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Papaya Fruit Ripening: Response to Ethylene and 1-Methylcyclopropene (1-MCP)

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Ripening affects the quality and nutritional contents of fleshy fruits, and papayas are climacteric fruits very susceptible to postharvest losses due to the fast softening caused by ethylene. This paper reports the changes in respiration, ethylene production, and pulp color and firmness, along with the contents of soluble sugars and major carotenoids, during ripening of 'Golden' papaya, an important Brazilian cultivar that has been exported to North American and European markets. The results obtained for nontreated and ethylene- or 1-MCP-treated papaya suggest that 1-MCP can decrease the quality of treated fruit and that even the use of ethylene for triggering or inducing homogeneous ripening can result in lower quality when compared to that of fruit allowed to ripe naturally.

KEYWORDS: Papaya; ethylene; 1-methylcyclopropene; climacteric; soluble sugars; carotenoids; fruit ripening

INTRODUCTION

Ripening of fleshy fruits affects the quality and nutritional contents in different ways. For climacteric fruits, such as bananas, tomatoes, pears, mangos, and papayas, the changes take place very quickly (I). In this way, climacteric fruits are more susceptible to postharvest losses due to the fast ripening caused by the ripening trigger ethylene, which, in turn, could come from any climacteric ripe fruit stored in the same environment with any climacteric green fruit (2). Thus, to minimize these effects, fruits must be stored away from ethylene sources or the hormone level in the atmosphere should be decreased by oxidation by potassium permanganate or ultraviolet light, although these approaches have limited commercial application (3).

Recently, cyclopropene-type inhibitors of ethylene action (4), especially 1-methylcyclopropene (1-MCP), have been employed in attempts to increase the shelf life of some climacteric fruits (5). By binding to the ethylene receptor (4), 1-MCP acts as an efficient ethylene antagonist, and its effects can persist for a long time. In fact, the effects of 1-MCP have already been evaluated for pears (6), avocados (7), nectarines (8), and papayas (3, 9), although the results were quite diverse for each fruit in terms of effectiveness for commercial use.

Papaya fruit (Carica papaya) is a commercially relevant crop but has a reduced shelf life due to the rapid pulp softening. The 'Golden' papaya is an important Brazilian cultivar of this fruit, which has been exported to both North American and European markets. This variety is very appreciated for its pleasant flavor and taste qualities, such as rich pulp sweetness, redness, and softness. Because papaya is a climacteric fruit, postharvest handling is targeted to avoid conditions that would favor increases in respiration and ethylene production rates. To prevent the nonhomogeneous ripening or the sudden softening of the fruit flesh caused by the exposure to exogenous ethylene or poor postharvest handling, fruit producers have been trying to employ 1-MCP as a ripening delayer to circumvent all of these problems. However, the optimum conditions for the commercial use of this inhibitor are far from being standardized, and there are several concerns regarding the quality and the appearance of the treated fruit.

This paper reports experiments to evaluate physicochemical parameters that would be important for both shelf life and quality of 'Golden' papaya. The respiration and ethylene production rates and measurements of pulp color and firmness, along with the contents of soluble sugars and the three major carotenoids during ripening, are presented for nontreated (control) and ethylene- or 1-MCP-treated 'Golden' papaya. The results obtained suggest that 1-MCP can decrease the quality of treated fruit and, surprisingly, even the ethylene-induced ones can be of lower quality when compared to the naturally ripened fruit.

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MATERIALS AND METHODS

Plant Material. Papaya fruit (C. papaya cv. 'Golden') were obtained from a producer in Sooretama and Linhares cities, Espírito Santo State, Brazil. Papaya fruits were harvested at color break to one-fourth yellow (around 150 days after anthesis). Soon after their arrival in the laboratory (2 days after harvest), fruits were randomly divided into three groups. Papayas from the control group were left to ripen spontaneously in a 240 dm³ chamber with controlled temperature and humidity (25 \pm 0.1 °C and 95%, respectively). The other two groups were treated with ethylene or 1-MCP. For ethylene treatment (2 days after harvest), papayas were left in a 240 dm³ chamber and exposed to a concentration of 100 ppm (100 μ L L⁻¹) of ethylene in a synthetic air mixture in a constant flow-through system during 2 h (for gas saturation) and 10 h in a closed system. The third group was left in a 240 dm³ chamber and treated with 1-MCP (2 days after harvest) at a concentration of 100 ppb (100 nL L^{-1}), for 12 h in a closed system. The 1-MCP gas was generated by the dissolution of, approximately, 18 mg of EthylBloc (Floralife, Inc.) powder (0.14% active ingredient) in 5 L of distilled water inside the box containing the papayas. After both treatments, fruits were ventilated and left to ripen in separate chambers under the same conditions of temperature and humidity described for the control group.

Respiration and Ethylene Production. A minimum number of four fruits from each group were individually placed in airtight 1.7 L jars equipped with a rubber stopper and left at 25 °C for 1 h. After this time, samples of 10 mL for ethylene analysis and 1 mL for CO₂ analysis were taken using a gastight syringe, and the composition of gases was determined by gas chromatography (Agilent Technologies, model HP-6890). A flame ionization detector was employed for ethylene analysis and a thermal conductivity detector for CO2 analysis. For both gases, the column used was an HP-Plot Q (30 m, i.d. = 0.53 mm, Agilent Technologies); injector and detector temperatures were both set at 250 °C, and an isothermal program was run at 30 °C. The helium carrier gas flows were 1 mL min⁻¹ for ethylene and 4 mL min⁻¹ for CO₂. The injections were made in pulsed splitless mode for ethylene and split mode for CO₂ analysis (50:1). Ethylene and CO₂ standards, both in synthetic air (Air Liquid), were used for the preparation of calibration curves. These analyses were conducted on a daily basis, soon after the arrival of the fruit in the laboratory until the end of the experiment.

Pulp Firmness. The same four fruits used for measurement of respiration and ethylene production were analyzed by a TA-XT2 texturometer using the "blade with knife" tool (Stable MicroSystems). The fruits were cut longitudinally, and three cylindrical pulp sections of 1 cm diameter were excised from the middle region of one of the halves of each fruit. After removal of 0.5 cm from the inner and outer pulp regions, including the placenta, the attached seeds, and the peel, a cylindrical section of 1 cm diameter and 1 cm height was cut with constant force and velocity (20 gF and 2 mm/s, respectively). Pulp resistance values were measured, and the maximum values were registered. After placenta and seed removal, the remaining halves of the four fruits analyzed were peeled, sliced, immediately frozen in liquid N₂, and pooled before storage at -80 °C for further analysis.

Soluble Sugars. Soluble sugars were extracted three times with 80% ethanol at 80 °C. After centrifugation, the supernatants were combined and the ethanol was evaporated under vacuum. The residues were reconstituted with water, filtered through 0.22 μ m membrane filters, and analyzed by a high-pressure liquid chromatography with pulse amperometric detection (HPAE-PA; Dionex, Sunnyvale, CA), using a PA₁ column (Dionex) in an isocratic run of 18 mM NaOH during 25 min. Total soluble sugars were obtained as the sum of glucose, fructose, and sucrose values.

Pulp Color Characterization. About 20 g of defrosted papaya homogenized pulp was put into a 20 mm transmission cell, and the visual color was measured using the HunterLab ColorQuest XE instrument (Hunter Associates Laboratories) in terms of *L* (lightness), *a* (redness and greenness), and *b* (yellowness and blueness). The reference illuminant was D65 (standard daylight), diffuse/8° geometry, and observation angle of 10°; the instrument was calibrated with a standard white tile (L = 92.03; $a^* = -0.88$; $b^* = 0.63$), and reflectance measurements were used. Postprocess Hunter L^* , a^* , and b^* values

were recorded, and pulp color measurements were taken five times. Differences in Δa^* and Δb^* values were calculated according to the following formula: $\Delta a^* = a_f - a_i$ and $\Delta b^* = b_f - b_i$, where the values for a_i^* and b_i^* were taken from the control sample 2 days after harvesting. The hue (*h*) value was defined by the following formula: $h = \tan^{-1}(b^*/a^*)$.

Carotenoid Determination. The carotenoids were exhaustively extracted with acetone from 10 g of defrosted homogenized papaya pulp used in the color measurements, transferred to petroleum ether/ diethyl ether, and saponified with 10% methanolic KOH according to the method of De Rosso and Mercadante (10). All extractions were conducted in duplicate, and immediately before HPLC-PDA analysis, the crude dried extracts were solubilized in ethyl acetate/acetonitrile (50:50) and further filtered through a 0,22 μ m Millipore filter. Separation was achieved using a Waters HPLC (Waters Corp., Milford, MA) coupled to a PDA detector (Waters, model 996), equipped with a quaternary solvent delivery system (Waters, model 600), an online degasser, a Rheodyne injection valve with a 20 μ L loop, and an external oven. Data acquisition and processing were performed by the Millennium Waters software. Carotenoid separation was carried out on a C18 Nova-Pak ODS, 300 mm \times 3.9 mm (4 μ m particle size) column, using as mobile phase a linear gradient of acetonitrile containing 0.1% triethylamine (TEA)/H₂O/ethyl acetate starting at 88:2:10 to 85:15:0 (v/v) in 15 min, maintaining this proportion for 25 min, at a flow rate of 1 mL/min and a column temperature set at 25 °C. Chromatograms were processed at 450, 400, and 350 nm, and the spectra were obtained between 250 and 600 nm. The major carotenoids were identified according to the following parameters: chromatographic behavior on the C₁₈ HPLC column, UV-visible spectra (λ_{max} and shape) features compared to literature data (11-13), and cochromatography with authentic standards. For quantification, calibration curves were constructed for all-trans-lycopene, all-trans-\beta-cryptoxanthin, and all-trans- β -carotene with a minimum of seven concentration levels, and the concentration levels were chosen to include those of the samples. Carotenoid quantification was performed by comparison of peak area of the sample with that of the standard peak area, injected daily.

RESULTS

Papayas were harvested at the preclimacteric stage, as demonstrated by the typical climacteric profile concerning CO_2 and ethylene productions achieved in control fruit (**Figure 1**). The endogenous ethylene peaked around day 4 and preceded the respiration burst by 1 day. In the ethylene-treated fruit, the climacteric was anticipated, and although the peak of endogenous ethylene was slightly lower, the respiration rate was considerably higher than that of the control. On the other hand, 1-MCP treatment resulted in climacteric inhibition of papaya fruit as denoted by the basal level of ethylene production and the only marginal rate in respiration.

The contrasting effects of exogenous ethylene and 1-MCP treatment were also apparent in the texture of the fruit pulp (**Figure 1**). During control-fruit ripening, the decrease in flesh firmness was concomitant with the increase in ethylene production and respiration. As expected, this significant softening of the pulp was anticipated in 1 day by exogenous ethylene treatment, taking only 12 h to change from 10 to 1 N cm⁻², whereas the use of 1-MCP kept the flesh firmness at higher levels through the end of the 1-MCP-treated fruit texture experiment.

Total soluble sugars content (Figure 2) in the pulp of papaya fruit increased 2.5 times during ripening, regardless of the treatment employed. For control fruit, the maximum level of soluble sugar was coincident with the climacteric respiration peak and the significant decrease in firmness (Figure 1). Although ethylene treatment anticipated the increase of soluble sugars content, levels similar to that of the control were achieved



Figure 1. Ripening analysis of papaya fruits and their response to ethylene (100 μ L L⁻¹) and 1-MCP (100 nL L⁻¹) treatment. The ripening of control fruits (control) and gas-treated fruits (ethylene and 1-MCP) were compared on the basis of the following parameters: top row, amount of CO₂ produced by fruits measured by GC-TCD (CO₂, mg kg⁻¹ h⁻¹); middle row, amount of ethylene produced by fruits measured by GC-FID (ethylene, μ L kg⁻¹ h⁻¹); bottom row, pulp firmness measured with a texturometer (N cm⁻²). Both vertical lines in ethylene and 1-MCP columns show the end of gas treatments. Error bars indicate SE of the mean (*n* = 4).



Figure 2. Soluble sugars content measured during ripening of untreated and treated papaya fruits. Papaya fruits were exposed to 100 μ L L⁻¹ of ethylene and 100 nL L⁻¹ of 1-MCP, and the content of soluble sugars was measured during untreated (control) and gas-treated (ethylene and 1-MCP) fruit ripening. Quantities of total soluble sugar (top row), sucrose (bottom row, columns), and glucose + fructose (bottom row, lines) in pulp fruit were measured by HPLC. Both vertical lines in ethylene and 1-MCP columns show the end of the gas treatments. Error bars indicate SE of the mean (n = 3).

only at late stages of ripening. In the case of 1-MCP-treated fruit, there was a persistent accumulation of sugars through the period covered by the experiment, which resulted in a total amount of sugar similar to that of the control.

When the main sugars that contribute to the total soluble sugars content were analyzed (**Figure 2**), it was noted that glucose and fructose content increased in the three groups during the covered experiment time. Although the timing was different

Table 1. Calculated Δa^* , Δb^* , and *h* Values from Pulp Samples of *Carica papaya* Cv. 'Golden'

color		days after harvesting					
parameter	2	2.5	3	4	5	7	
			Control				
Δa^*		3.95	1.18	7.18	8.95	4.66	
Δb^*		-1.66	-1.89	-8.06	-1.14	-0.16	
h	63.9	58.0	61.2	48.9	53.0	58.3	
			Ethylene				
Δa^*		4.40	5.06	7.82	7.02	7.06	
Δb^*		-1.23	0.71	-3.27	-0.71	2.67	
h		57.8	58.4	52.5	55.3	57.6	
			1-MCP				
Δa^*		6.94	5.08	0.72	6.28	7.51	
Δb^*		-1.95	-2.97	-0.04	-5.50	-1.59	
h		54.4	55.7	63.0	52.3	54.1	

for the accumulation of each monosaccharide, the profiles of glucose and fructose were quite similar in shape for control and ethylene- and 1-MCP-treated fruit. In contrast, significant differences between groups were observed for sucrose content, not only in the shape of curves but also in relation to the maximum amounts of the disaccharide. Whereas sucrose decreased at late stages of ripening for the control fruit, its end amount in 1-MCP-treated fruit increased more than twice at day 7 after harvest. Ethylene-treated fruit also presented high amounts of sucrose (**Figure 2**) but an even more dramatic change in disaccharide content during ripening.

Analysis of color (**Table 1**) showed that the pulp became darker during ripening during all treatments. This was verified by the slight decrease in the L^* values, along with an increase in pulp color saturation indicated by the decrease in hue values for all samples related to the first control fruit point. Pulp color of control and ethylene- and 1-MCP-treated fruit changed from moderate to fully red during ripening, as indicated by the increasing positive Δa^* values and, except for the ethylenetreated fruit, they also became less yellow saturated than the first samples, as shown by the negative Δb^* values.

The contents of the three main carotenoids, *all-trans*-lycopene, *all-trans*- β -cryptoxanthin, and *all-trans*- β -carotene, that contribute to the color of papaya pulp were evaluated. The results (**Figure 3**) showed that all of them increased during papaya ripening, *all-trans*-lycopene being the most abundant one with a concentration increment of 2.5 times, reaching the maximum value at approximately 1200 μ g mg⁻¹ of fresh weight (FW) on the fifth day postharvest. Both treated fruits, with ethylene or with 1-MCP, showed carotenoid contents lower than that in the control fruit. The most significant effect was observed in *all-trans*-lycopene; the initial levels apparently remained constant during the whole period covered by the experiment, these levels being almost half the amount of those reached by control fruit.

DISCUSSION

Papaya fruits were harvested at the preclimacteric stage, and ripening was clearly affected by the treatments. Whereas the application of exogenous ethylene induced most of the changes normally observed during ripening, the climacteric was almost abolished as a consequence of exposure to 1-MCP. The typical softening of papaya fruit during ripening was also impaired by the presence of the ethylene competitor, giving papaya pulp fruit an undesirable hardness. The ripening of 1-MCP-treated fruit was followed for additional days (data not shown), and no additional softening occurred, indicating that the negative effect of 1-MCP on fruit softening could not be reversed. Although there were changes in peel and pulp color and fruit started to deteriorate, no additional softening was observed. Apparently, papaya fruit could not recover from 1-MCP treatment and became sensitive to ethylene. This impairment of pulp softening suggests a large dependency of the enzymatic apparatus for cell wall and lamella media disassembly on the presence of ethylene. Because there was still a marginal decrease in pulp firmness, it is also possible to consider that the enzymes involved would be affected at different stages and degrees, although maximum softening could be achieved only by the concerted action of several enzymes, mainly those largely ethylene-dependent, such as polygalacturonase, β -galactosidase, and pectinesterase (14). These three examples of ethylene-dependent enzymes had their activity previously characterized, and their combined action could achieve the maximum softening as the fruits had ripened (15, 16), showing that cell wall and lamella media disassembly is particularly dependent on the enzymatic apparatus.

Besides pulp softening, sugar content is another important quality attribute of papaya fruit. In contrast to the effect on the firmness, inhibition of ethylene perception by 1-MCP did not preclude the accumulation of sugars. However, the differences observed can provide some clues to the metabolism of soluble sugars during ripening. Apparently, sucrose synthesis is operative during ripening, although rates of synthesis were lower than those described for fruit development (17). Moreover, when the results were compared to those of papaya fruit exposed to radiation (18), the same conclusion of an operative sucrose synthesis during ripening can be achieved. Because the trace amounts of starch in the pulp of papayas could not account for the accumulation of soluble sugars, it is possible to speculate that some mechanisms of cell wall disassembly (15, 19) could provide a source of carbon for sugar synthesis during ripening, including sucrose.

The similar profiles for glucose and fructose could be an indication that those sugars come from the accumulated sucrose, especially by the action of invertases in fully ripe fruits (20, 2I). In fact, an increase in monosaccharides was concomitant with decreased disaccharide content, and for both control and ethylene-treated fruit, a significant decrease in sucrose was noted at the peak of ethylene production, which suggests a positive effect of this hormone on the activity of invertases. The intermittent sucrose level increase in 1-MCP-treated fruit would also be in agreement with this idea. Additionally, the observed proportions between sucrose, glucose, and fructose content increase in 1-MCP-treated fruit could be an indication of an additional source besides sucrose. As discussed above, an additional supply of carbon could come from the cell wall disassembly or even organic acids.

Carotenoid determination of control fruits had results similar to those described by Chandrika et al. (22) and Wall (23), who found that *all-trans*-lycopene, *all-trans-*\$-cryptoxanthin, and *alltrans*- β -carotene concentrations increased in fully ripe fruits. Although the color analysis had indicated that papaya pulp became darker in color, the treatment with ethylene or 1-MCP impaired the accumulation of all carotenoids, mainly all-translycopene. Because the amounts of *all-trans-\beta*-carotene and *alltrans-\beta*-cryptoxanthin were lower than those of the control, it is possible to consider that the biosynthesis of their precursor was strongly inhibited. In fact, ζ -carotene desaturase, one of the enzymes responsible for lycopene synthesis, was one of the EST clones represented in a cDNA library from papaya fruit (24), suggesting its expression increases during normal fruit ripening. The inhibitory effect of 1-MCP on pigment synthesis would not be unexpected because blockage of ethylene percep-



Figure 3. Carotenoid contents measured during ripening of untreated and treated papaya fruits. Papaya fruits were exposed to 100 μ L L⁻¹ of ethylene and 100 nL L⁻¹ of 1-MCP, and the contents of the three major carotenoids were measured during untreated (control) and gas-treated (ethylene and 1-MCP) fruit ripening. Amounts of *all-trans-* β -cryptoxanthine (top row), *all-trans*-lycopene (middle row), and *all-trans-* β -carotene (bottom row) in pulp fruit were measured by HPLC. Vertical lines in the second and third columns show the end of gas treatments. Error bars indicate the deviation standard of the mean (n = 2).

tion has a negative action on several other events related to the climacteric ripening. However, the lower levels of carotenoids in fruit pulp exposed to exogenous ethylene are quite surprising, because the hormone would be supposed to have the same trigger effect as happens during noninduced ripening. This apparent contradictory effect could be taken as an indication that the accumulation of *all-trans*-lycopene is finely tuned by the ethylene level or time induction. In this way, the blockage of ethylene perception by 1-MCP would preclude the natural ethylene burst and induction of carotenoid synthesis. On the other hand, the massive supply of ethylene by exogenous application could disturb the concatenation of the entire events involved in the carotenoid synthesis, which would be signaled by the hormone. Another possibility would be the anticipation of events playing a negative or inhibitory effect on the biosynthesis of all-trans-lycopene or one of its very early precursors. On the basis of the results of Marty et al. (25) using apricot fruit, carotenoid biosynthesis can be under complex regulation and the ethylene effect on gene expression can also be diverse. These authors found that phytoene synthase and phytoene desaturase genes, genes upstream of the phytoene and phytofluene accumulation steps, were clearly up-regulated by ethylene, whereas downstream genes, such as β -carotene and ζ -carotene desaturase, were ethylene-independent.

The parallel analysis and comparison of the data from papaya fruit submitted to the three different conditions of ripening presented in this paper provided some interesting information regarding the main physical-chemical changes that have significant effects on the quality of this crop. Differences in fruit softening, total amount of soluble sugars, color development, and content of carotenoids with provitamin A or other functional properties were affected by the treatments, although this can be considered a good model for studying ripening events mechanisms. Another important point was the fact that some physical-chemical changes were differently affected by the ethylene level or perception. This could be an indication that, although highly coordinated, some events are more or less ethylene-independent. More specific studies at the biochemical or molecular level would provide interesting information on the enzymes or genes affected by the treatments and their contribution to the quality of fruit.

When compared to control fruit, both ripening induction by exogenous ethylene and ripening delay by 1-MCP resulted in a decrease in quality and nutritional aspects, at least for some attributes, such as pulp firmness and provitamin A content. In fact, the use of the ethylene antagonist to extend the shelf life of papaya cv. 'Golden' would rely on the finding of the proper conditions to avoid these negative effects. One could argue that 1-MCP treatment could be performed after the start of the climacteric ethylene production, as a way to circumvent the decrease in quality caused by the excessive hardness of the fruit. However, this would not be a feasible alternative because the pulp firmness changes too quickly as a consequence of the increase in ethylene production. Another possibility would be to wait for the fruit to become ethylene sensitive again. However, the results obtained showed that the negative effect of 1-MCP could not be reversed before the fruit started to deteriorate. The results are in favor of spontaneous ripening of papayas, avoiding any accumulation of ethylene as a consequence of poor handling, and they also reinforce the need for continuous development of postharvest ripening-delaying strategies, such as the use of cyclopropenes.

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