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Sweet and nonsweet taste discrimination of nectarines using visible and near-infrared spectroscopy

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ABSTRACT

The feasibility of using visible and near-infrared spectroscopy technology combined with multivariate analysis to discriminate cv. 'Big Top' and cv. 'Diamond Ray' nectarines has been studied. These varieties are very difficult to differentiate visually on the production line but show important differences in taste that affects the acceptance by final consumers. The relationship between the diffuse reflectance spectra and the two nectarine varieties was established. Five hundred nectarine samples (250 of each variety) were used for the study. Tests were performed by using a spectrometer capable of measuring in two different spectral ranges (600–1100 nm and 900–1700 nm). These spectral ranges were used to develop two accurate classification models based on linear discriminate analysis (LDA) and partial least squares discriminate analysis (PLS-DA). Later, selection techniques were applied to select the most effective wavelengths. The results showed that the PLS-DA model achieved better accuracy and less latent variables than LDA model, and specifically, good results with 100% classification accuracy were obtained using only the 600–1100 nm spectral range for the two models and eight selected wavelengths. These results places visible and near-infrared spectrocopy as an accurate classification tool for nectarine varieties with a very similar appearance but different tastes that could be potentially used in an automated inspection system.

1. Introduction

Nectarine and peach fruit [*Prunus persica* (L.) Batch] are the second most important fruit crop in the European Union (EU) after apple (Iglesias and Echeverría, 2009). Recently, significant innovations have been made in the field of fruit varieties that seek improvements in colour and size, consistency of pulp, texture, taste and flavour (Jha et al., 2012, 2006, 2005; Picha, 2006; Jha and Matsuoka, 2004). New varieties obtained show an attractive range of colours, tastes and forms as well as having an extended maturity schedule, which have given rise to excellent acceptance by consumers in both national and international markets (Iglesias, 2013; Iglesias and Casals, 2014).

The most appreciated attributes among fruit consumers have been described as being taste, food safety (absence of pesticides), ease of consumption and cost (Wandel and Bugge, 1997; Radman, 2005; Dragsted, 2008). Regarding taste consumers generally prefer sweet and balanced tastes, except in some countries like Germany or England, where there is preference for nonsweet tastes (Cembalo et al., 2009). In fact, the introduction of 'Big Top' nectarine variety intro the market represented a remarkable innovation for its sweet taste (< 6 g L-1 of malic acid) and excellent consistency, and has been widely accepted by national and international markets.

Recently, new varieties of nectarines completing the collection period from late May to late September have been introduced into the market. This varietal range is complemented by new or existing varieties showing a similar appearance, but a balanced or nonsweet taste (> 6 g L-1 of malic acid), as occurs in the case of the 'Diamond Ray' variety. In nectarine fruit, it is essential to differentiate the varieties from in processing line, which would allow the consumer to choose the ones that best adapt to their pReferences

The application of visible and near-infrared spectroscopy for the analysis of fruit has allowed the prediction of chemical composition, notably sugar content (Li et al., 2013; Reita et al., 2008), and textural parameters (Lee et al., 2012; Sánchez et al., 2011), as well as the identification of varieties (Li et al., 2016; Guo et al., 2016) and the measurement of quality-related parameters (Pérez-Marín et al., 2011). This technique is relatively rapid, simple, cost-effective, non-destructive, and environmentally friendly. Its application in combination with chemometrics has been successfully used in non-destructive discrimination between varieties of agricultural products such as peach

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(Guo et al., 2016), bayberry (Li et al., 2007), orange (Suphamitmongkol et al., 2013), and pummelos (Li et al., 2016).

This study aimed to evaluate the ability of visible and near-infrared spectroscopy to discriminate between two varieties of nectarine (cv. 'Big Top' and cv. 'Diamond Ray'), which, because there are similar in colour and appearance, are very difficult to differentiate visually on the production line but show important differences in taste, thereby affecting the acceptance by the final consumers. Two supervised methods such as linear discriminate analysis (LDA) and partial least squares discriminate analysis (PLS-DA) were used for this purpose.

2. Materials and methods

2.1. Experimental procedure

A total of 500 nectarines with commercial maturity and uniform size and the absence of any external damage were harvested in a commercial orchard in Lérida, Spain. They were then stored at 0.1 °C with 87% relative humidity to prevent the evolution of maturity during the experiment and to extend their shelf-life (Gorny et al., 1998). Half of the total samples belonged to the variety 'Big Top' and the other half to the variety 'Diamond Ray'. These varieties were selected because they are grown in the same period and have a similar evolution and physical appearance, although they differ critically in some of their organoleptic properties.

On arrival at the laboratory, fruits were cleaned, individually numbered and each variety was randomly divided into five sets of 50 fruits. The visible and near-infraed spectra of the fruits in each set were collected and their physicochemical properties (soluble solids, firmness and flesh and external colour) were analysed by standard destructive methods (Cortés et al., 2016; Martins et al., 2016; Li et al., 2013; Hernández et al., 2006).

2.2. Visible and near-infrared spectra acquisition

Diffuse visible and near-infraed reflectance spectra of intact nectarines were collected using a multichannel spectrometer platform (AvaSpecAS-5216 USB2-DT, Avantes BV, The Netherlands) equipped with two detectors. The first detector (AvaSpec-ULS2048 StarLine, Avantes BV, The Netherlands) included a 2048-pixel charge-coupled device (CCD) sensor (SONY ILX554, SONY Corp., Japan), 50 µm entrance slit and a 600 line mm-1 diffraction grating covering the visible and near-infrared range from 600 nm to 1100 nm (VNIR) with a spectral FWHM (full width at half maximum) resolution of 1.15 nm and a spectral sampling interval of 0.255 nm. The second detector (AvaSpec-NIR256-1.7 NIRLine, Avantes BV, The Netherlands) was equipped with a 256 pixel non-cooled InGaAs (Indium Gallium Arsenide) sensor (Hamamatsu 92xx, Hamamatsu Photonics K.K., Japan), with a 100 µm entrance slit and a 200 line mm-1 diffraction grating covering the near-infrared range from 900 nm to 1700 nm (NIR) with a spectral FWHM resolution of 12 nm and a spectral sampling interval of 3.535 nm.

The measurements were performed using a bi-directional fibre-optic reflectance probe (FCR-7IR200-2-45-ME, Avantes BV, The Netherlands). The probe was configured fitted with an illumination leg which connects to a stabilised 10 W tungsten halogen light source (AvaLight-HAL-S, Avantes B0 V, The Netherlands) and the other leg of the fibre-optic probe was connected to both detectors for simultaneous measurement. A personal computer equipped with software (AvaSoft version 7.2, Avantes, Inc.) was used to control both detectors and to acquire the spectra. The integration times were adjusted for each spectrophotometer using a 99% reflective white reference tile (WS-2, Avantes BV, The Netherlands), so that the maximum reflectance value over each wavelength range was around 90% of saturation (Lorente et al., 2015). The white reference tile for reflectance measurements was a 32 mm diameter and 10 mm thick block of white polytetrafluoroethylene (PTFE). The white reference tile was placed at a distance of 5 mm from the probe to make a reference measurement. The dark spectrum was obtained by turning off the light source and completely covering the tip of the reflectance probe. The integration time was set to 120 ms for the VNIR detector and 550 ms for the NIR detector due to the different features of the two detectors. For both detectors, each spectrum was obtained as the average of five scans to reduce the thermal noise of the detector (Nicolaï et al., 2007). The average reflectance measurements of each sample (S) were then converted into relative reflectance values (R) with respect to the white reference using dark reflectance values (D) and the reflectance values of the white reference (W), as shown in Eq. (1):

$$R = \frac{S - D}{W - D} \quad (1)$$

Prior to the spectral measurements, the temperature of the nectarines was stabilised at a room temperature of 22 ± 1 °C. All the measurements were taken at two points on each side of the fruit and mean values of the spectra were used for the analysis.

2.3. Determination of the quality attributes

Destructive methods were performed immediately after the spectral acquisition to determine the quality attributes for use as reference values. Both the external and the flesh colours were measured using a spectrocolorimeter (CM-700d, Minolta Co., Tokyo, Japan) every 10 nm between 400 and 700 nm. The colour was evaluated using the L*, a* and b* space proposed by the International Commission on Illumination (CIE). L*a*b* were determined from the reflectance spectra, considering standard illuminant D65 and standard observer 10°. L* refers to the luminosity or lightness component, a* (intensity of red (+) and green (−)) and b* (intensity of yellow (+) and blue (−)) are the chromaticity coordinates. The total colour difference (ΔE) between the 'Big Top' samples and the 'Diamond Ray' samples was calculated by Eq. (2).

$$\Delta E = \sqrt{(L^*_{BT} - L^*_{DR})^2 + (a^*_{BT} - a^*_{DR})^2 + (b^*_{BT} - b^*_{DR})^2} \quad (2)$$

where subscript 'BT' refers to the colour reading of the 'Big Top' samples and 'DR' refers to the colour reading of the 'Diamond Ray' samples.

Nectarine firmness was measured using a Universal Testing Machine (TextureAnalyser-XT2, Stable MicroSystems, Haslemere, England) to perform puncture tests using a 6 mm diameter cylindrical probe (P/15ANAMEsignature) to a relative deformation of 30% at a speed of 1 mm s-1. Two measurements were performed for each fruit on opposite sides along the equator. The fracture strength (F_{max}) was analysed for all samples as the maximum force applied to break up the sample, being expressed in Newtons.

Immediately after firmness measurements, juice samples were extracted to estimate the total soluble solids content (TSS) and titratable acidity (TA). The TSS was determined by refractometry (%) with a digital refractometer (set RFM330+, VWR International Eurolab S.L Barcelona, Spain) at 20 °C with a sensitivity of ± 0.1 %. Samples were analysed in triplicate and average values were calculated. The analysis of the TA was performed with an automatic titrator (CRISON, pH-burette 24, Barcelona, Spain) with 0.5 N NaOH until a pH of 8.1 (UNE34211:1981), using 15 g of crushed nectarine, which was diluted in 60 mL of distilled water. The TA was determined based on the percentage of citric acid, which was calculated using Eq. (3).

$$TA\,[g citric acid/100 g of sample] = (((A \times B \times C)/D) \times 100)/E \quad (3)$$

where A is the volume of NaOH consumed in the titration (in L), B is the normality of NaOH (0.5 N), C is the molecular weight of citric acid (192.1 g mol-1), D is the weight of the sample (15 g) and E is the valence of citric acid (E = 3).