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Hydrogen ion concentration affects quality retention and modifies the effect of calcium additives on fresh-cut 'Rocha' pear

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ABSTRACT

'Rocha' pear (*Pyrus communis* L.) was used as a model system to assess the effect of pH of dipping solutions on quality retention of fresh-cut fruit and its interaction with calcium additives. Pear slices were dipped for 60 s in a buffer solution at pH 3.0, 5.0 or 7.0 and stored at 4.5 °C for 13 days. In other experiments, pear slices were dipped for 60 s in buffer solutions containing 250 mM of calcium ascorbate, lactate, chloride, and propionate, at pH 3.0 or 7.0, and stored at 4.5 °C for 6 days. Browning and softening were more intense in slices dipped in a solution at pH 3.0 than at pH 5.0 or 7.0, but microbial growth was lower in slices treated at pH 3.0. The effect of calcium additives depended on the anion and significant interactions between the effects of calcium salt and pH were observed. Calcium ascorbate was very effective in preserving color and reducing microbial growth irrespective of pH, but enhanced pectin solubilization and tissue softening at pH 3.0. Slices treated with 250 mM calcium propionate or calcium lactate were softer and had higher electrolyte efflux when treated at pH 3.0 than at pH 7.0. Calcium lactate enhanced browning and reduced microbial growth at pH 3.0 but did not affect color or microbial counts at pH 7.0. All calcium treatments enhanced electrolyte leakage. pH of the dipping solution can affect, *per se*, the quality of fresh-cut fruit. The choice of calcium additives to prevent undesirable changes on visual and sensory quality of cut produce should involve pH ranges that provide the expected benefits.

1. Introduction

Fresh-cut produce are very perishable, even when processed and marketed with the best technology available. Preservation of fresh-cut fruit involves refrigeration and modified atmosphere packaging to reduce metabolic rate, water loss, and microbial growth (Lamikanra, 2002; Farber et al., 2003). Additional treatments, such as acid additives to lower the pH, are often used to reduce microbial growth (Karaibrahimoglu et al., 2004; Simón et al., 2010). In some fruit and vegetables, additives are also required to improve firmness and to prevent enzymic browning (Toivonen and Brummell, 2008).

Textural properties, such as firmness and juice retention, are very important to the appearance and flavor perception of fresh-cut fruit. A few water-soluble calcium salts (ascorbate, chloride, lactate, propionate, and gluconate), and even the less soluble calcium carbonate, have been successfully used to reduce softening in fresh-cut fruit (Dong et al., 2000; Luna-Guzmán and Barrett, 2000; Saftner et al., 2003; Aguayo et al., 2008). Calcium enhances the mechanical strength of the cell wall (Mignani et al., 1995) and reduces the autolytic release of pectins from cell walls (Wehr et al., 2004) by binding to the negative charges of demethylated galacturonic residues of pectins (Toivonen and Brummell, 2008). In addition, calcium can stabilize cell membranes by delaying galactolipid breakdown (Picchioni et al., 1995). Calcium additives are also thought to inhibit endopolygalacturonase (PG; EC 3.2.1.15) activity (Poovaiah, 1986), although evidence suggests that the effect of calcium is not on the catalytic activity of PG but, instead, on the solubilization of the products of PG-mediated hydrolysis (Almeida and Huber, 2007).

Enzymic browning is a major limiting factor of shelf-life on some fresh-cut fruit and vegetables. Tissue browning following wounding is a result of oxidative reactions mediated by polyphenoloxidase (PPO; EC 1.14.18.1). Phenolic compounds are oxidized by PPO into *o*-quinones polymerize leading to the formation of brown pigments (Martinez and Whitaker, 1995). Several categories of additives are used to prevent or reduce enzymic browning in susceptible produce, including carboxylic acids (e.g. citric acid), chelators, reductants (e.g. ascorbate), thiol-containing compounds (e.g. cysteine, glutathione) or specific enzyme inhibitors such

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as 4-hexylresorcinol (Martinez and Whitaker, 1995; Arias et al., 2007).

The use of additives is likely to alter, intentionally or unintentionally, the surface pH of fresh-cut produce. pH is a measure of hydrogen ion concentration, a chemical variable that interferes with many quality attributes of fresh-cut fruit: it affects PPO activity (Siddiq et al., 1994; Arias et al., 2007), modulates cell wall metabolism and texture (Knee, 1982; Chun and Huber, 1998; Gorny et al., 2002; Pinheiro and Almeida, 2008), and interferes with microbial growth (Bhagwat et al., 2004; Karaibrahimoglu et al., 2004). Despite the effects of pH *per se* and the interaction between pH and calcium additives on several quality attributes of fresh-cut fruit (Ponting et al., 1971; Pinheiro and Almeida, 2008), these remain largely ignored in the literature. The pH of the coatings and dipping solutions used to carry the additives is often not reported and the role of pH is seldom recognized as an explanatory variable for the effects of dipping or coating treatments.

This study was designed to evaluate the effect of pH *per se* and its interaction with calcium additives on quality attributes of fresh-cut pear. Treatments were applied by dipping according to the standard practice in fresh-cut industrial processing. Pear was chosen as a model fruit due to its susceptibility to browning and softening.

2. Materials and methods

2.1. Plant material

Pear (*Pyrus communis* L. 'Rocha') fruit were harvested at commercial maturity from an orchard in the Oeste Region, Portugal, selected by hand for uniform size, washed and stored at −0.5 °C, 90–92% RH. All the fruit used in the experiments were drenched prior to storage with 636 mg L^{-1} diphenylamine and 375 mg L^{-1} imazalil, the standard postharvest treatments used by the 'Rocha' pear industry. Fruit removed from the cold rooms were allowed to ripen at 20 °C to an edible texture and then cooled to 4 °C before processing. Whole fruit firmness was measured after skin removal with a penetrometer mounted on a stand drill and equipped with an 8-mm probe. Fruit used as raw material for the pH experiments were processed with flesh firmness of 57 ± 1 N and pears with 58 ± 2 N were used in the experiment with calcium additives. Both experiments were performed in duplicate with similar results.

2.2. Minimal processing and storage conditions

Fruit were processed at 10 °C in a sanitized cold room and handled with gloved hands during processing. Whole fruit were surface sanitized with 2 mM sodium hypochlorite (pH 6.5) for 2 min and rinsed with tap water before processing. Pears were cut by hand into longitudinal slices (*ca.* 10–20 mm thick) with a sharp stainless steel knife. After cutting, the pear slices were dipped for 60 s in the treatment solutions, and allowed to drain for 2 min before being packed.

After the dipping treatments, slices were randomly distributed in vented plastic (polyethylene terephthalate) clamshells with 500 cm^3 containing ten slices each (*ca.* 200 g). The containers were covered but a circular perforation (5 mm in diameter) in the lid assured that the atmospheric composition inside the package was not modified. The vent was plugged with cotton to reduce microbial contamination. O_2 and CO_2 concentrations inside the package were monitored throughout storage with a gas analyzer (CheckMate II, PBI Dansensor, Ringsted, Denmark) to assure that no relevant deviation from normal atmospheric level occurred. The containers were stored at 4.5 ± 0.5 °C for 13 days in the experiment to assess the effect of pH and for 6 days in the experiment designed to evaluate the interaction between pH and calcium salts.

2.3. Buffers and calcium solutions

The effect of pH *per se* was evaluated in a buffer solution prepared with 100 mM citric acid–200 mM sodium phosphate and pH adjusted to 3.0, 5.0 or 7.0.

Different buffers were required in the experiment designed to evaluate the interaction between pH and calcium to assure the complete solubility of calcium salts. Two buffers were used for each pH to allow the distinction between the effects of pH and the chemical composition of the buffer. Buffer solutions at pH 3.0 were 100 mM citric acid–100 mM sodium citrate and 100 mM citric acid–200 mM sodium phosphate. At pH 7.0 the buffers were 100 mM Mops–NaOH and 100 mM Tris–100 mM HCl. In each of these buffer solutions, four calcium salts – ascorbate, chloride, lactate and propionate – were dissolved to a final concentration of 250 mM of calcium (1% Ca^{2+}). Buffer solutions without calcium salt were used as controls.

2.4. Color measurement

Color of the cut surface was measured in the CIE L*a*b* color space with a Konica-Minolta CR-400 chromameter (Osaka, Japan) equipped with a D_{65} illuminant and the observer at 2°. Lightness (L*), chroma (C*) and hue angle (h°) and the metric-hue difference between the initial reading and the observation date (ΔH*) were analyzed. Metric-hue difference was calculated as $\Delta H^* = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 - (\Delta C^*)^2}$, where a* and b* are the Cartesian color coordinates. One measurement was made in each of six slices sampled from three replicated clamshells per pH treatment or on 30 randomly selected slices per buffer × pH × calcium salt treatment

2.5. Firmness assessment

Firmness was measured using a TA-XT2 Plus texture analyzer (Stable Micro Systems, Surrey, UK). In the experiment designed to evaluate the effect of pH *per se*, firmness was evaluated by compression. Disks (10 mm diameter) were excised from the central region of a pear wedge and cut to a uniform thickness of 10 mm. Disk firmness (compression force) was measured using a 30 mm diameter flat-plate probe (Pinheiro and Almeida, 2008) travelling at a speed of 1.5 mm s^{-1} for 4 mm. One measurement was made in each of six slices sampled from three replicated clamshells. In the experiments with calcium additives, firmness was measured by puncture, the method commonly used to assess firmness in fresh-cut pear (Gorny et al., 2000, 2002; Soliva-Fortuny et al., 2004). Maximum peak force required to force a 3 mm flat head probe 5 mm into de slice with a travel speed of 1.5 mm s^{-1} was registered. One measurement was made on 30 slices per treatment and a paired measurement in the same slice was made after 6 days in storage to reduce sample variation.

2.6. Electrolyte efflux

Representative slices from three clamshells per treatment were sampled after 6 days in storage. Disks with 13 mm diameter and 5 mm thickness were excised from pear slices with a cork-borer, rinsed with an isotonic mannitol solution and blot dried. Four disks (*ca.* 2.5 g) were immersed in 25 mL of 700 mM mannitol and incubated for 2 h at 20 °C with agitation. Electrical conductivity of the incubation solution was measured with a Con 510 meter (Eutech Instruments, Nijkerk, The Netherlands) immediately after immersion of disks (EC_0) and after the 2 h incubation period (EC_f). After incubation, the solution containing the disks was frozen for 24 h then thawed and boiled for 30 min and cooled to room temperature before the measurement of total electrical conductivity (EC_t). Electrolyte leakage