance spectra were measured in wavelength ranges of 400–2,498 nm at 2 nm intervals. Thirty-two repetitive scans were averaged, transformed to log(1/Reflectance) and were then stored in a microcomputer file, forming one spectrum per measurement.

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Honey samples were divided into a calibration set and a validation set. Samples were ranked by values of invert sugar and each set was selected by increasing rank, evenly. Half the total samples were selected for the calibration set and the other 50% were reserved for the validation set. The calibration set was used during model development and the validation set was used to predict quality properties from unknown spectra.

The method of partial least square (PLS) analysis was used to determine the quality properties of honeys. A unique set of PLS loading vectors (factors) was developed. Multiplicative scatter correction (MSC) pre-treatment was applied to all spectra to minimise sample-to-sample light scatter differences. A commercial software package, the Unscrambler (CAMO ASA, Norway), was used to perform the PLS analyses. For each constituent, up to 20 factors were examined. Cross-validation was performed during model development, where calibration samples were removed, one at a time, from the calibration set. The standard error of calibration (*SEC*) was considered to determine the optimal number of factors during calibration. On completion of the calibration, the model was used to predict quality properties of honey from the validation set. Model performance was reported as the correlation coefficient (r), the standard error of prediction (*SEP*) and the average difference between measured and predicted values (bias).

Results and discussion

The minimum, maximum and average values of quality properties of the tested honey are listed in Table 1. The average moisture content of the honey was 19.9% with the range from 17.0 to 27.3%. Moisture content is an important constituent to determine the quality of honey, because it bears direct relation to undesired fermentation. About 90% of tested samples had less than 21.0% moisture content. The ash in the honey ranged from 0.05 to 0.22% with average value of 0.12%. All samples satisfied the Food Code requirements for ash content.

The sugar content is the most important constituents for honey quality. The average invert sugar in honey was 68.4% with the range from 55.7 to 77.3%. About 91% of samples exceeded 65.0% of invert sugar. The average sucrose content of the honey was 5.7% with a wide range from 2.2 to 15.4%. The Food Code requirement for sucrose is less than 7.0%, and 92% of samples were less than limit. The F/G ratio ranged from 1.04 to 2.04 with average value of 1.27.

The average HMF in honeys was 14.4 mg kg^{-1} with the range from 10.0 to 24.9 mg kg^{-1}. The most samples (99%) met the requirement of the honey standards regarding HMF content. The carbon isotope (C12/C13) ratio of honey showed some indication of quality of grading. The C12/C13 ratio

Table 1. Quality properties of honey tested.

	N	Average	Maximum	Minimum
Moisture (%)	394	19.9	27.3	17.0
Ash (%)	393	0.121	0.22	0.05
Invert sugar (%)	394	68.4	77.3	55.7
Sucrose (%)	394	5.7	15.4	2.2
F/G ratio	394	1.27	2.04	1.04
HMF (mg kg^{-1})	208	14.4	24.9	10.0
C12/C13 ratio	359	–19.1	–11.2	–28.3

Table 2. Results of PLS Calibration for honey.

	Wavelengths (nm)	Factor	Correlation	SEC
Moisture (%)	1100 ~ 2200	5	0.985	0.297
Ash (%)	1400 ~ 1800	11	0.873	0.802
Invert sugar (%)	1100 ~ 1300, 1600 ~ 1800	6	0.959	0.794
Sucrose (%)	1100 ~ 1300, 1600 ~ 1800	7	0.966	0.440
F/G ratio	1100 ~ 1300	8	0.988	0.033
HMF (mg kg^{-1})	1100 ~ 1300	8	0.802	2.420
C12/C13 ratio	1100 ~ 1300, 1400 ~ 1800, 1900 ~ 2200	12	0.968	0.092

Table 3. Results of PLS Validation for honey.

	Correlation	SEP	Bias
Moisture (%)	0.973	0.390	0.057
Ash (%)	0.900	0.012	0.000792
Invert sugar (%)	0.942	0.862	0.022
Sucrose (%)	0.952	0.456	–0.035
F/G ratio	0.967	0.042	0.000619
HMF (mg kg^{-1})	0.628	3.320	0.961
C12/C13 Ratio	0.948	1.067	–0.036

ranged from –28.3 to –11.2 with an average value of –19.1. It was found that only 19% of samples were less than –23.0 of C12/C13 ratio.

The PLS analyses showed good correlation between reflectance spectra and quality properties of the honey. As shown in Tables 2 and 3, the PLS model using raw spectra without pre-processing

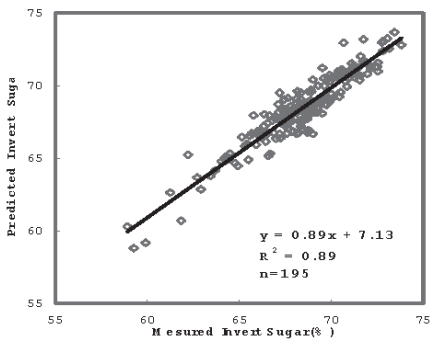

Figure 1. Comparison of actual and predicted values of invert sugar of honey.

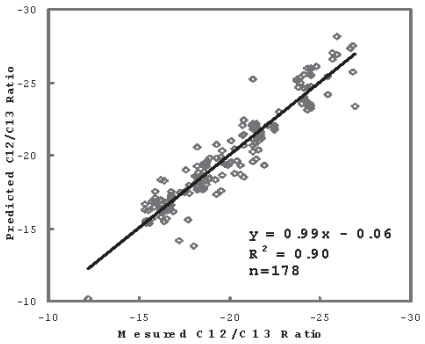

Figure 2. Comparison of actual and predicted values of C12/C13 ratio of honey.

showed the best results in the NIR ranges, but some constituents used many factors. It means that models may include systematic noise to predict the constituents from unknown honey samples. The PLS model for moisture content showed the best performance by using five factors. The moisture content model had a correlation coefficient of 0.973 and an *SEP* of 0.390%. The PLS model for invert sugar had a correlation of determination (R^2) of 0.89 and an *SEP* of 0.862%, as shown in Figure 1. The PLS model for C12/C13 ratio had a coefficient of determination (R^2) of 0.90 and an *SEP* of 1.067, as shown in Figure 2.

The PLS model, using raw reflectance spectra, showed good performance to predict moisture content, ash, invert sugar, sucrose, F/G ratio and C12/C13 ratio of honey in the wavelength range of 1100–2200 nm. However, the PLS analysis was not good enough to predict the hydroxymethyl furfural (HMF) content of the honey. The HMF model had a correlation coefficient of 0.628 and an *SEP* of 3.32 mg kg^{-1}, as shown in Table3.

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