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Evaluation of chemical components and properties of the jujube fruit using near infrared spectroscopy and chemometrics

Ying Guo [a], Yongnian Ni [a,b,*], Serge Kokot [c]

[a] College of Chemistry, Nanchang University, Nanchang 330031, China
[b] State Key Laboratory of Food Science and Technology, Nanchang University, Nanchang 330047, China
[c] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, QLD University of Technology, Brisbane 4001, Australia

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ABSTRACT

Near-infrared spectroscopy (NIRS) calibrations were developed for the discrimination of spectra of the jujube (*Zizyphus jujuba Mill.*) fruit samples from four geographical regions. Prediction models were developed for the quantitative prediction of the contents of jujube fruit, i.e., total sugar, total acid, total phenolic content, and total antioxidant activity. Four pattern recognition methods, principal component analysis (PCA), linear discriminant analysis (LDA), least squares-support vector machines (LS-SVM), and back propagation-artificial neural networks (BP-ANN), were used for the geographical origin classification. Furthermore, three multivariate calibration models based on the standard normal variate (SNV) pretreated NIR spectroscopy, partial least squares (PLS), BP-ANN, and LS-SVM were constructed for quantitative analysis of the four analytes described above. PCA provided a useful qualitative plot of the four types of NIR spectra from the fruit. The LS-SVM model produced best quantitative prediction results. Thus, NIR spectroscopy in conjunction with chemometrics, is a very useful and rapid technique for the discrimination of jujube fruit.

1. Introduction

Jujube (*Zizyphus jujuba Mill.*) fruit belongs to the Rhamnaceae group of cultivars, and is widely grown, e.g., in southwest Europe, India, China and the Middle East [1]. This fruit is nutritious and also has some medicinal properties. It contains nutrients such as carbohydrates, proteins, minerals, and vitamins (especially vitamin C) among many other compounds [2,3]. Also, the jujube fruit is an important Chinese herb, and is claimed to prevent cancer, epilepsy and insomnia among many other illness [4].

The quality of this fruit in the market place is variable because it is a function of the geographical environment, cultivar, cultivation methods, post-harvest processing and storage conditions. For consumers, it is the taste and nutrition parameters, which determine the fruit variety a consumer prefers. In this context, it is the organic acids, sugar, and phenolic compounds, which are the important ingredients that influence the flavor and sensory characteristics of the jujube fruit [2]. In particular, the phenolic compounds are important because of their antioxidant properties and ability to alleviate chronic disease [4].

The conventional methods of analysis for the determination of both the quality attributes and nutritional properties are often based on either colorimetric or chromatographic techniques [5–7]. Generally, these require complex sample preparation, are time consuming, and need expensive instruments. Thus, in China, the commercial quality standards of jujube products are mainly related to their varietal characteristics, such as shape, size, color and freshness. Generally, physical and chemical composition tests include only the soluble solids, moisture content, total sugar, total acid, and vitamin C. The total phenol content and total antioxidant activity are not considered. To improve the quality control procedures for the jujube products quality control, it is necessary for us to find a better and simple way for its control.

Ideally, the quality assessment methods routinely used in food manufacturing, should be non-invasive, non-destructive, rapid and reliable. Near-infrared spectroscopy (NIRS) is a readily available analytical technique, which has been used for analysis of agricultural and food samples [8]. However, the NIR absorption bands are often broad, and lack detailed structure required for analysis. Such spectra can be readily resolved with the use of chemometrics data analysis [9]. Thus, NIRS combined with chemometrics has been used for food authentication and origin as well as for tracing and verification of food products. Haughey et al. [10] detected the adulteration of melamine in soya bean products, and they also combined NIRS with Raman spectroscopy to detect chili powders adulterated with Sudan dye [11]. Other applications of the NIRS in this context include the detection of bioactive components in foods, e.g., evaluation of: post-harvest quality of passion fruit [12], the agave syrups from natural sweeteners [13], soluble solids

* Corresponding author at: College of Chemistry, Nanchang University, Nanchang 330031, China.
E-mail addresses: ynni@ncu.edu.cn (Y. Ni), s.kokot@qut.edu.au (S. Kokot).

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content of citrus fruit [14], total anthocyanins content in flowering tea [15], grain protein content in barley [16], and antioxidant activity of mint [17].

The aims of this study were: to research and develop a non-destructive NIRS method for the analysis of jujube fruit collected from four different geographical origins (Shandong, Xinjiang, Hebei, and Henan provinces); to apply selected, unsupervised and supervised pattern recognitions methods for the classification of different unprocessed jujube samples (chemometrics methods include principal component analysis (PCA), linear discriminant analysis (LDA), least squares-support vector machines (LS-SVM), and artificial neural networks (ANN)), and finally, to apply the linear partial least squares (PLS) as well as the non-linear LS-SVM and BP-ANN methods for the prediction of a selected number of important chemical compounds in the jujube samples.

2. Materials and methods

2.1. Chemicals and reagents

Folin–ciocalteu reagent (FCR, 2.0 mol L^{-1}), 2,2-diphenyl-1-picrylhydrazyl radical (DPPH), gallic acid, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate) diammonium salt (ABTS), 2,4,6-tris (2-pyridyl)-s-triazine (TPTZ), and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were obtained from Sigma-Aldrich (St. Louis, MO, USA); hydrochloric and sulfuric acids, sodium carbonate, phenol and phenolphthalein, ferric chloride ($FeCl_3 \cdot 6H_2O_2$), sodium acetate, and potassium persulfate were purchased from Xilong Chemical Co., Guangzhou, China; sodium hydroxide and methanol were obtained from Damao Chemical Reagent Factory, Tianjin, China; and glucose was purchased from Donghong Chemical Reagent Factory, Guangzhou, China. All reagents and solvents were Analytical Grade or HPLC grade reagents, and fresh, doubly distilled water was used throughout this work.

2.2. Jujube samples and sample preparation

Jujube samples (97; dried under the sun) were collected from four, different, cultivated regions in China: 25 from Shandong (SD), 17 from Hebei (HB), 20 from Henan (HN) and 35 from Xinjiang (XJ). The cores of the jujube fruit were removed manually. The samples were further dried at 40 °C for 48 h, ground to powder using a grinder, and finally passed through a 40-mesh sieve. To eliminate the interference from moisture, the samples were dried at 40 °C for another 24 h before chemical analysis and NIRS sampling.

2.3. Chemical analysis of total sugar

Total sugar (TS) content was determined according to the phenol sulfuric acid method [18]. An accurately weighed, powdered fruit sample (0.08 g) was transferred to a 100 mL conical flask, water (15.0 mL) and hydrochloric acid (1.0 mL) were added, and the sample was hydrolyzed in a thermostatic vibrator at 100 °C for 60 min. Subsequently, the sample was cooled to room temperature and filtered through a #202 filter paper (Whatman Co., Hangzhou, China). The flask was rinsed twice with 30 mL water, and all filtrates were pooled and diluted to volume in a 100 mL volumetric flask for sugar determination. Standard solutions containing 100 mg L^{-1} glucose were prepared. Aliquots of 0, 0.1, 0.2,…,0.9 mL were transferred to ten separate 10 mL glass tubes and diluted to 1.0 mL with water, respectively. Each solution was then mixed with 1.0 mL 5% phenol and 5.0 mL sulfuric acid. The absorbance of each solution was then measured in a 1.0 cm quartz cuvette after standing for 20 min at 30 °C at 487 nm, with a model 8453 spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). A standard glucose absorbance curve was then obtained from such measurements. A 0.1 mL aliquot of each jujube fruit sample solution was then measured as described above for the standard glucose solutions. Results were expressed as grams of glucose equivalent/100 g dry weight (g glucose/100 g DW).

2.4. Chemical analysis of total acid

Analysis of the total acid content (TA) was carried out according to a procedure in the Chinese Pharmacopeia [19]. Jujube fruit powder (1.0 g) was extracted in 15.0 mL water with the use of a magnetic stirrer at 25 ± 0.2 °C for 30 min. The supernatant was separated, and the residue was re-extracted by repeating the above steps. The two filtrates were combined, diluted to 100 mL in a volumetric flask, and titrated with 0.1 mol L^{-1} sodium hydroxide and a phenolphthalein indicator was added. Since 1.0 mL of 0.1 mol L^{-1} NaOH is equivalent to 6.4 mg citric acid, the results were expressed as grams citric acid equivalent/100 g dry weight (g citric acid/100 g DW) of the fruit sample. Titrations were performed in duplicate, and the average of two determinations was used for further interpretation.

2.5. Chemical analysis of the total phenolic content (TPC)

Powdered jujube samples (each 0.2 g) were extracted in an ultrasonic bath with 20 mL 80% methanol for 30 min. The resulting supernatant was separated, and the residue was re-extracted by repeating the above procedure. The extracts were combined, filtered through a filter paper, and transferred to a 50 mL volumetric flask; the sample was then diluted to the mark with 80% methanol and stored at 4 °C.

The Folin–ciocalteu reagent (FCR) was diluted 10-fold with water. Aliquots (1.0 mL each) of jujube extracts or standard solutions of gallic acid (50, 100, 150, 200, and 250 mg mL^{-1}) were added to separate 25 mL tubes [20]; the diluted Folin–ciocalteu reagent (5.0 mL) was added to each tube and mixed thoroughly. The tubes were allowed to stand for 4 min at 25 ± 0.2 °C; 4.0 mL of 7.5% sodium carbonate (w/v) solution was added, and the treated sample was then immediately diluted to 25 mL with water and mixed thoroughly. This mixture was kept for 90 min at 25.0 ± 0.2 °C in the dark and was then transferred to a 1.0 cm quartz cuvette for absorbance measurement at 750 nm against a water blank. The TPC was analyzed in duplicate and expressed as grams gallic acid equivalent/100 g dry weight (g gallic acid/100 g DW) of sample with the use of a gallic acid calibration plot.

2.6. Chemical analysis of total antioxidant activity

The total antioxidant activity (TAA) of the samples is generally determined by three common chemical methods, which are summarized below:

TAA-FRAP assay [21]: The FRAP reagent was prepared with an acetate buffer (300 mM, pH 3.6), 2,4,6-tris (2-pyridyl)-s-triazine (TPTZ, 10 mM in 40 mM HCl), and $FeCl_3$ (20 mM), and the proportions of acetate buffer, TPTZ, and $FeCl_3$ were 10:1:1 (v:v:v). For the determination of the antioxidant activity, the FRAP reagent (4.00 mL) was mixed with 1.0 mL of the sample extract (obtained as described for the TPC method above), and a Trolox standard or control (80% CH_3OH). The reaction was kept at 37 °C for 4 min and then the absorbance of the sample was measured at 593 nm.

Antioxidant activity was expressed in terms of Trolox (0.15 mg mL^{-1}), and 20, 40, 60, 80, and 100 μL aliquots of standard solutions were used to establish a calibration curve. All measurements were made in duplicate and the TAA here was expressed as micromoles of Trolox/g dry weight of sample (μmol Trolox/g DW).

TAA-DPPH assay: In general, the DPPH method involves the free radical of 2,2-diphenyl-1-picrylhydrazyl (DPPH) [22]. The jujube extract