



A model approach revealed the relationship between banana pulp acidity and composition during growth and post harvest ripening



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ARTICLE INFO

Article history:

Received 14 May 2013

Received in revised form 5 August 2013

Accepted 8 August 2013

Keywords:

Musa

Organic acids

Mineral elements

Cultivars

Titrateable acidity

pH

ABSTRACT

Titrateable acidity and pH are important chemical traits for the organoleptic quality of banana since they are related to the perception of sourness and sweetness. Banana fruit has the particularity of having separate growth and ripening stages, during which pulp acidity changes. A modeling approach was used to understand the mechanisms involved in changes in acidity during pulp growth and post harvest ripening. Changes in pH and titrateable acidity were modeled by solving a set of equations representing acid/base reactions. The models were built using data from growth and post harvest ripening of three dessert banana cultivars with contrasting acidity. For each model, calculated values were compared to observed values. These models allowed the prediction of pH ($R^2 = 0.34$; RMSE = 0.75, biais = 0.05) and of titrateable acidity ($R^2 = 0.81$, RMSE = 2.05, biais = -1.44) during fruit growth and post harvest ripening. The sensitivity analyses showed that among acids, malic, citric and oxalic acids are the main contributors to banana pulp acidity, and that among soluble minerals, potassium also plays an important role. Studying the factors that affect the accumulation of organic acids (citric, malic, and oxalic acids) and potassium in banana pulp could be a relevant area of research with the objective of modifying banana fruit acidity.

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1. Introduction

Fruit acidity is a topic of primary importance in improving fruit quality since it influences the perception of both sourness and sweetness (Bugaud et al., 2011; Esti et al., 2002). These two attributes are major drivers of consumer preferences for fruit (Lyon et al., 1993), and are thus important traits to consider in breeding programs. Understanding the elaboration of fruit acidity is also important because acidity controls numerous enzyme activities (Madshus, 1988).

Fruit acidity is commonly measured using two chemical parameters: titrateable acidity (TA) i.e. the amount of weakly bound hydrogen ions that can be released from the acids, and pH, the activity of free hydrogen ions. Fruit acidity is due to the acidity of the vacuole which represents about 90% of the volume of most

mature fruit cells (Etxeberria et al., 2012). The acidity of the vacuole is the result of its ionic composition, mainly organic acids and mineral cations that determine the vacuolar pH and TA (Etienne et al., 2013). Banana pulp contains three major organic acids, malic acid, citric acid, and oxalic acid, whose concentrations undergo marked changes during growth and ripening (John and Marchal, 1995; Jullien et al., 2008) and phosphoric acid (Bugaud et al., 2013). Banana pulp contains soluble minerals, mainly potassium (K), and to a lesser extent magnesium (Mg), calcium (Ca), and chloride (Cl) (John and Marchal, 1995). During post harvest ripening, mineral content can still change due to migration between the peel and the pulp (Izonfuo and Omuaru, 1988).

There are considerable differences in pH and TA among dessert banana cultivars and among post-harvest ripening stages (Bugaud et al., 2013; Chacón et al., 1987), and the origins of these differences remain unclear. Quantifying the relations between pulp acidity and pulp ionic composition using a modeling approach, would advance our understanding of the determinants of banana acidity. Models of pH and TA predictions have been developed for peach (Lobit et al., 2002) and proved to be powerful tools to understand the mechanisms underlying changes in acidity during peach development. The objective of the present work was to apply and validate these models on banana fruit, in which other ionic species than those

Abbreviations: TA, titrateable acidity; RMSE, root mean squared error; K, potassium; Mg, magnesium; Ca, calcium; Cl, chloride; P, phosphorus; IDN 110, Indonesia 110; JB, Pisang Jari Buaya; PL, Pisang Lilin; FW, fresh weight; mEq, milliequivalents; LMM, linear mixed model; SI, sensitivity index.

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found in peach need to be taken into account, and to throw light on the determinants of the changes in pH and TA that occur during the life of the banana pulp, i.e. from growth on the plant through post harvest ripening.

2. Materials and methods

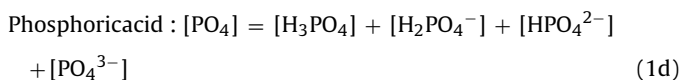
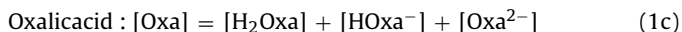
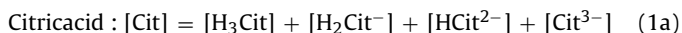
2.1. Model development

2.1.1. pH model

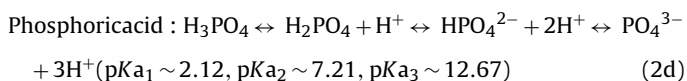
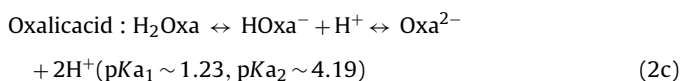
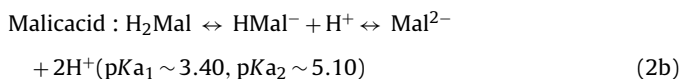
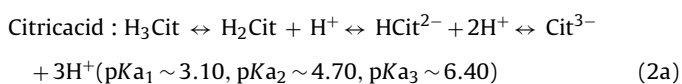
The model used for pH prediction was adapted from Lobit et al. (2002). Banana pulp can be considered as a concentrated aqueous solution of weak acids, mainly malic, citric, oxalic and phosphoric acids, and mineral cations, mainly potassium, magnesium, calcium and chloride. Other acids can be found in banana pulp but were not taken into account in the present study. Weak acids are partly in free form and partly dissociated to form salts with monovalent cations. Proton exchange reactions occur between acids and bases until equilibrium state is reached, which determines the pH and the concentrations of all ionic species. So, to predict the pH of banana pulp solution, the concentrations of the different chemical forms of the weak acids need to be calculated.

2.1.1.1. Acid/base equilibrium. The equilibrium state of a solution containing several acid/conjugate base pairs and cations in known amounts can be computed by solving a system consisting in the following sets of equations:

2.1.1.1.1. Equations of conservation. The total amount of an acid is equal to the sum of the concentrations of all the ionic species formed by its dissociation:



2.1.1.1.2. Equations of dissociation. The dissociation reactions of the weak acids considered in the model are the following:



If HA/A⁻ is an acid/base pair characterized by an acidity constant K_a, the equilibrium between the concentrations of the protonated and the dissociated form can be written as a function of pH and of the activity of the ionic species involved in the reaction: K_a = (A⁻h)/(HA), where (HA) and (A⁻) are the activities of the conjugated acid and base, respectively; h = (H⁺) = 10^{-pH} is the hydrogen ion activity, and K_a = 10^{-pK_a} is the acidity constant.

In diluted solutions (concentrations below 10⁻² molL⁻¹), activities can be considered equal to concentrations. In more concentrated solutions like fruit juice, they are less than concentrations: (HA) = a_{HA}[HA] and (A⁻) = a_{A⁻}[A⁻], where [HA] and [A⁻] are the concentrations of the acid and its corresponding base respectively, and a_{HA} and a_{A⁻} are the activity coefficients, which depend on the ionic composition of the solution. So, the dissociation equilibrium can be written by introducing an apparent acidity constant: [A⁻]h/[HA] = K'_a, where K'_a is the apparent constant of acidity defined as:

$$K'_a = K_a a_{HA} / a_{A^-} \quad (3)$$

2.1.1.1.3. Activity coefficient of ions. The activity coefficients of each acid and conjugated base have to be computed to estimate the apparent acidity constants. In a solution that contains n ionic species S_i with electric charges z_i and at concentrations C_i (i < n), an ion S with a charge z has an activity coefficient a_s that depends on the ionic strength (μ) of the medium. The ionic strength of the solution is the total concentration in ionic species, given by the following equation:

$$\mu = 1/2 \left(\sum_i z_i^2 C_i \right) \quad (4)$$

In the case of an aqueous solution with a ionic strength of up to 1 M, a_s can be calculated by the equation of Davies (1962):

$$\log(a_s) = -0.509z^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right) \quad (5)$$

2.1.1.1.4. Ionic balance. The neutrality of the electrical solution in pulp cell implies that the algebraic sum of cationic and anionic charged must be null:

$$\begin{aligned} &[\text{H}_2\text{Cit}^-] + 2 * [\text{HCit}^{2-}] + 3 * [\text{Cit}^{3-}] + [\text{HOxa}^-] + 2 * [\text{Oxa}^{2-}] \\ &+ [\text{Hmal}^-] + 2 * [\text{Mal}^{2-}] + [\text{H}_2\text{PO}_4^-] + 2 * [\text{HPO}_4^{2-}] \\ &+ 3 * [\text{PO}_4^{3-}] + [\text{OH}^-] + [\text{Cl}^-] - [\text{H}^+] - [\text{K}^+] - 2 * [\text{Mg}^{2+}] \\ &- 2 * [\text{Ca}^{2+}] = 0 \end{aligned} \quad (6)$$

[OH⁻] is expressed as a function of the pH: [OH⁻] = 10^(pH-14)

2.1.1.2. Algorithm of the pH model. Combinations of Eqs. (1) and (2) give the following set of equations that all depend on the apparent acidity constants and the pH:

$$\begin{aligned} [\text{Cit}^{3-}] &= (K'_{\text{cit1}} K'_{\text{cit2}} K'_{\text{cit3}} / (h^3 + h^2 K'_{\text{cit1}} + h K'_{\text{cit1}} K'_{\text{cit2}} \\ &+ K'_{\text{cit1}} K'_{\text{cit2}} K'_{\text{cit3}})) [\text{Cit}] \end{aligned} \quad (7a)$$

$$\begin{aligned} [\text{HCit}^{2-}] &= (h K'_{\text{cit1}} K'_{\text{cit2}} / (h^3 + h^2 K'_{\text{cit1}} + h K'_{\text{cit1}} K'_{\text{cit2}} \\ &+ K'_{\text{cit1}} K'_{\text{cit2}} K'_{\text{cit3}})) [\text{Cit}] \end{aligned} \quad (7b)$$

$$\begin{aligned} [\text{H}_2\text{Cit}^-] &= (h^2 K'_{\text{cit1}} / (h^3 + h^2 K'_{\text{cit1}} + h K'_{\text{cit1}} K'_{\text{cit2}} \\ &+ K'_{\text{cit1}} K'_{\text{cit2}} K'_{\text{cit3}})) [\text{Cit}] \end{aligned} \quad (7c)$$

$$[\text{H}_3\text{Cit}] = (h^3 / (h^3 + h^2 K'_{\text{cit1}} + h K'_{\text{cit1}} K'_{\text{cit2}} + K'_{\text{cit1}} K'_{\text{cit2}} K'_{\text{cit3}})) [\text{Cit}] \quad (7d)$$

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