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Non-destructive prediction of color and pigment contents in mango peel

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ABSTRACT

The pigment content of mango peel is an important quality determinant due to its involvement in the nutritional value and coloration of the fruit. In addition, pigment content in the peel is related to the fruit maturity stage and has been suggested as a reliable harvest criterion. Measurements of pigment content by vis-spectrophotometry and chromatography methods are destructive, time-consuming and expensive. This study deals with the potential of reflectance measurements as a non-destructive method to assess pigment content and color in mango fruit peel. We also investigated the relationship between the pigment content of the peel and its color. Eight mango cultivars, i.e., Cogshall, Kent, Caro, Sensation, Tommy Atkins, Nam Doc Mai, Irwin and Heidi, were studied. Hue angle distribution was used to characterize and to compare cultivar colors. The peel contents in anthocyanin, carotenoids, chlorophyll *a* and chlorophyll *b* were predicted using Partial Least Square Regressions based on reflectance indexes and compared between cultivars. Our results showed that reflectance measurements can accurately ($R^2 \geq 0.91$, RMSE ≤ 5.74 μg gFW^{-1}) predict the contents of the main pigment contained in the mango peel. Further studies are nevertheless required to increase PLSR robustness. Significant differences were found in the hue angle distribution and the predicted peel pigment content between the eight mango cultivars studied. All relationships between pigments and hue angle values were found to be cultivar-dependent. The highest correlations between hue angle values and pigment contents were found for anthocyanin content in red cultivars ($0.76 \geq R^2 \geq 0.58$), and chlorophyll content in green cultivars ($0.88 \geq R^2 \geq 0.62$). Results showed that reflectance measurements could be used to predict mango quality determinants such as the fruit maturity stage according to the peel chlorophyll content, the fruit coloration and the content of valuable components, i.e., anthocyanins and carotenoids.

1. Introduction

The chlorophyll content in mango peel was recently found to be a reliable indicator of the mango maturity stage (Léchaudel et al., 2010). In addition, anthocyanins and carotenoid pigments of mango fruit have been the object of increasing interest since they are known to provide health benefits due to their antioxidant activity (Ajila et al., 2007a,b, 2010; Berardini et al., 2005a,b). Spectrophotometric and HPLC measurements were used to measure pigment content in mango peel and revealed their variations between cultivars (Ajila et al., 2007a; Berardini et al., 2005a,b; Ketsa et al., 1999) and fruit maturity stages (Ketsa et al., 1999; Medlicott et al., 1986). However, these methods are destructive, time-consuming and expensive. Non-destructive measurements of surface reflectance in the visible range have been suggested to predict the pigment content of leaves and apple skin (Merzlyak et al., 2003a; Mielke et al., 2012; Gitelson et al., 2001; Sims and Gamon, 2002; Zude, 2003). Such measurements could also be used to assess the content of the main pigments of mango fruit peel, i.e., chlorophyll *a*, chlorophyll *b*, carotenoids and anthocyanins (Medlicott et al., 1986). These pigments are involved in the photosynthesis activity, in the photo-protection of the fruit (Merzlyak et al., 2002; Steyn et al., 2002) and in the fruit coloration (Lancaster et al., 1997). Fruit color is an important factor for market acceptance (Nguyen et al., 2004; Vásquez-Caicedo et al., 2002; Litz, 2009) and could be used as a tool to describe mango cultivars (Ayala-Silva et al., 2005) or to predict mango maturity stages (Jha et al., 2007). Colorimetric coordinates can be deduced from reflectance measurements

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using color-matching functions (Vos, 1978). These functions make it possible to calculate the quantity of red, green and blue colors of a reflectance spectrum in order to reproduce the sensitivity of the human eye (Abbott, 1999). Several authors found relationships between colorimetric measurements and pigment content in the skin (Lancaster et al., 1997; Iglesias et al., 2012; Steyn et al., 2004) or flesh tissues (Ornelas-Paz et al., 2008; Vásquez-Caicedo et al., 2005; Sánchez et al., 2006) for various fruits and vegetables.

In this paper, reflectance measurements were used to evaluate the relationships between the color and the pigment content of mango peel. The study is based on eight mango cultivars in order to ensure a wide range of variation in fruit colors and pigment contents.

2. Materials and methods

2.1. Fruits samples, measurements of reflectance spectra and color determination

The study was carried out on 61, 60, 79, 60, 51, 51, 51, and 58 mangoes from cv. Cogshall, Kent, Caro, Sensation, Tommy Atkins, Nam Doc Mai, Irwin and Heidi, respectively. Fruits were grown during the 2012–2013 production season in the CIRAD orchard collection of Reunion Island (20°52′48″ S, 55°31′48″ E), consisting of 7-year-old trees grafted on 'Maison Rouge' cultivars. Trees were well-irrigated, spaced 5 m × 6 m, and approximately 3 m high. Fruits were randomly chosen on the tree in order to represent the variability of sun exposure conditions, and harvested at the optimal harvest stage for the local market, considering that fruits are at their prime during the next 3–5 days (Léchaudel and Joas, 2006). Just after the harvest, approximately four NIR spectra of fruit peel surface at random locations on each fruit were monitored from 350 to 2500 nm with the contact probe of a portable spectrometer (LABSPEC 2500, Analytical Spectral Devices, Inc., Boulder, CO, USA). For 33 supplementary samples representing the observed color variability observed within the studied cultivars, pigment concentrations in the peel were determined after extraction by vis-spectrophotometry in order to develop predictive models based on reflectance spectra. NIR spectra were monitored on these skin samples prior to their destructive analysis to determine pigment content.

XYZ colorimetric coordinates of skin color were obtained from its reflectance spectra in the visible range (Colorimetry, 2004), where $S(\delta)$ is the spectral reflectance of the measured mango peel, $I(\delta)$ is the spectral irradiance of the illuminant, and $\overline{x(\delta)}$, $\overline{y(\delta)}$ and $\overline{z(\delta)}$ are the color-matching functions. The CIE standard illuminant, D65, was used in this paper ($Xn = 0.9503$, $Yn = 1$ and $Zn = 1.0891$). The calculated *XYZ* color coordinates were then converted to CIELAB coordinates, and the hue angle value (H°) was calculated from a^* and the b^* coordinates using Eq. (2).

$$\begin{cases} X = \dfrac{1}{N}\displaystyle\int_{380}^{700} I(\delta) \times \overline{x(\delta)} \times S(\delta) \times d\delta \\ Y = \dfrac{1}{N}\displaystyle\int_{380}^{700} I(\delta) \times \overline{y(\delta)} \times S(\delta) \times d\delta \\ Z = \dfrac{1}{N}\displaystyle\int_{380}^{700} I(\delta) \times \overline{z(\delta)} \times S(\delta) \times d\delta \end{cases} \quad (1)$$

where $N = \int_{380}^{700} I(\delta) \times \overline{y(\delta)}$,

$$h_{ab} = \arctan\left(\frac{b^*}{a^*}\right) \quad (2)$$

2.2. Determination of peel pigment concentration

The photosynthetic pigments, chlorophylls *a* and *b*, as well as the total carotenoids ($x+c$), were extracted with 100% dimethylsulfoxide (DMSO). Approximately 5 cm^2 of mango peel samples were removed with a peeler on each fruit studied, and then immediately frozen in liquid nitrogen and stored in an ultra-freezer (−80 °C) until chlorophyll and carotenoid extraction and quantification were performed. Approximately 0.5 g of the mango peel samples were extracted with 5 ml of DMSO after incubation in the dark, in a dry bath at 65 °C for 5 h. Heated samples were removed from the dry bath and allowed to reach room temperature. The absorbance (A) of supernatants was then measured at 480, 649, and 665 nm with a VIS scanning spectrophotometer (Helios Epsilon, Thermo Fisher Scientific, USA). To calculate the chlorophyll *a* ($[C_a]$), chlorophyll *b* ($[C_b]$) and total carotenoid ($[C_{x+c}]$) content, the equations of Wellburn (1994) were used (Eq. (3)).

$$\begin{aligned} [C_a] &= 12.47 \times (A_{665}) - 3.62 \times (A_{649}) \\ [C_b] &= 25.06 \times (A_{649}) - 6.5 \times (A_{665}) \\ C_{x+c} &= (1000 \times (A_{665}) - 1.29 \times [C_a] - 53.78 \times [C_b]/220) \end{aligned} \quad (3)$$

Anthocyanin pigments were extracted according to the procedure described by Jing and Giusti (2007). Briefly, approximately 0.5 g of crushed mango peel was added to 4 ml of deionized water. The sample was shaken in a dry bath at 50 °C for 1 h. The resulting extract was filtered through a Whatman No.1 filter paper under a vacuum using a Büchner funnel. Extraction with deionized water provides the highest yield in comparison to other extraction solvents (Jing and Giusti, 2007).

The monomeric anthocyanin content of the mango peel was measured using a spectrophotometric pH differential protocol (Lee et al., 2005). A VIS scanning spectrophotometer (Helios Epsilon, Thermo Fisher Scientific) was used to measure absorbance at 520 and 700 nm against a distilled water blank. Anthocyanin content was expressed as micrograms of cyanidin-3-glucoside equivalent per gram of fresh mango peel.

2.3. Prediction of peel pigment content using reflectance spectra

In order to non-destructively predict the peel contents in pigments using reflectance spectra, a model based on Partial Least Square Regression (PLS) was established. The tested preprocessing methods (first and second derivations) did not improve the models accuracy so no transformed spectral data (log(1/reflectance)) were used to build models.

Model calibrations were performed from the destructive measurements of pigment content of the 33 epidermis samples. As proposed by several authors (Merzlyak et al., 2003a; Mielke et al., 2012; Gitelson et al., 2001; Sims and Gamon, 2002), the PLS regression was calculated from reflectance indexes based on optical pigment features. The number of latent variables for the PLSR model was obtained by using leave-one-out cross-validation to avoid over-fitting of the equation. The procedure provided by the PLS package (Mevik and Wehrens, 2007) developed in R software (Team, 2012) and fully described by Cornillon (2010) was applied.

Model prediction error was evaluated using the Root Mean Square Error (RMSE) and the coefficient of determination (R^2) as indicators. Calculation of the RMSE is described in Eq. (4), where y_t is the t-th observed or reference value, $\hat{Y}_t$ is the t-th simulated value, and n is the number of observed or simulated values.

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{t=1}^{n}(y_t - \hat{y}_t)^2}{n}} \quad (4)$$