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QUALITY, BIOACTIVE COMPOUNDS AND ANTIOXIDANT ACTIVITY DURING MATURATION OF ORANGES PRODUCED IN THE BORBOREMA TERRITORY[1]

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ABSTRACT – The family farming from the Borborema Territory-PB, Brazil, produces sweet oranges that supply the regional market. In this context, it is necessary to define standards of identity and quality, as well as to quantify the bioactive compounds in the fruit, in view of adding value and creating more competitive markets. This work sought to evaluate the quality, bioactive compounds and total antioxidant activity (TAA) of oranges from family farming. A 3×3 factorial completely randomized design was used, with three cultivars (Baía, Comum, Mimo-do-Céu) and three maturity stages (predominantly green, green/yellow, yellow), with 60 replications of 1 fruit for the physical evaluations, and 4 of 15 fruit for the others. The whole fruits were evaluated by color index, length, diameter, fresh weight and firmness. The juice was assessed for yield, pH, soluble solids (SS), titratable acidity (TA), SS/AT ratio, and ascorbic acid. Total extractable polyphenols (TEP) and $ABTS^{•+}$ and $DPPH^{•}$ total antioxidant activity (TAA) were measured in the juice and albedo. The 'Baía' and 'Mimo-do-Céu' oranges presented quality parameters aligned with the CEAGESP standards. On average, the ascorbic acid content was higher than 45 mg 100 g^{-1}, with 'Mimo-do-Céu' presenting the highest content (50.26 mg 100 g^{-1}). During maturation, the firmness decreased, and the SS, TEP and TAA of the juice and the albedo increased. In general, the TEP content was about eight-fold higher in the albedo than juice, corresponding to the much higher TAA in this portion, thereby highlighting its higher functional potential, especially for 'Baía' orange.

Keywords: *Citrus sinensis.* Quality standards. Albedo. Functional potential. Adding value.

QUALIDADE, COMPOSTOS BIOATIVOS E ATIVIDADE ANTIOXIDANTE DURANTE A MATURAÇÃO DE LARANJAS PRODUZIDAS NO TERRITÓRIO DA BORBOREMA

RESUMO - A agricultura familiar do Território da Borborema-PB, produz laranjas doces que supre o mercado regional. Nesse contexto, se faz necessária a definição de padrões de identidade e qualidade, bem como quantificar os compostos bioativos nas porções do fruto buscando a agregação de valor, visando mercados mais competitivos. O objetivo deste trabalho foi avaliar a qualidade, compostos bioativos e atividade antioxidante de laranjas da citricultura familiar. Utilizou-se um DIC, fatorial 3x3, com três cultivares ('Baía', 'Comum' e 'Mimo-do-Céu'), três estádios de maturação C1 (predominantemente verde); C2 (verde amarelado) e C3 (amarelo), com 60 repetições de um fruto para as avaliações físicas e 4 de 15 frutos para as demais. As avaliações no fruto inteiro foram: índice de coloração, comprimento, diâmetro, massa fresca e firmeza. No suco foram avaliados: rendimento, pH, sólidos solúveis, acidez titulável, SS/AT e ácido ascórbico. Os polifenóis extraíveis totais (PET) e atividade antioxidante total (AAT) foram determinados pelos métodos $ABTS^{•+}$ e $DPPH^{•}$ no suco e albedo. As laranjas 'Baia' e 'Mimo-do-Céu' apresentam parâmetros de qualidade que se enquadram nas Normas do CEAGESP. Em média o teor de ácido ascórbico foi superior a 45 mg.100g^{-1}, sendo a 'Mimo–do-Céu' com maior teor (50,26 mg.100g^{-1}). Durante a maturação a firmeza diminuiu e os sólidos solúveis, PET e a AAT do suco e do albedo aumentaram. Em geral, o albedo apresentou teor de PET cerca de oito vezes superior ao do suco, que refletiu em AAT bem superior nesta porção que, portanto, se destacou pelo elevado potencial funcional, principalmente na laranja 'Baia'.

Palavras-chave: *Citrus sinensis.* Padrões de qualidade. Albedo. Potencial funcional. Agregação de valor.

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INTRODUCTION

The orange [*Citrus sinensis* (L.) Osbeck] belongs to the Rutaceae family and is one of the most cultivated fruit trees. Its fruit are among the most commercialized and consumed, and Brazil is the largest producer in the world (SOUSA et al., 2016). Approximately 80% of the national citrus production is concentrated in the southeast region, in the state of São Paulo. However, the northeast is the second largest producing region of the country, contributing to 11% of the national production (CNA, 2018; IBGE, 2018). In the Borborema Territory, state of Paraíba, citriculture is the major activity of the family farming, generating employment, income and development for the region (BRASIL, 2018), by producing table oranges to meet the demands of the regional market, with particular attention focused on Baía, Comum and Mimo-do-Céu cultivars (LOPES et al., 2007).

However, it is necessary to establish standards of identity and quality for the classification of fruits intended for the local market, allowing to add value to the product and improve profits for the producers. Furthermore, it is necessary to evaluate the content of the bioactive compounds and the antioxidant activity of each edible portion of the fruit, seeking to add value not only to the juice, but also to other edible portions of the fruit that are usually discarded (LADO; GAMBETTA; ZACARIAS, 2018; RODRIGO et al., 2013).

Oranges are recognized as a source of vitamin C, carotenoids and phenolic compounds that have high antioxidant capacity both in the juice and its byproducts, such as the albedo (mesocarp), which can be consumed fresh associated with the pulp (endocarp) or used in the preparation of products with functional properties for human consumption (YOO; MOON, 2016). The antioxidant substances present in the albedo can inhibit reactive free radicals and, consequently, protect other molecules against oxidation, generating health-promoting effects in the prevention of degenerative diseases, including cancer (CIRMI et al., 2016; YOO et al., 2004).

In this sense, the albedo of the citrus, usually discarded, also contains dietary fiber in higher quantity and quality than cereal fibers, in addition to bioactive compounds (flavonoids, carotenoids and vitamin C), which provide additional health benefits (LADO; GAMBETTA; ZACARIAS, 2018). The citrus albedo has a higher content of total dietary fiber due to a higher soluble fiber fraction than the peeled pulp. Certain water-soluble fibers, such as pectin, reduce the postprandial serum-cholesterol and the blood glucose in humans. Insoluble fibers (lignin, cellulose and some hemicelluloses) serve almost exclusively as bulking agents that promote less intestinal transit time and increase the fecal mass, thereby improving the efficiency of the intestine and colon, and reducing the risk of colorectal cancer (BILGIÇLI; AKTAŞ; LEVENT, 2014).

Maturation induces changes that are influenced by environmental factors and agronomic practices, and the study of these changes is fundamental to define the maturity and quality indices of fruits (DANTAS et al., 2016; WANG et al., 2016). Regardless of whether the orange is intended for the industry or fresh consumption, some physical aspects, such as coloring, fresh weight, pulp yield, besides the functional potential, should be deeply considered for standardization, classification and adding value to the product. In this way, differential criteria for quality can be assigned, which will support the practice of fair prices while enabling more competitive markets (LADO; GAMBETTA; ZACARIAS, 2018).

Based on the above, this study aimed to evaluate the quality, bioactive compounds and antioxidant activity of the sweet orange cultivars Baía, Comum and Mimo-do-Céu, produced in the Borborema Territory-PB, harvested at three distinct stages of maturity.

MATERIAL AND METHODS

The fruits were harvested from a commercial orchard of the family farming, conducted under usual cultural practices of cleaning, pruning, organic fertilization and rescue irrigation, located in the municipality of Alagoa Nova, Borborema Territory region, Paraiba state, Brazil. The rural property has predominant soil type ARGISSOLO RED Eutrophic abrupt (SANTOS et al, 2018). The predominant tropical climate is "As", according to the classification of Köppene Geiger, with annual average temperature of 22.2 °C and average annual rainfall of 1317 mm, with higher rainfall intensities in the winter (ALVARES et al., 2014).

Oranges of the cultivars Baía, Comum and Mimo-do-Céu were randomly harvested from the orchard, between 6 and 8 A.M., in 3 maturity stages by selection of peel coloration, corresponding to the Subclasses: C1 - predominantly green; C2 - green/ yellow; C3 - yellow peel (Figure 1), according to CEAGESP (2011) standards, as well as the absence of pests, diseases and apparent injuries. At the time of harvest the fruits were packed in high density polyethylene boxes, protected with bubble wrap and transported to the laboratory for the analysis.

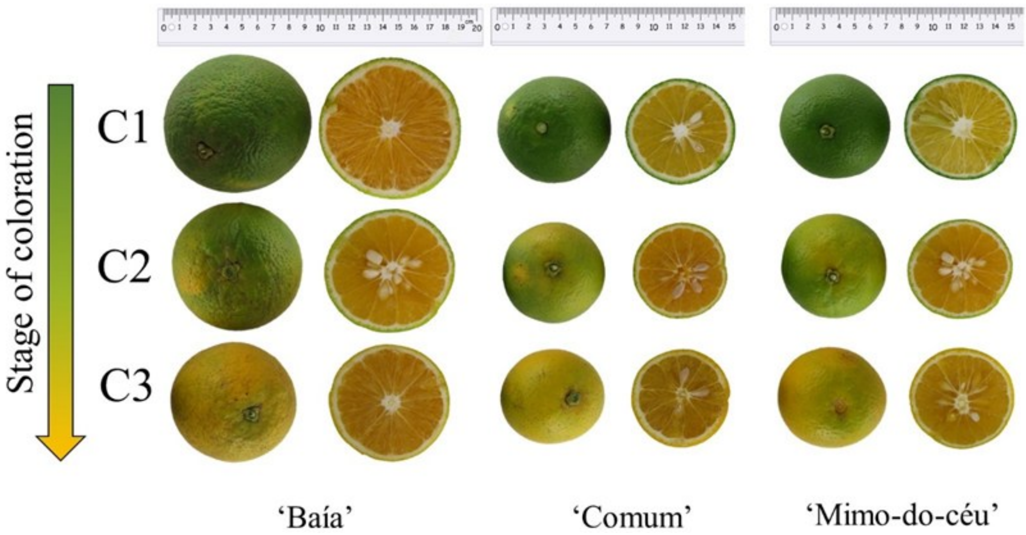

Figure 1. Appearance of whole and halved fruits of 'Baía', 'Comum' and 'Mimo-do-Céu' oranges harvested in three maturity stages (C1 - predominantly green; C2 - green/yellow; C3 – yellow), based on the color of the peel, from the Territory of Borborema – PB, Brazil.

The experiment was conducted in a completely randomized design (CRD) and arranged in a simple 3x3 factorial scheme, with three orange cultivars (Baía, Common and Mimo do Céu) and three stages of peel coloration (C1, C2 and C3). For the physical characteristics, 60 fruits per maturity stage of each cultivar were used, each fruit being considered a replication, totaling, therefore, 60 replications per maturity stage and 180 fruit per cultivar. For the physicochemical characteristics, bioactive compounds, and antioxidant activity, 4 replications of 15 fruit per maturity stage were used for each cultivar.

In the laboratory, the physical characteristics evaluated for fruits of each cultivar were: fresh mass (g), obtained with the help of a semi analytical scale; longitudinal and transverse diameters (mm) measured with the aid of a caliper; juice yield, determined by the ratio between the total fresh fruit mass and the mass of the peel, seeds and pulp residue (%); firmness (N), determined in two points in the equatorial region of each fruit with a bench penetrometer, and the evolution of the peel color through an objective evaluation, using a Minolta digital calorimeter, which expresses the color in the parameters: L* (corresponds to the clarity/ brightness); a* (defines the transition from the green color (-a*) to the red color (+ a*) and b* (represents the transition from the blue color (-b*) to the yellow color (+ b*), and the farther from the center (= 0), the more saturated is the color. Afterwards, these parameters (L, a *, and b *) were used to calculate the color index (CI), which indicates the degree of green/yellow variation of the fruits, according to the equation proposed by Camelo and Gomes (2004), $IC=2000^{*}(a^*)/L^* \sqrt{(a^*)^2 + (b^*)^2}$.

For the physicochemical evaluations, bioactive compounds and antioxidant activity, the fruits were separated into four replications of 15 fruits. The evaluations after extraction and homogenization of the juice were: pH; soluble solids (SS%); titratable acidity (AT%) and SS/AT ratio by the quotient between SS and TA, according to the methodologies described by Silva et al. (2014), and ascorbic acid content (AA mg.100 g^{-1}) as measured by titration with DFI (STROHECKER; HENNING, 1967).

The total extractable polyphenols content (Galic Acid Equivalent – GAE) and the antioxidant activities by the sequestration capacities of the 2,2'-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid radical cation ($ABTS^+$) and the stable free radical 2,2 -diphenyl-1-picrylhydrazil (DPPH) were evaluated in the juice and albedo, according to methodology described by Dantas et al. (2015) and the results were expressed as μM Trolox (Trolox Equivalent - TE) g^{-1} fresh weight. The antioxidant activity was determined by the DPPH method, according to Rufino et al. (2010) and its antioxidant capacity was expressed as the antioxidant concentration required to reduce the amount of free radicals by 50% (EC_{50}), with the values expressed in g fruit/g DPPH.

The data of the evaluations were submitted to analysis of variance (ANOVA) and the means of the varieties, the stages, and the unfolding of the interaction x variety were submitted to the Tukey test up to 5% probability. In order to perform these analyzes, the Emmeans software package R version 5.1 was used (LENTH, 2018).

RESULTS AND DISCUSSION

The physical changes occurring during the maturation of the orange cultivars evaluated are presented in Table 1. Notably, the color index (CI) of the fruits evolved significantly with the advance of maturation, indicating that the coloration transformed from green to completely yellow. However, this evolution was less pronounced in cultivar Baía, whose CI increased from -6.87 for fruit harvested in the C1 stage (green coloration) to 3.23 in the C3 stage (yellow). For Comum orange, the CI varied from -10.45 (at C1) to 3.83 (at C3). In turn, the most pronounced transformation in the coloration was observed for Mimo-do-Céu, with a CI spanning from 14.93 (at C1) to 4.85 (at C3). These changes correspond to the transition of the coloration of the peel, from green to yellow/orange, due to the degradation of chlorophyll and synthesis of carotenoid pigments (DING et al., 2015). During maturation, changes in fruit color are expected, and there may be an expressive increase in the CI from the intermediate phase of ripening (DANTAS et al., 2015).

Table 1. Physical characteristics of Baía, Comum e Mimo-do-Céu orange fruit cultivars harvested in three maturity stages, based on the color of the peel.

		Maturity Stage	Color index	Length (mm)	Diameter (mm)	Fresh weight (g)	Firmness (N)
Cultivar	Baía	C1	-6.87 cA	89.41 aA	86.63 aA	363.23 aA	49.14 aA
		C2	-2.17 bA	81.72 bA	80.03 bA	283.41 bA	40.15 aA
		C3	3.23 aA	79.91 bA	78.69 bA	263.13 bA	27.09 bA
		Mean	-1.94	83.68	81.78	303.26	38.79
		CV %	31.28	10.14	9.68	17.34	45.64
	Comum	C1	-10.45 cB	73.79 aB	77.55 aB	143.71 aB	27.12 aB
		C2	-4.02 bB	59.02 bB	61.61 bB	125.03 aB	20.7 abB
		C3	3.83 aA	57.63 bC	60.63 bC	113.86 aC	16.18 bB
		Mean	-3.54	63.48	66.60	127.53	21.33
		CV %	36.25	8.09	8.61	18.12	44.7
	Mimo-do-Céu	C1	-14.93 cC	60.84 aC	64.06 aC	129.53 aB	44.97 aA
		C2	-4.68 bB	62.44 aB	65.13 aB	144.07 aB	19.88 bB
		C3	4.85 aA	62.81 aB	66.69 aB	148.62 aB	25.53 bA
		Mean	-4.92	62.03	65.29	140.74	30.12
		CV %	38.41	6.66	5.91	17.69	47.54

In the column, means followed by the same lowercase letter within each cultivar among maturity stages, and by the same capital letter for each maturity stage among cultivars, do not differ, by the Tukey test: $p \leq 0.05$. n = 60.

For 'Baía' and 'Comum' oranges, the largest fruit, based on length (89.41 and 73.79 mm) and diameter (86.63 and 77.55 mm), were observed in the first maturity stage (C1). For 'Mimo-do-Céu', the length and diameter did not differ among the three maturity stages evaluated. However, according to the CEAGESP classification standards (2011), the oranges of these three cultivars from the Borborema Territory are classified as medium-sized, and, under this criteria, meet the demands of more competitive markets for quality. Size is one of the characteristics used by the CEAGESP to classify fruits by caliber and, thus, define the marketing prices.

The overall mean fresh weight of the fruits was 303.26 g, and the highest was found for 'Baía' orange, with 363.23 g in the C1 stage (Table 1). 'Baía' fruit presented a reduction in fresh weight during maturation. Conversely, the fresh weight of oranges of the cultivars Comum and Mimo-do-Céu did not differ between maturity stages, with mean values of 127.53 and 140.74 g, respectively. Growing conditions, soil, water availability and the supply of the essential nutrients for the crop influence the fresh weight, size and general quality of the fruits (LADO; GAMBETTA; ZACARIAS, 2018).

Regarding the firmness, oranges harvested in the C1 stage were firmer, mainly for 'Baía' (49.14 N) and 'Mimo do Céu' (44.97 N), and the less firm was 'Comum' in the C1 (27.12 N) and C3 (16.18 N) maturity stages. Possibly, these differences in firmness among cultivars are associated with the different thicknesses and polymeric structure of the peel (LADO; GAMBETTA; ZACARIAS, 2018), among other factors. For 'Ponkan' mandarin at maturity stage C3, Silva et al. (2014) reported a mean firmness of 11.78 N. In the present study, the orange firmness declined as maturity advanced. This effect can be justified because the firmness is directly related to the solubilization of pectic substances present in the orange albedo (RODRIGO et al., 2013) and so the firmer the fruit, the less these polymers are solubilized (DING et al., 2015). Firmness is one of the most important factors in defining the amount of fruit per box during packaging operations, in addition to the types of packaging that can be used for the transport and storage (PAREEK, 2016).

The juice yield (Table 2) did not differ among maturity stages within the cultivars. However, Baía orange showed the lowest juice yield (43%), and the highest yield was derived from Mimo-do-Céu (66.83%) in the C3 stage. The percentage of juice yields for 'Baía' and 'Comum' oranges are close to the pulp yields of 48.6 to 53.8%, reported by Emmanouilidou and Kyriacou (2017) for 'Delta' orange from different rootstocks, at different maturity stages. In comparison, 'Mimo-do-Céu' orange, herein, was far superior regarding this characteristic. In addition, for these three cultivars from the Borborema Territory, evaluated at the three maturity stages, the juice yield was higher than that established by the CEAGESP (2011) in the Classification Standards for Table Citrus. A high juice yield in oranges is extremely important, both for the juice industry and for fresh consumption, and may even add value to the fruit (PAREEK, 2016), as a result of this desirable characteristic for consumption, which impacts positively on the yields of the industrialized product and consumer satisfaction of fresh fruit.

Table 2. Physicochemical characteristics of Baía, Comum e Mimo-do-Céu orange fruit cultivars harvested in three maturity stages, based on the color of the peel.

		Maturity Stage	Juice (%)	pH	Soluble Solids (%)	Titratable Acidity (g.100g¹)	SS/TA
Cultivar	Baía	C1	37.44 aB	3.73 aB	9.31 cA	0.52 bB	17.90 aB
		C2	46.96 aB	3.59 abB	10.94 bA	0.62 abB	17.65 aB
		C3	45.10 aB	3.52 bB	12.31 aAB	0.65 aB	18.93 aB
		Mean	43.17	3.61	10.85	0.60	18.16
		CV %	9.29	2.74	3.28	6.05	6.90
	Comum	C1	52.98 aA	3.28 aC	8.75 cAB	1.07 aA	8.18 aB
		C2	50.83 aB	3.36 aC	9.94 bB	0.83 bA	11.98 aB
		C3	50.97 aB	3.27 aC	12.00 aB	1.04 aA	11.54 aB
		Mean	51.59	3.30	10.23	0.98	10.57
		CV %	8.81	1.40	9.95	9.34	7.80
	Mimo-do-Céu	C1	57.95 aA	5.88 aA	8.06 bC	0.07 aC	115.14 bA
		C2	62.13 aA	5.76 aA	11.43 bA	0.07 aC	163.29 aA
		C3	66.83 aA	5.85 aA	13.13 aA	0.10 aC	131.30 bA
		Mean	62.30	5.83	10.88	0.08	136.58
		CV %	8.98	1.60	5.76	21.78	7.21

In the column, means followed by the same lowercase letter within each cultivar among maturity stages, and by the same capital letter for each maturity stage among cultivars, do not differ, by the Tukey test: $p \leq 0.05$. n = 4.

The pH of the 'Baía' orange decreased during maturation from 3.73 (at C1) to 3.52 (at C3), but did not differ among the maturity stages for 'Common' and 'Mimo-do-Céu', with mean pH values of 3.30 and 5.83, respectively. Considering that the lower the pH value, the more acidic the orange, 'Comum' was the most acidic while 'Mimo-do-Céu' was the less acidic orange. 'Mimo-do-Céu' is classified as a orange of the group, characterized by low acidity (SOUSA et al., 2016), which explains why its pH is much higher than those of the other evaluated cultivars.

The soluble solids (SS%) content, an indirect indicator of the sugar level of the fruit, increased significantly as maturation advanced. For 'Baía' orange, the SS content increased from 9.31 to 12.31%, 'Comum' from 8.75 to 12%, and 'Mimo-do-Céu' from 8.06 to 13.13%, respectively. The CEAGESP (2011) Standards for Table Oranges establish a minimum SS of 10% for commercialization. Thus, at the more advanced maturity stages (C2 and C3), orange cultivars Baía and Mimo-do-Céu from the Borborema Territory exceed the CEAGESP standards in these criteria, whereas, for Comum, only the C3 stage complied with this regulation, which characterizes this cultivar as acid and not sweet, and, in turn, explains its lower SS/TA ratio, and, consequently, lower perceived sweetness. In this sense, according to Ding et al. (2015); and Pareek (2016), the SS content may vary depending on several factors, such as the cultivar, the climate, the soil and the growing region.

The TA of 'Baía' orange increased during maturation from 0.52 g citric acid 100 g^{-1} (at C1) to

0.65 g 100 g^{-1} (at C3). 'Comum' recorded the highest TA. 'Mimo-do-Céu' presented the lowest, and the values did not differ according to the stage of maturity, ranging from 0.07 (C1) to 0.10 (C3) g citric acid 100 g^{-1}. As mentioned above, 'Mimo-do-Céu' is a sweet orange with low acidity compared with 'Lima' orange, which is considered the sweetest of this group (SOUSA et al., 2016). Indeed, Couto and Canniatti-Brazaca (2010); and Silva et al. (2016) reported TA values for 'Lima' orange of 0.23 and 0.34 g citric acid 100 g^{-1}, respectively, well above that of 'Mimo-do-Céu' of the Borborema Territory, evaluated in this work.

For the SS/TA ratio, Baía and Comum cultivars did not differ among the three maturity stages. On the contrary, 'Mimo-do-Céu' orange showed a significant increase in the SS/TA from stage C1 (119.62) to stage C2 (172.97). In 'Ponkan' mandarin, Silva et al. (2014) used the SS/TA ratio to describe the maturity and quality for acceptance and consumption of this citrus fruit. In this context, 'Comum' presented the lowest SS/TA ratio (10.60) while 'Mimo-do-Céu' showed a much higher SS/TA ratio (143.99), characterizing its very sweet and low acid flavor.

The ascorbic acid content (Table 3) of 'Baía' and 'Comum' oranges increased from 40.51 and 42.63 mg 100 g^{-1} at the C1 maturity stage, to 49.17 and 49.24 mg 100 g^{-1} at C3, respectively. Conversely, 'Mimo-do-Céu' orange differed from the others since its ascorbic acid content decreased during maturation. However, this cultivar was distinguished by having the highest mean content of vitamin C (50.26 mg 100 g^{-1}) (ascorbic acid + dehydroascorbic acid), which was more than that reported for 'Lima' orange (*C. sinensis* (L.) Osbeck) in the Brazilian Table of Food Composition (NEPA, 2011), of 41.3 mg 100 mL^{-1} of juice.

The ascorbic acid contents of the three cultivars examined in this study were higher than that in 'Valencia' orange juice (29.2 to 39.8 mg 100 g^{-1}; ESCOBEDO-AVELLANEDA et al., 2014), lower than those in 'Pêra', 'Lima', 'Natal', 'Valencia' and 'Baía' oranges (62.50, 64.58, 84.03, 78.47 and 80.03 mg 100 g^{-1}, respectively; COUTO; CANNIATTI-BRAZACA, 2010) but close to the vitamin C content reported by Lado, Gambetta and Zacarias (2018), which ranged from 46 to 60 mg 100 g^{-1} in sweet orange varieties. These variations can be due to the region of cultivation, cultural management, climate and year of production, besides the degree of maturation of the fruit (ALÓS; RODRIGO; ZACARÍAS, 2014; COUTO; CANNIATTI-BRAZACA, 2010; YOO; MOON, 2016).

Table 3. Ascorbic acid and total extractable polyphenols (TEP) content of the juice and albedo portions of Baía, Comum e Mimo-do-Céu orange fruit cultivars harvested in three maturity stages, based on the color of the peel.

		Maturity Stage	Ascorbic acid (mg.100g¹)	TEP (mg GAE.100g^{-1}) Juice	TEP (mg GAE.100g^{-1}) Albedo
Cultivar	Baía	C1	40.51 bB	19.82 bA	138.75 bC
		C2	46.92 aA	23.37 abA	159.09 bC
		C3	49.17 aA	23.88 aB	211.80 aA
		Mean	45.53	22.35	169.88
		CV %	3.74	12.21	6.14
	Comum	C1	42.63 bB	21.41 cA	216.19 aA
		C2	44.55 abA	26.74 bA	228.99 aA
		C3	49.24 aA	31.26 aA	234.61 aA
		Mean	45.47	26.47	226.60
		CV %	4.74	5.95	9.36
	Mimo-do-Céu	C1	53.19 aA	19.84 cA	172.58 bB
		C2	46.19 bA	26.56 bA	189.43 bB
		C3	47.38 bA	31.18 aA	222.20 aA
		Mean	50.26	25.86	194.73
		CV %	9.83	7.89	5.37

In the column, means followed by the same lowercase letter within each cultivar among maturity stages, and by the same capital letter for each maturity stage among cultivars, do not differ, by the Tukey test: $p \leq 0.05$. n = 4. GAE = Galic Acid Equivalent.

The total extractable polyphenols (TEP) of the juice and albedo increased with the maturation of the evaluated cultivars (Table 3). In the juice of 'Baía', 'Comum' and 'Mimo-do-Céu' oranges, the TEP content increased from 19.82, 21.41 and 19.84 mg (at C1) to 23.88, 31.26 and 31.28 mg GAE 100 g^{-1} (at C3), respectively, denoting the increased content of compounds with claimed functional properties (CIRMI et al., 2016) during maturation.

In the fruit albedo, the TEP contents ranged from 138.75 to 211.80 mg 100 g^{-1} for 'Baia', and from 172.58 to 222.20 mg 100 g^{-1} for 'Mimo-do-Céu', respectively. The TEP content in 'Comum' orange, although not differing among maturity stages, increased from 216.19 (at C1) to 234.61 mg GAE 100 g^{-1} (at C3), which was the cultivar that showed the highest overall PET contents among the cultivars analyzed in this study. These results corroborate with Wang et al. (2016), who verified a significant increase in the TEP content in the citrus epicarp (albedo + flavedo). These data also corroborate those detected in the epicarp of different orange cultivars, which ranged from 104.2 to 223.2 mg 100 g^{-1} (ZEFANG et al., 2016), and from 66.10 to 407.55 mg 100 g^{-1} (GHASEMI; GHASEMI; EBRAHIMZADEH, 2009). However, these amounts are lower than those indicated in 'Valencia' orange albedo that ranged from 553.1 to 730.0 mg 100 g^{-1} (ESCOBEDO-AVELLANEDA et al., 2014), yet close to that observed in 'Sweet' orange epicarp, of 288.17 mg 100 g^{-1} (CASQUETE et al., 2015).

For total antioxidant activity (TAA) evaluated by the $ABTS^{\bullet+}$ method, there was no significant difference among maturity stages in the juice of the oranges, independently of the cultivar (Table 4). However, 'Mimo-do-Céu' presented the highest value, with 3.33 μM TE g^{-1} at C1 stage, and a general mean of 2.91 μM TE g^{-1}, possibly explained by its higher content of ascorbic acid and TEP than the other cultivars. For 'Baía' and 'Comum' oranges, the mean values were 2.04 and 1.91 μM TE g^{-1}, respectively.

Given that the highest TAA by the $DPPH^{\bullet}$ assay is characterized by the lowest content of material required to capture 1 g of this radical, the TAA of the juice, although it increased with maturation, was very low (higher values), notably for cultivar 'Mimo-do-Céu'. In contrast, the juice of 'Comum' orange at the C3 maturity stage stood out as displaying the highest TAA (lower value) among the cultivars considered (Table 4).

The three major groups of compounds responsible for the beneficial effects attributed to the natural antioxidants found in fruits and vegetables are ascorbic acid, phenolics and carotenoids (ALVES et al., 2010). The phenolic compounds present in plants have recognized beneficial effects that contribute to preventing against degenerative diseases (CIRMI et al., 2016; DEL RIO et al., 2013; ZOU et al., 2016). Fruits and vegetables have phenolic contents that vary, depending on the species, genetics, environmental conditions, agronomic management and maturity stages (LADO; GAMBETTA; ZACARIAS, 2018), among other factors. Thus, the lowest TAA by the $DPPH^{\bullet}$ method in 'Mimo-do-Céu' orange juice might be due to the low content of PET and other antioxidants.

In the albedo, 'Baia' cultivar presented the highest TAA by the $ABTS^{\bullet+}$ radical assay, followed by 'Comum' and 'Mimo-do-Céu', with 26.27, 17.76 and 16.04 μM TE g^{-1}, respectively. However, there was no significant difference in TAA between maturity stages when comparing 'Baía' with 'Comum' and 'Mimo-do-Céu' oranges. Although, the TAA values of 'Baia' albedo, in all three maturity stages, were superior to the other oranges. Casquete et al. (2015) noted 3.4 mg TE g^{-1} in sweet orange epicarp, well below that of the oranges evaluated herein, which may be due to edaphoclimatic conditions, cultural practices and other factors (LADO; GAMBETTA; ZACARIAS, 2018), indicating the ability of the Borborema Territory to produce oranges of distinct functional potential.

According to Ferreira, Silva and Nunes (2018), the high antioxidant activity of citrus peel extracts may be explained by their phenolic composition, such as hesperidin, naringin, rutin, and caffeic and chlorogenic acids. As mentioned by Bilgiçli, Aktaş and Levent (2014); and Liew et al. (2018), the bioactive phytochemicals present in the citrus peel can be exploited for various applications, such as the extraction of natural antioxidants, food additives and dyes for the food industry. These antioxidants act to protect against the accumulation of reactive oxygen species, eliminating them from the system through irreversible dehydrogenation. For instance, ascorbic acid reacts directly with O_2^-, HOO^- and OH^-, eliminating $^1O_2$ (ZOU et al., 2016). Furthermore, recent research suggests that *C. reticulata* peel has therapeutic potential and a chemopreventive effect against breast cancer (FERREIRA; SILVA; NUNES, 2018). In this sense, the albedo of the oranges produced in the Borborema Territory could add value to the marketed product, in light of its highlighted functional potential.

Table 4. Antioxidant activity of juice and albedo of orange fruit of Baía, Comum e Mimo-do-Céu orange cultivars harvested in three maturity stages, based on the color of the peel, by the $ABTS^{\bullet+}$ and $DPPH^{\bullet}$ methods.

		Maturity	$ABTS^{\bullet+}$ (µM TE.g^{-1})		$DPPH^{\bullet}$ - EC_{50} (g pulp.g DPPH^{-1})	
		Stage	Juice	Albedo	Juice	Albedo
Cultivar	Baía	C1	1.78 aB	26.76 aA	5777.43 aB	1704.98 bB
		C2	2.54 aA	25.22 aA	4489.99 aB	2225.82 aAB
		C3	1.80 aA	26.84 aA	4599.09 aB	1913.04 abA
		Mean	2.04	26.27	4955.50	1947.95
		CV %	12.43	5.8	14.7	14.18
	Comum	C1	1.71 aB	15.82 bB	4393.76 aB	2387.04 abA
		C2	1.85 aA	17.21 abB	4172.96 aB	2578.69 aA
		C3	2.17 aA	20.25 aB	2907.99 aC	1976.35 bA
		Mean	1.91	17.76	3824.90	2314.03
		CV %	15.06	13.83	21.63	15.11
	Mimo-do-Céu	C1	3.33 aA	15.51 abB	13263.15 aA	2717.75 aA
		C2	2.62 aA	14.32 bB	9591.76 bA	2020.30 bB
		C3	2.76 aA	18.30 aB	6422.31 cA	1700.74 bA
		Mean	2.91	16.04	10492.40	2146.26
		CV %	12.44	12.07	11.95	8.48

In the column, means followed by the same lowercase letter within each cultivar among maturity stages, and by the same capital letter for each maturity stage among cultivars, do not differ, by the Tukey test: $p \leq 0.05$. n = 4. TE = Trolox Equivalent.

By the $DPPH^{\bullet}$ method, the antioxidant activity (TAA) of the juice of Baía and Comum cultivars did not differ among maturity stages, with general means of 4955.50 and 3824.90 g pulp g DPPH^{-1}, respectively. For Mimo-do-Céu, the EC_{50} significantly decreased as maturation progressed, presenting 13263.15 (at C1) to 6422.31 g pulp g DPPH^{-1} (at C3), indicating that the TAA increased about two-fold during maturation. In general, the increase in antioxidant capacity with maturation substantiates the findings of Wang et al. (2016) that also verified an increase in the antioxidant activity as maturation evolved, as much in the juice as in the peel of citrus.

Although much higher than for the juice, the albedo of ‘Baía’ and ‘Comum’ oranges at C2 stage, presented the lowest antioxidant activity by the $DPPH^{\bullet}$ radical scavenging assay, requiring 2225.82 and 2578.69 g of pulp, respectively, to eliminate 1 g of DPPH. The albedo of ‘Mimo-do-Céu’ had a comparatively lower EC_{50} value (1700.74 g pulp g DPPH^{-1}) and, consequently, higher antioxidant activity at the C3 stage. From literature studies, the residues of the citrus agroindustry contained TAA values of 11035 µM TE g^{-1} (BARBOSA; RUVIARO; MACEDO, 2018), and 9188 µM TE g^{-1} (MADEIRA JR; MACEDO, 2015) whereas, in citrus peels, the $DPPH^{\bullet}$ radical scavenging activity ranged from 8.35 to 18.20 mg TE g^{-1} (LIEW et al., 2018), depending on the extraction technique. These differences may be a result of the different analytical protocols of the extraction method, production region, cultivar and maturation stage (FERREIRA; SILVA; NUNES, 2018).

Antioxidants act on free radicals through two main mechanisms: (i) transfer of hydrogen atoms, wherein the antioxidant donates hydrogen atoms to stabilize the free radical species, preventing them from progressing in the reactions, and (ii) by transferring electrons, so that free radicals are reduced by the donation of an electron from antioxidant compounds (CRAFT et al., 2012).

The antioxidant activity in orange depends on the cultivar and maturity stage of the fruit. In addition, the change in antioxidant activity is related to the metabolism of polyphenols, ascorbic acid, flavonoids and carotenoids (BARBOSA; RUVIARO; MACEDO, 2018; WANG et al., 2016). As Zou et al. (2016) stated, pre-/postharvest and processing factors influence the chemical structure and antioxidant capacity of citrus fruits. This activity further depends on the composition of the extract, as well as on the conditions and mechanisms of the test used (LIEW et al., 2018).

CONCLUSION

'Baía' and 'Mimo-do-Céu' oranges presented quality parameters that fit into the CEAGESP standards. During maturation, the firmness decreased, and the SS, TEP and TAA of the juice and albedo increased. 'Baía' orange had the largest size and fresh weight. However, it presented the lowest juice yield, due to the high thickness of the peel, leading to a greater amount of residue that could be used for the extraction of bioactive compounds since the albedo presented much higher functional potential. In general, the albedo presented about eight-fold as much TEP than the juice, and this meant a higher TAA in that portion, which was the most functional aspect of the fruit, especially for 'Baía' orange. These results highlight the potential of the Borborema Territory in producing differentiated oranges with high functional potential.

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