Postharvest Biology and Technology 101 (2015) 58–65

Contents lists available at ScienceDirect

Postharvest Biology and Technology

journal homepage: www.elsevier.com/locate/postharvbio

Optical properties, ethylene production and softening in mango fruit

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ARTICLE INFO

Article history:
Received 21 July 2014
Received in revised form 4 November 2014
Accepted 6 November 2014

Keywords:
Mango
Maturity
Ethylene
Absorption
Scattering
Time-resolved reflectance spectroscopy

ABSTRACT

Firmness decay, chlorophyll breakdown and carotenoid accumulation, controlled by ethylene, are major ripening events in mango fruit. Pigment content and tissue structure affect the optical properties of the mesocarp, which can be measured nondestructively in the intact fruit by time-resolved reflectance spectroscopy (TRS). This work is aimed at improving the maturity assessment in mango (*Mangifera indica* L. cv Haden) from Brazil, using TRS absorption in both the carotenoid and chlorophyll regions in order to develop a model for fruit ripening. Scattering and absorption in the 540–900 nm spectral range by TRS, ethylene production and respiration rate, and firmness, were measured in one day on each individual fruit of a sample covering the range of maturity. The fruit displayed a variability which was attributed to the different biological age. Absorption spectra showed two peaks at 540 and 670 nm, corresponding respectively to the tail of carotenoid absorption and to chlorophyll-*a* absorption. Carotenoids increased substantially only in fruit where chlorophyll had almost disappeared. The absorptions at 540 and 670 nm, which described the maturity state of each fruit relative to the range of each wavelength, were combined in one index of biological age (biological shift factor) for each fruit and used in logistic models of ethylene increase and firmness decay respectively. The model explained about 80% of the variability in ethylene production rate. A similar result was obtained for firmness when scattering was added in the model. The combination of absorption at 540 and 670 nm measured by TRS in the intact fruit can be used to classify mango fruit according to maturity and to predict the ripening of individual fruit.

1. Introduction

The ripening process of climacteric fruit such as mango (*Mangifera indica* L.) is regulated by genetic and biochemical events that result in changes in color, texture, aroma, nutritional content and flavor of the fruit (Giovannoni, 2004). Ethylene plays a major role in controlling these events. During ripening, ethylene production becomes autocatalytic, being stimulated by ethylene itself. Loss of firmness (softening), change of exocarp and mesocarp color, and development of volatiles are among the most obvious symptoms of ripening. During fruit ripening, chloroplasts differentiate into chromoplasts by disintegration of the thylakoid membranes and by the development of new pigment-bearing structures, as observed in pepper (Camara and Brangeon, 1981) and mango (Vásquez-Caicedo et al., 2006). This process is accompanied by biochemical changes such as degradation of chlorophyll and accumulation of carotenoids, which cause the characteristic bright yellow–orange mesocarp coloration in ripening mangoes (Vásquez-Caicedo et al., 2005). Ethylene accelerates chlorophyll breakdown and stimulates biosynthesis of carotenoids and their precursors (Rodrigo and Zacarias, 2007; Montalvo et al., 2009). Ethylene and carotenoid synthesis and chlorophyll degradation pathways are integrated in that they share some common regulating factors (Lee et al., 2012; Luo et al., 2013). The most abundant carotenoids in mango are all-*trans*-β-carotene, all-*trans*-violaxanthin and 9-*cis*-violaxanthin. Ripe 'Haden' fruit has been characterized by a high content of all-*trans*-β-carotene and all-*trans*-violaxanthin as compared to other cultivars (Ornelas-Paz et al., 2007). The concentrations of these carotenoids increased in an exponential manner during fruit ripening and were highly correlated with the color coordinate a^* (positive) and H° (negative) values of the mesocarp (Ornelas-Paz et al., 2008).

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http://dx.doi.org/10.1016/j.postharvbio.2014.11.008
0925-5214/

Mango, as other climacteric fruit, is generally harvested at the preclimacteric, mature-green stage, and its ripening process is completed in the postharvest phase. Fruit harvested in a ripe condition has better quality for direct consumption, but a shorter shelf-life. For long supply chains, the maturity stage at harvest must prevent ripening during transport, while ensuring acceptable potential for subsequent ripening. Fruit harvested too early may be unable to ripen, as the ripening ability of a fruit is acquired on the tree (Joas et al., 2012).

The determination of reliable maturity indexes is therefore of paramount importance for the mango fruit industry. Commonly, in practice the shape and appearance of the fruit is used, which can be subjective. According to Kienzle et al. (2011), titratable acidity, mesocarp yellowness and dry matter are the most useful indices to specify harvest maturity. Exocarp color changes with maturity, but it is not always well correlated to the other maturity indices, which are related to the mesocarp properties. The best tools to assess changes in the mesocarp during ripening are the penetrometer, followed by flesh a^* value and total soluble solids content (Padda et al., 2011). Unfortunately all these measurements are destructive, so they can be applied only to a sample of a fruit batch. To overcome the problem, and make possible the individual measurement of each fruit in a batch, nondestructive methods are needed, recently reviewed by Nicolaï et al. (2014). Among optical methods, continuous wave NIR or Vis–NIR spectroscopy has been widely used to estimate established maturity parameters of mango, following them during fruit ripening: e.g., dry matter, starch (Saranwong et al., 2004), total soluble solids, color (Subedi et al., 2007), firmness (Subedi and Walsh, 2009) and a combined maturity index (Jha et al., 2014) were predicted from NIR spectra using partial least squares regression. The latter approach predicts maturity parameters indirectly, and the robustness of the prediction model depends on the extent and variation of the population used for calibration. The direct nondestructive measurement of relevant parameters in the mesocarp by means of time-resolved reflectance spectroscopy (TRS) could be an improvement to the standard Vis–NIR approach. TRS and space-resolved reflectance spectroscopy (SRS), differently from continuous wave methods, can separate the effects of light absorption (due to chemical compounds such as pigments or water) and light scattering (due to microscopic changes in refractive index caused by membranes, air, vacuoles, starch granules, organelles, etc.). With TRS, the absorption (μ_a) and reduced scattering (μ_s') coefficients are quantified by measuring photon time-of-flight distribution with picosecond temporal resolution. In nectarines, the absorption at 670 nm (μ_a670), near the chlorophyll-*a* peak, has been shown to be an effective maturity index, which, at harvest, allowed the prediction of softening rate during ripening (Eccher Zerbini et al., 2006). An interesting feature of TRS is that it measures optical properties at a depth of 1–2 cm in the sample with no or limited influence from the skin (Cubeddu et al., 2001; Torricelli et al., 2008), while continuous wave spectrophotometers have a useful penetration depth of a few mm, depending on wavelength (Lammertyn et al., 2000). When measurements of peeled and intact mangoes were compared, TRS absorption spectra were fairly identical in the two cases, and correlated with spectrophotometric measurements only in peeled fruit, indicating that TRS measured internal properties, while spectrophotometer measured rather superficial features (Spinelli et al., 2012, 2013; Vanoli et al., 2011a, 2013). Scattering spectra can be interpreted with Mie theory: under the hypothesis that the scattering centers are homogeneous spheres behaving individually, Mie theory predicts the wavelength dependence of the scattering and the relation between scattering and sphere size and density. Scattering has been related to textural properties of fruit. In apple fruit μ_s' at 750 and 780 nm were positively correlated to the intercellular space volume, and negatively to firmness (Vanoli et al., 2007), and were related to pectin composition showing a high and positive correlation to galacturonic acid content in water soluble pectin fraction, and a negative correlation to residue insoluble pectin and protopectin index (Vanoli et al., 2009). A significant positive correlation was found between firmness and μ_s'880 in ripening 'Tommy Atkins' mangoes (Vanoli et al., 2013). TRS measurements in the chlorophyll absorption region (near 670 nm) have been used to obtain a direct indication of harvest maturity and to model fruit ripening on an individual fruit basis, taking into account the variability of fruit. In fact fruit maturity at the tree level is heterogeneous owing to variations in flowering time as well as to variability in environmental conditions of the fruit-bearing branches (Léchaudel and Joas, 2007). This variance may be seen as a disadvantage for fruit industry which looks for uniform batches of produce; however, it can also be managed in order to treat each fruit in the most suitable way, e.g., directing the less mature fruit to long distance transport and the more mature ones to direct consumption in the near or gourmet markets. In the last decade, biological variation has been studied by many authors (Hertog, 2002; Tijskens et al., 2003; Hertog et al., 2004; Schouten et al., 2004; De Ketelaere et al., 2006). The concept of biological shift factor allows reducing many different aspects of variation in postharvest behavior to that of a different biological age of individuals which share a common behavior at constant conditions (Tijskens et al., 2005). In nectarines μ_a670, decreasing with maturity, was considered an index of the fruit biological age (Tijskens et al., 2007) and, converted into the biological shift factor, was successfully used to predict fruit softening rate during shelf-life,

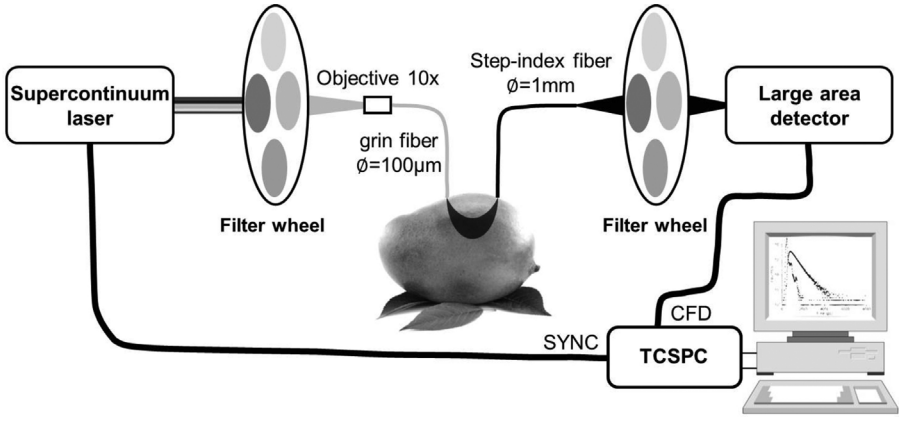

Fig. 1. Scheme of the TRS instrumental setup. TCSPC: time-correlated single-photon counting board; SYNC: synchronization signal; CFD: constant fraction discriminator.