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Effect of citric acid and calcium on quality and shelf-life of fresh-cut banana (*Musa paradisiaca* L.)

Efecto del ácido cítrico y calcio en la calidad y vida útil del banano (*Musa paradisiaca* L.) mínimamente procesado

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Abstract

The objective of this study was to evaluate the quality attributes and respiratory activity of banana slices during storage at 13 ± 2 °C and 92 ± 2 % relative humidity (RH), simulating marketing conditions. The bananas were selected, washed, sanitized, and cut into slices. Then, they were divided into four groups to which different treatments were applied: 1 % (w/v) calcium chloride ($CaCl_2$) + 0.92 % citric acid (abbreviated as CaAc); 1 % (w/v) $CaCl_2$ (abbreviated as Ca) alone; 0.92 % (w/v) citric acid (abbreviated as Ac) alone; and fruit without application of calcium chloride and citric acid as control (C). Physicochemical analyses were performed using standard methodologies, such as ICONTEC norms. pH values, titratable acidity, color, total soluble solids, weight loss, firmness, and respiration rate were evaluated every 2 days until Day 17. The combined treatment of 1 % (w/v) $CaCl_2$ + 0.92 % citric acid (w/v) significantly decreased respiration rate, weight loss, and browning, and preserved quality attributes during storage. The combination of refrigeration and the application of 1 % (w/v) $CaCl_2$ + 0.92 % (w/v) Ac can extend the shelf life of banana slices up to 9 days.

Keywords: Antioxidant, banana, cold storage, post-harvest, respiration rate.

Resumen

El objetivo de este trabajo fue evaluar el comportamiento de los atributos de calidad y la actividad respiratoria de rodajas de banano almacenadas a 13 ± 2 °C y 92 ± 2 % de humedad relativa (HR), simulando las condiciones de comercialización. Los bananos fueron seleccionados, lavados, higienizados y cortados en rodajas, después se dividieron en cuatro grupos a los que se les aplicaron diferentes tratamientos: 1 % (p/v) cloruro de calcio ($CaCl_2$) + 0.92 % (p/v) ácido cítrico; 1 % (p/v) $CaCl_2$ solo; 0.92 % (p/v) ácido cítrico solo; y fruta sin ácido cítrico ni $CaCl_2$ denominada control. Se utilizaron métodos de análisis fisicoquímicos bajo metodologías consagradas como las normas ICONTEC. Se evaluaron valores de pH, acidez titulable, color, sólidos solubles totales, pérdida de peso, firmeza e intensidad respiratoria, cada dos días y hasta el día 17. Se encontró que el tratamiento combinado de 1 % (p/v) $CaCl_2$ + 0.92 % (p/v) ácido cítrico disminuyó considerablemente la intensidad respiratoria, la pérdida de peso y el pardeamiento, y permitió conservar los atributos de calidad durante el almacenamiento. La combinación de refrigeración y la aplicación de 1 % (p/v) $CaCl_2$ + 0.92 % (p/v) ácido cítrico puede alargar hasta 9 días la vida útil de las rodajas de banano.

Palabras clave: antioxidante, almacenamiento refrigerado, banano, intensidad respiratoria, poscosecha.

Introduction

Banana (*Musa acuminata*) of the Cavendish variety is a fruit of significant importance in the global market due to its high content of vitamins and other nutrients, antioxidant properties, and benefits for human health in disease prevention (Chang *et al*., 2022). Banana pulp consists of approximately 70 % water, is rich in easily digestible carbohydrates, contains low percentage of proteins and fats, and serves as a good source of vitamins A, B1, B2, and C (Zahra *et al*., 2021). Approximately 15 million tons of bananas are exported each year, making them the fifth most important agricultural product in global trade after cereals, sugar, coffee, and cocoa (Sarifudin *et al*., 2021). Colombia is one of the world's largest producers of the *Musa* genus, ranking fifth in total production and second in exports after Ecuador, with a production volume of 2 554 287 tons in 2020 (FAO, 2023). Bananas are a strategic crop for Colombian food security and are also of great economic importance in the market. Therefore, the deterioration of whole or cut bananas can have a significant economic impact.

Globally, approximately 14 % of food—with an estimated value of USD 400 billion—is lost between harvest and distribution, and another 17 % is wasted during distribution and among final consumers (FAO, 2023). Fresh-cut fruits are emerging as a response to consumer demand for fresh, healthy, high-quality products that require little preparation time while maintaining their original organoleptic (color, flavor, and aroma) and nutritional (vitamins, minerals, and nutrients) properties.

Banana is a climacteric fruit, and its natural ripening process is rapid. This factor affects the quality of the fruit and the long-term storage conditions (Yildiz, 2018). It undergoes post-harvest alterations in both the fresh and fresh-cut state. In the case of fresh-cut bananas, softening and darkening occur due to the polyphenol oxidase (PPO) enzyme, whose activity increases when plant tissues are cut and exposed to oxygen (Yildiz, 2018). Various agents, such as ascorbic acid, tartaric acid, calcium chloride, and citric acid, are commonly applied to prevent these alterations in plant tissues, as they are considered safe for human consumption (Arora *et al*., 2021).

Studying the biochemical and physiological changes that occur during the ripening of fresh-cut fruits enables the development of appropriate handling procedures, operational strategies, equipment, and packaging systems to prevent or delay the senescence of the product. The research question is: Does the application of calcium and citric acid to banana slices affect the physicochemical properties, color, and respiration rate of the fruit during cold storage? Therefore, the objective of this research was to evaluate the quality attributes and physiological responses of fresh-cut bananas subjected to various post-harvest treatments with calcium chloride and citric acid during storage under commercial conditions.

Materials and methods

Local and raw material

The experimental process was developed in the Laboratory of Fruits and Vegetables at the Universidad Nacional de Colombia, Palmira campus, at an average temperature of 23 °C, a relative humidity of 89 %, and an altitude of 1000 m. a. s. l. Banana fruits of the Cavendish variety (*Musa acuminata*), sourced from the village of El Bolo Arsenal in Pradera (Valle del Cauca), were used at ripening stage 5, corresponding to yellow fruits with green tips, as defined by Guzmán-Bortolini (2021). The fruits were transported to the laboratory in 20 kg plastic baskets.

Fruit selection and classification

The initial quality of the fruits was defined in accordance with the norm NTC 1190 (ICONTEC, 1999). Therefore, medium-sized bananas weighing approximately 110 to 129 g, classified as extra quality—without stains, cracks or deep stripes —were selected and classified. It was also ensured that the bananas did not have signs of pest infestation, disease, rotting, or bruising.

Minimal processing

The fruits were washed by immersion in potable water, and subsequently disinfected using a sodium hypochlorite solution at 200 µL/L1 for 2 minutes. After disinfection, the fruits were peeled and manually cut into slices with a diameter of 40 mm and a thickness of 3 mm. These slices were then divided into four groups corresponding to the treatments described in Table 1. Citric acid and calcium chloride were applied by immersing the slices in 20 L of the solution for 2 minutes.

Table 1. Different treatments for fresh-cut bananas

Abbreviation	Treatment
CaAc	1 % calcium chloride ($CaCl_2$) (w/v) + 0.92 % citric acid (w/v)
Ca	$CaCl_2$ 1 % (w/v)
Ac	Citric acid 0.92 % (w/v)
C	Control (without application of calcium chloride and citric acid)

Fruit packaging and storage

The banana slices were packed in polystyrene trays (15 cm × 1.3 cm) and sealed with a 16 µm thick polyvinyl chloride film, thus creating a modified atmosphere. Approximately 500 g of fresh-cut bananas was packed in each tray. The samples were stored for 17 days at 13 ± 2 °C and 92 ± 2 % relative humidity (RH), simulating refrigeration conditions on supermarket shelves. Quality attributes were evaluated every two days and analyzed in triplicate.

Physicochemical analysis

Weight loss () was determined gravimetrically by calculating the difference between the initial weight () and the final weight () of the fruit at the end of storage (Equation 1). The results are expressed as the cumulative weight loss (%) during refrigerated storage.

$$\%PP = \frac{P_i - P_f}{P_i} * 100 \qquad \textbf{(Eq. 1)}$$

The pH was measured using a potentiometer following the NTC 4592 standard (ICONTEC, 1999). Titratable acidity was determined by titration with 0.1 N sodium hydroxide (NaOH), according to the method established in NTC 4623 (ICONTEC, 1999), and expressed as a percentage of malic acid per gram of banana pulp juice (% malic acid/g). Total soluble solids (TSS) of banana juice at a 2:1 water-to-fruit ratio were measured using a manual refractometer, following NTC 4624 (ICONTEC, 1999). TSS values were corrected by the dilution factor and are presented in degrees Brix (° Brix). Firmness was assessed as the force required to penetrate the center of the banana slices using the piston of a Wagner penetrometer (model POB 1217, stainless steel punch Φ = 6 mm).

Color evaluation

The color of the samples was evaluated using a photographic comparison method. In the following equations, the L, a, and b values were obtained using Adobe Photoshop PCS4, following the methodology reported by Yam and Papadakis (2004). These values were then used to calculate the CIE L* a* CO_2 color coordinates according to Equations 2, 3, and 4. The browning index (BI) (Equation 5) and the total color difference (Equation 6) were calculated according to the procedures of Aimi-Azira *et al.* (2021) and Pathare *et al.* (2013).

$$L^* = \frac{L}{255} * 100 \qquad \textbf{(Eq. 2)}$$

$$a^* = \frac{240a}{255} - 120 \qquad \textbf{(Eq. 3)}$$

$$b^* = \frac{240b}{255} - 120 \qquad \textbf{(Eq. 4)}$$

$$BI = \frac{100\,(x - 0.31)}{0.17}\ ;\ x = \frac{a^* + 1.75L^*}{5.645L^* + a^* - 0.3012b^*} \qquad \textbf{(Eq. 5)}$$

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \qquad \textbf{(Eq. 6)}$$

Subscript 1 corresponds to the sample at Day 1, and subscript 2 corresponds to Day 17 of storage of the banana slices.

Respiration rate

The respiration rate was determined using a respirometer titration method, based on the reaction of carbon dioxide (CO_2) with a basic sodium hydroxide (NaOH) solution. A compressor was adapted to supply external air for 30 minutes through the initial CO_2 trap, ensuring the elimination of CO_2 present in the air. This CO_2-free air was first passed through a moisture trap to remove water vapor, and then directed into desiccators containing previously weighed banana samples. The desiccators were hermetically sealed to prevent the air from escaping from the respiration of the fruits. After 30 minutes, airflow was stopped, and the secondary CO_2 traps were removed from the system and sealed immediately. A 20 mL aliquot from each CO_2 trap was mixed with 10 % w/v $BaCl_2$ and four drops of phenolphthalein. The solution was immediately titrated with 0.1 N HCl. The respirometer was equipped with a refrigeration system to maintain the refrigeration temperature (13 ± 2 °C). Finally, calculations were performed using Equation 7.

$$IR\left(\frac{mg\ CO_2}{kg * h}\right) = \frac{(V_b - V_m) * N_{HCl} * 22 * f}{w * t}\ ;\ f = \frac{V_{NaOH\ en\ frasco}}{V_{alícuota}} \qquad \textbf{(Eq. 7)}$$

Where is the volume (mL) of HCl used in the titration of the blank; is the volume (mL) of HCl used in the titration of the sample; is the standard normality of HCl; is the weight of the sample; is the duration (h); 22 is the equivalent weight of CO_2 (g-meq); and is the sample factor.

Experimental design

A completely randomized design was employed, consisting of four treatments, each analyzed in triplicate. Different physicochemical parameters were assessed every 2 days during cold storage (1, 3, 5, 7, 9, 11, 13, 15, and 17 days). Data are presented as means. The results obtained were subjected to analysis of variance (ANOVA) to determine significant differences among treatments. Mean comparisons were performed using Duncan's multiple range test (*p*<0.05) applying the MEANS procedure of the SAS® statistical software version 9.1 (USA).

Results and discussion

Physicochemical properties

Figure 1 shows the cumulative weight loss of the banana slices stored for 17 days. Weight loss is primarily associated with increased respiratory activity and moisture loss during storage (Shehata *et al.*, 2020). The highest percentages of cumulative weight loss were observed in treatments C and Ac. In contrast, the lowest accumulated weight loss was recorded in samples treated with Ca and CaAc. These results showed that the cell wall integrity of the samples treated with $CaCl_2$ was preserved due to the formation of crossed bridges between the carboxylic groups of pectic acid and the divalent cation of calcium (Shehata *et al.*, 2020).

Calcium can also contribute to the stabilization of protein-pectin complexes in the middle lamina (Huang, 2023). In a study on banana fruit, Elbagoury *et al.* (2021) reported that calcium accumulation in tissues not only helps maintain firmness but also slows down weight loss. In addition, treatments with calcium salt may promote the formation of calcium pectate hydrogels that retain water and increase cellular hardness.

In banana slices, TSS showed an increasing trend along all treatments, with values rising until Day 7 of storage and remaining relatively stable until Day 17 (Figure 2). The increase in TSS may be due to the hydrolysis of starch into sugars like glucose, fructose, and sucrose during banana ripening (Deori *et al.*, 2020; Moreno *et al.*, 2021). Likewise, the sudden increase in TSS content observed in the samples from treatment C may be directly associated with rapid moisture loss, and consequently, a reduction in weight (Shehata *et al.*, 2020). Pleşoianu and Nour (2022) reported that, due to the application of coatings, the increase in solid concentration was reduced, since these treatments can slow down respiration and metabolic activity.

Figure 3 shows that the pH of the banana slices remained nearly constant throughout the investigation, ranging approximately from 5.25 to 5.70, with no significant decreases or increases. Similar results were reported by Siqueira *et al.* (2018) for 'Prata-Anã' banana pulp stored at 23 °C under different controlled and modified atmospheres. The pH was also a relevant factor, as it reflects an acidic medium suitable for microbial growth. Aimi-Azira *et al.* (2021) observed that minimal variations in pH are associated with reduced respiration rates, which may reflect the effectiveness of the treatments.

Regarding titratable acidity, a slight increase was observed in banana slices during the first three days of storage. This was followed by a decrease over the next two days, after which values remained relatively stable until Day 13 of storage (Figure 4), when a second decline was recorded, consistent with the findings by Deori *et al.* (2020). The increase in titratable acidity at the end of the storage period may be associated with microbial proliferation in the fresh-cut fruit. Additionally, there were no significant differences (*p*<0.05) between the different treatments after the application of $CaCl_2$ and citric acid, who did not affect the acidity of the banana slices.

$CaCl_2$ effectively maintained the firmness of the banana slices until Day 11 of refrigerated storage (Figure 5). This effect is attributed to the interaction between calcium and pectin, leading to the formation of calcium pectate, which strengthens plant tissue texture (Deori *et al.*, 2020). In contrast, the application of citric acid alone had no influence on fruit firmness. On the other hand, Figure 5 shows that the combined treatment of citric acid and calcium chloride exhibited better results. Mirshekari *et al.*

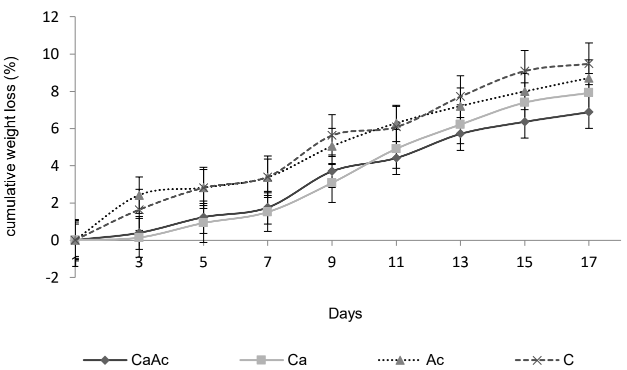

Figure 1. Changes in the cumulative weight loss percentage of fresh-cut bananas stored at 13 ± 2 °C and 92 ± 2 % RH.

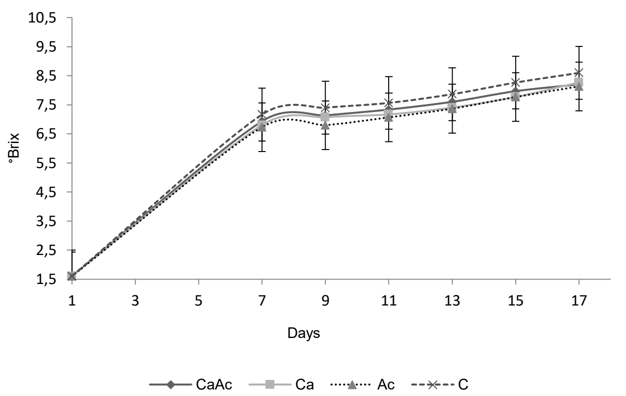

Figure 2. Changes in total soluble solid content (°Brix) of fresh-cut bananas stored at 13 ± 2 °C and 92 ± 2 % RH.

(2017) reported that a combined treatment with 1 % chitosan and 1 % calcium propionate maintained the firmness of 'Berangan' bananas over five days of storage at 5 °C, whereas bananas treated only with 1 % calcium propionate exhibited noticeable softening.

The incorporation of calcium into fruit tissues can delay color changes and reduce the activity of enzymes responsible for cell wall degradation, thereby helping to preserve fruit firmness. Furthermore, calcium contributes to reducing the incidence of certain physiological disorders (Jaime-Guerrero *et al.*, 2024).

Color parameters

The browning index (BI) is calculated from the CIE L* a* CO_2 coordinates and serves as an indicator of browning in foods. It is directly associated with the activity of the PPO enzyme (Pathare *et al.*, 2013). As shown in Figure 6, at the beginning of storage, BI values were lower for the samples treated individually and combined with citric acid. However, at the end of storage, these values increased markedly across all treatments. This increase is related to elevated PPO enzyme activity during the storage period due to intensified metabolic processes and the onset of senescence, consisted with observations by Yildiz (2018).

The a* parameter of the banana slices showed a slight increase during storage due to the emergence of brownish tones. From Day 11 onward, a* values began to approach the threshold associated with red hues (Figure 7). According to Pathare *et al.* (2013), the increase in a* values, and thus in orange or red pigments, is associated with the accelerated ripening and browning processes. Significant statistical differences ($p<0.05$) were observed between a* values of samples from the Ca treatment and those of the other treatments. Banana slices subjected to the combined treatment of citric acid and calcium chloride exhibited the highest a* values during the storage period, indicating a tendency towards reddish tones. In contrast, the highest b* values, that is, the ability to maintain the yellow hue, were observed in banana slices from the Ac and CaAc treatments (Figure 8).

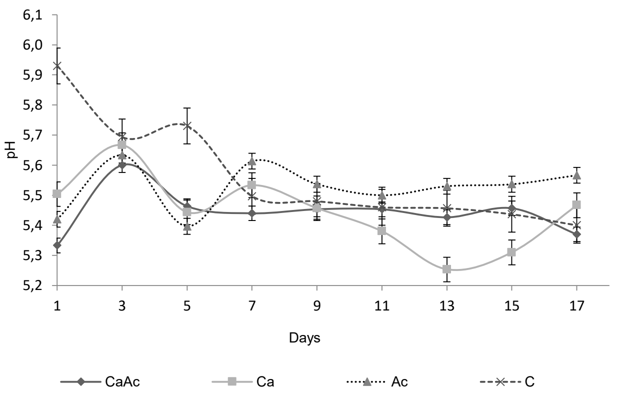

Figure 3. Changes in the pH values of fresh-cut bananas stored at 13 ± 2 °C and 92 ± 2 % RH.

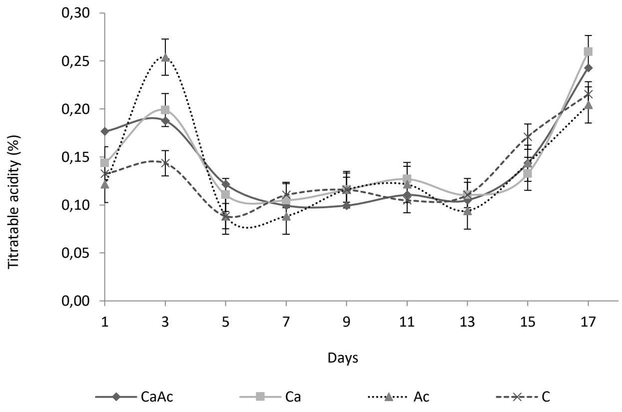

Figure 4. Increase in titratable acidity (%) of fresh-cut bananas stored at 13 ± 2 °C and 92 ± 2 % RH.

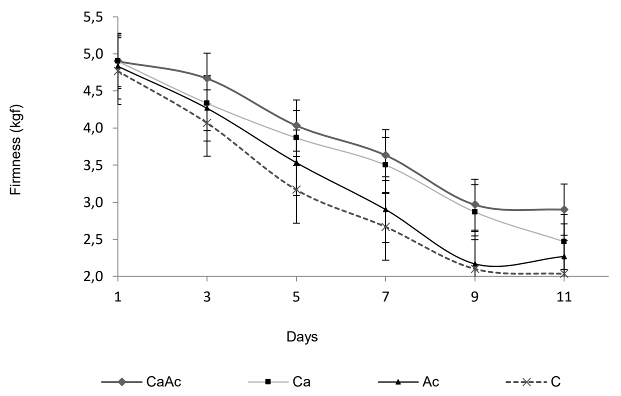

Figure 5. Increase in firmness (kgf) values of fresh-cut bananas stored at 13 ± 2 °C and 92 ± 2 % RH.

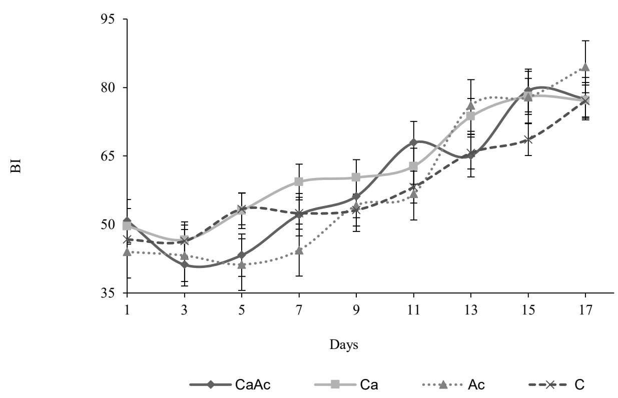

Figure 6. Increase in browning index (BI) values of fresh-cut bananas stored at 13 ± 2 °C and 92 ± 2 % RH.

Overall, the CO_2 levels of banana slices increased slightly during storage. The highest CO_2 values were recorded in samples treated with Ac, while the lowest values were observed in those treated with Ca (Figure 9). No statistically significant differences were found between the CO_2 values of the CaAc, Ac, and C treatments ($p<0.05$). Higher CO_2 levels were associated with the presence of yellow tones in the banana slices. In contrast, the rapid increase in CO_2 observed in the samples treated with Ac can be associated with accelerated maturation. The decrease in CO_2 may be attributed to the darkening of the fruit (Pathare *et al.*, 2013).

Regarding color parameters (L*, a*, and CO_2), noticeable color changes in the banana slices were observed throughout the storage period. The control (C) samples exhibited significant color variation over time ($p<0.05$). The Ca-treated samples showed the highest total color difference (ΔE) during storage, which was associated with a greater degree of browning. As reported by Yildiz (2018), $CaCl_2$ is not as effective as ascorbic acid in inhibiting the PPO enzyme in banana slices. Similarly, Pathare *et al.* (2013) reported significant differences ($p<0.05$) in color between the CaAc and Ac-treated samples compared to the control. The Ca-treated samples exhibited major differences in color in respect to the control. However, the combined treatment (CaAc) preserved the surface color characteristics of the banana slices.

Respiration rate

As shown in Figure 9, the respiration rate of banana slices during the first 6 days of storage was relatively constant or exhibited small variations. From Day 7, a marked increase in the respiration rate was observed, reaching a maximum peak before subsequently declining. This peak corresponded with the onset of senesce, characterized by the development of dark spots and the appearance of microorganisms. Overall, the respiration rate of banana slices tends to be elevated due to the cutting process, which is related to an acceleration of tissue metabolism caused by the stress induced by this operation (Yildiz, 2018).

The increase in respiration rate in the fresh-cut samples is attributed to the larger contact of the surface area of the slices with the surrounding atmosphere, which facilitates greater gas exchange during the experimental period. This response can also be influenced by endogenous ethylene production and the climacteric nature of the fruit (Shehata *et al.*, 2020). According to Figure 9, the climacteric peak of the banana slices occurred near Day 9 of storage. Although no statistical differences ($p<0.05$) were found in respiration rate among treatments, the samples treated with $CaCl_2$ presented the lowest values.

Considering the physicochemical properties, color attributes, and physiological behavior under simulated storage conditions, the applied treatments demonstrate potential for commercial application at the supermarket level.

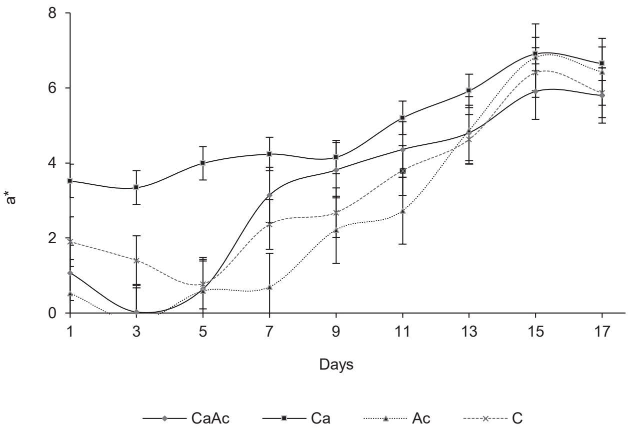

Figure 7. Increase in a* color values of fresh-cut bananas stored at 13 ± 2 °C and 92 ± 2 % RH.

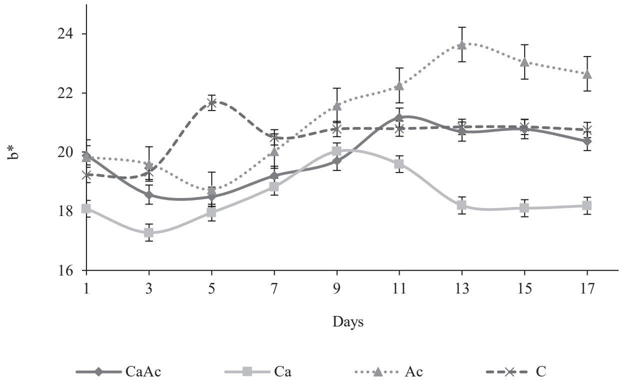

Figure 8. Increase in b* color values of fresh-cut bananas stored at 13 ± 2 °C and 92 ± 2 % RH.

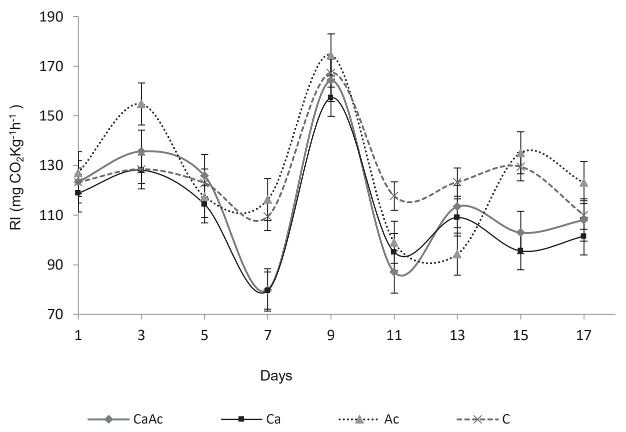

Figure 9. Increase in the respiration rate values (in mg $CO_2 Kg^{-1}h^{-1}$) of fresh-cut bananas stored at 13 ± 2 °C and 92 ± 2 % RH.

Conclusions

The treatments with $CaCl_2$ and citric acid effectively reduced firmness loss by 41 % and weight loss by 2 % in fresh-cut bananas by the ninth day of cold storage, since it acts as a barrier to transpiration. In addition, citric acid reduced browning and helped preserve the color characteristics of the banana slices. The combination of $CaCl_2$ and citric acid is suggested as the most effective treatment to extend the shelf life of fresh/cut bananas up to 9 days under simulated commercial conditions (13 ± 2 °C and 92 ± 2 % RH).

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