Ascorbic acid and pectin in different sizes and parts of citric fruits

Ácido ascórbico e pectina em diferentes partes de frutas cítricas de vários tamanhos

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Abstract

Citric fruits - in natura, as frozen pulp or even as juice - are one of the most important Brazilian exportation products. They are a source of ascorbic acid – a potent antioxidant, and pectin, which is used in the food industry and is an important dietary fiber. This project aims to quantify ascorbic acid and pectin contents in citric fruits, commercial oranges and tangerines, comparing them in sizes and varieties. Ascorbic acid amount was measured in juice comparing sizes, varieties and storage conditions, using a tritimetric method with 2.6-dichlorobenzenoindophenol indicator. Total and soluble pectin in each part of the fruits (peel, albedo, pulp and juice) were quantified using the polygalacturonic acid as a standard. Differences were found between the sizes. The highest content of vitamin C was found in the oranges (Bahia variety). Comparing the storage temperatures, the biggest loss was at room temperature. Albedo presented the highest content of pectin in all fruits. In juice, the total and soluble pectin contents increased as fruits size decreased. Oranges and tangerines differed in the amount of pectin.

Keywords: orange; tangerine; pectin; ascorbic acid; composition; size.

Resumo

Os produtos de frutas cítricas são de grande importância para as exportações do Brasil in natura, polpa congelada e ainda na forma de suco. São fonte de ácido ascórbico, potente antioxidante, e pectina, que é utilizada na indústria e também é importante fibra alimentar. A pesquisa teve como objetivo quantificar o ácido ascórbico em frutas cítricas, laranjas e tangerinas comerciais, comparando tamanhos e variedades. O teor de ácido ascórbico foi medido no suco comparando os tamanhos, variedades e condições de estocagem, usando método de titulação com 2,6-diclorobenzenoindofenol. A pectina total e solúvel foi quantificada em partes da fruta (casca, albedo, polpa e suco), sendo usado como padrão o ácido poligalacturônico. Foram encontradas diferenças entre tamanhos. As maiores quantidades de vitamina C foram encontradas nas laranjas (variedade Bahia). Comparando as temperaturas de estocagem, a maior perda ocorreu à temperatura ambiente. O albedo apresentou a maior quantidade de pectina em todos os frutos. No suco, o total de pectina solúvel e insolúvel aumentou com a diminuição do tamanho dos frutos. Laranjas e tangerinas diferiram quanto ao teor de pectinas.

Palavras-chave: laranja; tangerina; pectina; ácido ascórbico; composição; tamanho.

1 Introduction

Citric fruits are originally from Asia, especially from China and the Malaysian archipelago, and are of different shapes and colors. The fruiting occurs all year long, but mainly between April and September (GRUPO COLT, 2003).

There are several new citrus hybrids in the world (RAPISARDA et al., 2009). In Brazil, mutation of wild species has resulted in the production of an orange variety internationally known as Bahia orange or Washington Navel (HASSE, 1987; ASSOCIAÇÃO..., 2003).

Vitamin C, carotenoids, pectin and phenolic compounds are important components of citrus. The phenolic antioxidants of fruit juices protect the vitamin C content from oxidative degradation. The identifiable soluble phenolic compounds of orange are hesperidin and nanrirutin, but the major antioxidant is the ascorbic acid. Orange juice also contains carotenoids, mainly cryptoxanthis, lutein, anthoxanthin, violaxantin, which do not mix with the water soluble antioxidant components. Hesperidin and narirutin flavones are abundant in orange juice in a partially dissolved, partially suspended and partially colloidal form (DAUCHET et al., 2008; GHASEMI; GHASEMI; EBRAHINZADEH, 2009; XU et al., 2008).

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Among fruits and vegetables, citrus fruits are the ones with the highest pectin content in all their parts: peel, albedo, juice and pip (RAI et al., 2006).

Responsible for the firmness and texture of fruits and vegetables, pectin became important in food industries as gel forming and thickening agents (BRUMMELL, 2006; MAFRA et al., 2006). In food industries, pectic substances are widely used in the manufacture of jams, jellies, marmalades, and fruit preserves of all kinds, especially the natural pectin content of fruits, like orange peel (ZYKWINSKA et al., 2009).

There is a relationship between the consumption of fibers and the decrease of blood cholesterol (KANG et al., 2009).

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Pectin can alter the digestion and absorption of lipids (METZGER; BARNES; REED, 2009; OVODOV, 2009). The high methoxyl pectin is more effective than the low one for reducing blood cholesterol, 30-40 g reduce 10% of cholesterol level in blood (CIPRIANI et al., 2009; FIETZ; SALGADO, 1999; FRANCO, 2001). Piedade and Canniatti-Brazaca (2003) found out that fibers from leaves are not as effective, after comparing high methoxyl pectin and fibers from pineapple leaves in lowering of blood cholesterol.

This project aims to quantify the vitamin C contents in citric fruits, comparing sizes, varieties and storage conditions, and to compare the influence of varieties on the pectin levels of different citrus - in different parts and of different sizes.

2 Materials and methods

2.1 Material

Two dozen of each one of the following citrus varieties, in different sizes (small, medium and large), were used in this study. We also quoted their origin and collection date: Sample 1 – 'Pêra' orange; Sample 2 – 'Valência' orange; Sample 3 – 'Lima' orange; Sample 4 – 'Natal' orange; Sample 5 – 'Bahia' (Washington Navel) orange; Sample 6 – 'Ponkan' tangerine; Sample 7 – 'Murcote' tangor.

2.2 Methodology

Sample Standardization

All the samples were standardized by analyzing their proximal composition (water, ash, lipids, protein and carbohydrates) (ASSOCIATION..., 1995).

For these analyses, we used 6 fruits of each size (small, medium and large), except the peels. They were dried in stove (55 $^{\circ}$ C) and grinded before the analyses.

Determination of dietary fiber method

In these analyses, we used the albedo, pulp and seeds by Asp et al. (1983) method. It uses the α -amylase heat-stable enzyme (A-3306 Sigma^{**} St. Louis USA) to hydrolyze starch and pepsin (VETEC^{***} Rio de Janeiro RJ, Brazil) followed by pancreatin (From Porcine pancreas P-1625 Sigma^{***} St. Louis USA) for protein degradation.

For these analyses we used 6 fruits of each size (small, medium and large). They were dried in stove (55 °C) and grinded before the analyses.

Samples standardization

The maturation of samples was measured using total solid soluble (°Brix) and titratable acidity according to Pregnolatto (1985). The ratio between them was calculated.

The juice of three fruits was used after extraction and homogenization for each treatment.

Determination of Ascorbic acid

Ascorbic acid amount was measured in samples immediately after extraction of juice and after 24 hours. The storage was done at room temperature and at 4 °C in dark screw cap flask. Ascorbic acid was measured using a tritimetric method, 2.6-dichlorobenzenoindophenol indicator (JACOBS, 1958; LEME JUNIOR; MALAVOLTA, 1950).

The juice of three fruits was used after extraction and homogenization for each treatment.

Determination of pectin

Pectin (total and soluble) was quantified in juice, pulp, albedo and peel, through McCready and McComb (1952) method. Bitter and Muir (1962) technique was used for dosage, and the results were expressed in mg of polygalacturonic acid per 100 g of fresh fruit.

For all samples, we used 12 fruits of each size (small, medium and large), peeled and with all the parts separated manually, trying to keep the minimum of albedo in the peel and the most of it together with the pulp. The samples were dried in oven (55 $^{\circ}$ C) and then grinded. The juice was extracted manually and froze immediately.

Statistics

The delineation was made totally at random. The F Test was realized for average comparison and, if it were significant, the Tukey Test was performed - the SAS software (STATISTICAL..., 1996) was used. The significance level used was 5%.

3 Results and discusion

All the samples were of ripe fruits, but their different sizes were a result of factors such as water amounts (from soil, air, irrigation and rain), low temperatures, deficient or inappropriate plant nutrition, biological factors (plague, senile trees and excessive flowering) or tree location (BECERRA-RODRIGUEZ et al., 2008; LESTER; JIFON; ROGER, 2005; PESTANA et al., 2005).

The data showed by FCF (UNIVERSIDADE..., 2008), USDA (UNITED..., 2009), RLC/FAO (OFICINA...; FOOD..., 2004) and TACO/UNICAMP (UNIVERSIDADE..., 2006) are similar to the data found (Table 1) for some items of the fruits composition, but, in general, the results of this study were higher for items like proteins, ash and total fibers; the water amounts were lower and the lipids amounts were the nearest. 'Natal' orange stood out for its ash amounts. Lipids amounts in tangerine and tangor were higher than in three varieties of oranges, and the lipids amounts were similar in 'Valência' and 'Pêra'. The highest lipids amounts were found in 'Pêra' orange. For insoluble fibers, the highest amounts were found in 'Bahia' and 'Natal' oranges and in 'Ponkan' tangerine, although the lowest soluble fibers amounts were found in 'Natal' and 'Valência' oranges, too.

Changes in water amounts can occur because of long periods of rain and low temperatures, which can delay the fruits ripeness and influence their characteristics (Tables 1 and 2).

Table 2 shows smaller differences for water amounts between the sizes of tangerine and tangor, occurring only in oranges. The highest water amounts were found in the large size fruits and the lowest ones in the small size fruits, with significant differences in some varieties ($p \le 0.05$). The ash amounts were higher in the small size fruits, except in the 'Valência' orange. There were no statistical differences between sizes for 'Bahia' orange ($p \le 0.05$). A similar behavior is observed for lipids, the highest levels were detected in the smaller fruits and there were no significant statistical differences between the sizes, the same occurring in protein amounts. In this case, 'Lima' orange presented a reduction in the protein level despite the size increase; protein levels in 'Ponkan' tangerines were very close; and for 'Natal' orange, the medium sized fruits presented the highest values followed by the small sized ones and then, by the large sized. Culture treatments, pluviosity and weather conditions may influence these values (BECERRA-RODRIGUEZ et al., 2008; LESTER; JIFON; ROGER, 2005; PESTANA et al., 2005).

Analyzing the total fibers contents, the highest values were found in the small sized 'Pêra' and 'Lima' oranges.

Except for 'Bahia' orange, the soluble fibers content is lower than the insoluble one, as shown in Table 3. In most varieties, there was little values variation between the sizes. For oranges, the highest values for soluble fibers content were found in the small sized fruits; except for a few cases, there were no statistical differences ($p \le 0.05$) among the medium sized fruits. Tangerine soluble fibers content presented statistical differences (p \leq 0.05) between the sizes.

Table 3 shows the highest values for insoluble fibers content in the small sized oranges, and in the medium sized 'Ponkan' tangerine.

The varieties did not present significant differences in the total soluble solids contents (Table 4). The titratable acidity presented a significant difference ($p \le 0.05$) between the lime orange - with the lowest acid content, and 'Bahia' orange, which presented the highest titratable acidity.

Total solid soluble and titratable acidity in different sizes by variety are observed in Table 5.The medium and large sizes compared to the little size in lime oranges presented numerical differences. The large and medium sizes were harvested in rain season and lower temperature, retarding fruit maturation and altering the total soluble solids (Tables 4 and 5).

Sanchez-Moreno's et al. (2003) research on 'Valencia' variety found 11.3 soluble solids (°Brix at 20 °C), 1.12 % titratable acidity and 10.09 TSS/TTA levels. For 'Pera' variety, it was found a TSS of 10.43, a TTA of 2.2% and a TSS/TTA of 4.75, according to

Table 1. Proximal composition^{1,2} of Citrus fruits (g.100 g⁻¹).

Varieties	Water	Ash	Lipids	Protein	Insoluble Fiber	Soluble Fiber	HCO ³
Pêra	84.56 ± 3.1^{a}	$0.65\pm0.0^{\rm b}$	$0.32\pm0.1^{\text{abc}}$	1.61 ± 0.1^{a}	6.54 ± 1.1^{a}	2.45 ± 0.3^{abc}	3.86
Valência	89.21 ± 0.6^a	$0.73\pm0.2^{\mathrm{b}}$	0.31 ± 0.0^{abc}	$0.87 \pm 0.0^{\text{cde}}$	3.78 ± 0.8^{ab}	$0.39 \pm 0.2^{\circ}$	4.70
Lima	$86.27 \pm 3.3^{\mathrm{a}}$	$0.52\pm0.0^{\rm b}$	$0.18\pm0.1^{\circ}$	$1.03 \pm 0.2^{\text{bcd}}$	4.37 ± 2.2^{ab}	$1.32 \pm 1.6^{\text{abc}}$	6.30
Natal	$88.74\pm0.4^{\rm a}$	$1.49\pm0.4^{\rm a}$	$0.25\pm0.0^{\mathrm{bc}}$	$0.68\pm0.1^{\circ}$	1.77 ± 0.1^{b}	$0.84\pm0.1^{\mathrm{bc}}$	6.24
Bahia	$83.87 \pm 0.7^{\mathrm{a}}$	$0.67\pm0.0^{\mathrm{b}}$	$0.15\pm0.1^{\circ}$	$1.28\pm0.1^{\rm b}$	$3.12\pm0.5^{\rm b}$	3.08 ± 0.2^{a}	7.24
Ponkan	$88.36 \pm 1.0^{\rm a}$	$0.54\pm0.0^{\rm b}$	0.45 ± 0.1^{ab}	$0.83\pm0.0^{\rm de}$	$2.96\pm0.3^{\rm b}$	$1.04 \pm 1.1^{\mathrm{abc}}$	5.82
Murcote	84.28 ± 1.8^{a}	0.51 ± 0.1^{b}	0.45 ± 0.1^{a}	$1.15\pm0.0^{\mathrm{bc}}$	4.28 ± 0.3^{ab}	2.53 ± 0.4^{ab}	6.80

¹Average of the three sizes (small, medium and large) \pm standard deviation. ²Different lowercase letters in a column indicate statistic differences (p \leq 0.05) between the varieties, for each item (water, ash, lipids, protein, insoluble fiber, soluble fiber and carbohydrates). ³Carbohydrates (HCO).

Table 2. Citrus fruits proximal composition^{1,2} by different sizes without peel (g.100 g^{-1}).

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Vari	eties	Water	Ash	Lipids	Protein	Dietetic fiber	HCO ³
Pêra	Large	87.26 ± 0.0^{a}	$0.64 \pm 0.0^{\mathrm{b}}$	$0.23\pm0.0^{\mathrm{b}}$	1.61 ± 0.1^{a}	8.08	2.18
	Medium	$85.23\pm0.3^{\rm b}$	$0.61 \pm 0.0^{\circ}$	$0.26\pm0.0^{\mathrm{b}}$	1.51 ± 0.0^{a}	8.33	4.06
	Small	$81.18\pm0.4^{\circ}$	0.70 ± 0.0^{a}	0.48 ± 0.1^{a}	1.72 ± 0.2^{a}	10.57	5.35
Valência	Large	89.84 ± 0.1^{a}	0.95 ± 0.1^{a}	0.30 ± 0.0^{a}	$0.92\pm0.0^{\mathrm{a}}$	4.69	3.40
	Medium	88.78 ± 0.1^{b}	$0.67 \pm 0.0^{\mathrm{b}}$	0.33 ± 0.0^{a}	$0.85\pm0.0^{\text{a}}$	3.53	5.84
	Small	$89.02\pm0.2^{\rm b}$	$0.56 \pm 0.0^{\mathrm{b}}$	0.31 ± 0.1^{a}	$0.85\pm0.0^{\mathrm{a}}$	4.40	4.86
	Large	88.88 ± 0.1^{a}	$0.47\pm0.0^{\mathrm{b}}$	$0.14\pm0.0^{\circ}$	$0.84\pm0.0^{\circ}$	3.60	6.07
Lima	Medium	87.41 ± 0.1^{b}	0.54 ± 0.0^{a}	$0.17 \pm 0.0^{\mathrm{b}}$	$1.02\pm0.0^{\mathrm{b}}$	3.54	5.57
	Small	$82.51 \pm 0.1^{\circ}$	0.55 ± 0.0^{a}	$0.24\pm0.0^{\text{a}}$	1.24 ± 0.1^{a}	9.94	5.52
Natal	Large	89.22 ± 0.2^{a}	1.62 ± 0.2^{ab}	$0.21 \pm 0.0^{\mathrm{b}}$	$0.57 \pm 0.0^{\circ}$	2.46	5.92
	Medium	$88.58\pm0.1^{\rm b}$	$1.07 \pm 0.3^{\mathrm{b}}$	0.25 ± 0.0^{ab}	$0.76\pm0.0^{\mathrm{a}}$	2.51	6.83
	Small	$88.42\pm0.2^{\rm b}$	1.77 ± 0.2^{a}	$0.29\pm0.0^{\mathrm{a}}$	$0.70\pm0.0^{\mathrm{b}}$	2.86	5.96
Bahia	Large	84.65 ± 0.2^{a}	0.71 ± 0.0^{a}	$0.06 \pm 0.0^{\mathrm{b}}$	1.32 ± 0.1^{a}	5.68	7.58
	Medium	83.66 ± 0.1^{b}	0.63 ± 0.1^{a}	0.23 ± 0.1^{a}	1.22 ± 0.0^{a}	6.16	8.10
	Small	$83.29\pm0.0^{\rm b}$	0.66 ± 0.1^{a}	$0.16\pm0.0^{\mathrm{ab}}$	1.31 ± 0.1^{a}	6.76	6.03
Ponkan	Large	87.26 ± 0.1^{b}	0.56 ± 0.0^{a}	0.49 ± 0.0^{a}	$0.86\pm0.0^{\text{a}}$	5.04	5.79
	Medium	$88.95\pm0.2^{\rm a}$	$0.52\pm0.0^{\mathrm{b}}$	$0.38\pm0.0^{\mathrm{b}}$	$0.80\pm0.0^{\rm b}$	3.33	6.03
	Small	88.87 ± 0.1^{a}	0.55 ± 0.0^{ab}	$0.48\pm0.0^{\mathrm{a}}$	$0.82\pm0.0^{\mathrm{ab}}$	3.65	5.63
Murcote	Large	85.49 ± 0.0^{a}	$0.35\pm0.1^{\mathrm{b}}$	$0.40\pm0.0^{\mathrm{b}}$	1.09 ± 0.1^{a}	6.43	6.24
	Medium	$82.16 \pm 0.0^{\circ}$	0.56 ± 0.0^{a}	0.50 ± 0.0^{a}	$1.17 \pm 0.0^{\text{a}}$	7.53	8.08
	Small	$85.18\pm0.0^{\rm b}$	0.61 ± 0.0^{a}	$0.46\pm0.0^{\mathrm{a}}$	$1.18\pm0.2^{\mathrm{a}}$	6.48	609

¹Average of the three repitition \pm standard deviation. ²Different lowercase letters in a column indicate statistic difference (p \leq 0,05) between the sizes (large, medium and small), for the same variety, for each item (water, ash, lipids, proteins, dietetic fiber and carbohidrate). ³Carbohydrates (HCO).

Table 3. Soluble and insoluble dietary fiber ^{1,2} in Citrus fruits without peel (g.100 g ^{-1}).

Varieties		Soluble Fiber	Insoluble Fiber	Var	Varieties		Insoluble Fiber
Pêra	Large	2.21 ± 0.2^{a}	5.87 ± 0.2^{b}	Natal	Large	$0.75\pm0.1^{\mathrm{b}}$	$1.71 \pm 0.0^{\rm b}$
	Medium	2.42 ± 0.3^{a}	$5.91\pm0.5^{\mathrm{b}}$		Medium	$0.83\pm0.0^{\rm ab}$	$1.68\pm0.0^{\mathrm{b}}$
	Small	2.73 ± 0.5^{a}	7.84 ± 0.7^{a}		Small	$0.93\pm0.0^{\mathrm{a}}$	1.93 ± 0.1^{a}
Valência	Large	$0.15\pm0.0^{\rm b}$	4.44 ± 0.2^{a}	Bahia	Large	$2.84\pm0.2^{\rm b}$	$2.84\pm0.1^{\rm b}$
	Medium	$0.57\pm0.0^{\mathrm{a}}$	$2.96\pm0.0^{\mathrm{b}}$		Medium	3.29 ± 0.0^{a}	$2.87\pm0.0^{\rm b}$
	Small	$0.45\pm0.1^{\mathrm{a}}$	$3.95\pm0.3^{\mathrm{a}}$		Small	3.11 ± 0.2^{a}	3.65 ± 0.3^{a}
Lima	Large	$0.02\pm0.0^{\rm b}$	$3.58\pm0.0^{\mathrm{b}}$	Ponkan	Large	2.23 ± 0.2^{a}	$2.81\pm0.0^{\rm b}$
	Medium	$0.88\pm0.7^{\rm b}$	$2.66 \pm 0.0^{\circ}$		Medium	$0.07 \pm 0.0^{\circ}$	3.25 ± 0.0^{a}
	Small	3.06 ± 0.2^{a}	6.88 ± 0.2^{a}		Small	$0.83\pm0.0^{\mathrm{b}}$	$2.82\pm0.0^{\mathrm{b}}$
				Murcote	Large	$2.24\pm0.0^{\circ}$	4.19 ± 0.1^{a}
					Medium	2.95 ± 0.1^{a}	4.58 ± 1.1^{a}
					Small	$2.40 \pm 0.1^{\text{b}}$	$4.08\pm0.3^{\rm a}$

 1 Average of the three repitition \pm standard deviation. 2 Different lowercase letters in a column indicate statistic differences (p \leq 0,05) between the sizes (large, medium and small), for the same variety, for each item (insoluble and soluble fibers).

Souza et al. (2004). These variations are due to the climate and the maturation grade of the fruits.

'Pera', lime, 'Murcote' and 'Ponkan' fruits of small size presented the highest values of titratable acidity ($p \le 0.05$). According to Villas Boas et al. (2002), the same occurred to the total solid soluble, as presented for 4 varieties of oranges. 'Natal' variety had the highest amount of total solid soluble for the large sized, but with no significant difference. That was observed in other components, too. For tangerines, the highest total soluble solid amount corresponded to the medium sized fruits. Titratable acidity and total solid soluble amounts presented the same averages as those presented by Sugai et al. (2002) and Iemma et al. (1999) for 'Pêra' orange and Villas Boas et al. (2002) and Raveh et al. (2009) for 'Valência' orange. Duenhas et al. (2002) and Cano, Medina and Bernajo (2008), who studied different citrus varieties, found higher averages for the same variety. Only 'Pera' orange presented a significant difference ($p \le 0.05$) between sizes (Table 5), others presented a difference of one in relation to other two.

Ascorbic acid amount was higher than the average presented by USDA (UNITED..., 2009), Iemma et al. (1999) and TACO/UNICAMP (UNIVERSIDADE..., 2006), but tangerine values were lower than orange values, too, as shown in Table 6.

Johnston and Hale (2005) found values for commercial orange juices at 1 day and 8 days of storage (4 °C), 29 and 27 mg.100 mL⁻¹, respectively, and 38 and 49 mg.100 mL⁻¹ for frozen juice. The values are lower because the juices are reconstituted. Tiwari et al. (2009) concluded that different processes change the retention of ascorbic acid in orange juice during storage.

'Valencia' orange ascorbic acid amount was $40.64 \text{ mg}.100 \text{ mL}^{-1}$ for fresh juice (SÁNCHEZ-MORENO et al., 2003), similar to the results of this research (Table 6). For 'Pera' variety, Souza et al. (2004) found values between 50 and 60 mg.mL⁻¹, from time zero until 72 hours of storage at 4 °C.

Between varieties (Tabela 6), tangerines ('Murcote' and 'Ponkan') presented lower values immediately after extraction, similar to 'Valência' only. The same occurred after 24 hours at room temperature and at 4 °C. The highest amount of ascorbic acid at all times was found for 'Bahia' orange, which differ from others ($p \le 0.05$) after 24 hours of storage, but at the moment of

Table 4. Total titratable acidity (TTA) ^{1,2} and Total soluble solids (TSS) ^{1,2}	
in citrus varieties.	

Varieties	TTA (%)	TSS (%)	TSS/TTA
Pêra	$1.8\pm0.1^{\mathrm{ab}}$	13.43 ± 2.1^{a}	7.46
Valência	$1.3\pm0.0^{\mathrm{ab}}$	9.37 ± 0.8^{a}	7.21
Lima	$0.3\pm0.0^{\mathrm{b}}$	$10.47 \pm 4.0^{\mathrm{a}}$	34.90
Natal	$1.6\pm0.0^{\mathrm{ab}}$	10.03 ± 0.1^{a}	4.36
Bahia	2.3 ± 0.0^{a}	9.13 ± 2.3^{a}	3.97
Ponkan	1.6 ± 0.1^{ab}	$9.73 \pm 1.1^{\text{a}}$	6.08
Murcote	$1.2\pm0.0^{\mathrm{ab}}$	14.60 ± 1.5^{a}	12.17

¹Average of the three sizes (small, medium and large) \pm standard deviation. ²Values within a column with different superscripts are significantly different at $p \le 0.05$ by tukey test.

Table 5. Total titratable acidity (TTA) ^{1,2} and total soluble solids (TSS) ^{1,2}
in oranges and tangerines varieties by sizes.

e	e			
Var	ieties	TTA (%)	TSS (%)	TSS/TTA
	Large	$1.8\pm0.0^{\rm 1b2}$	$11.20 \pm 0.0^{\circ}$	6.22
Pêra	Medium	$0.5\pm0.0^{\circ}$	$13.80\pm0.0^{\rm b}$	27.6
	Small	2.8 ± 0.0^{a}	15.30 ± 0.0^{a}	5.46
Valência	Large	$1.2\pm0.0^{\mathrm{b}}$	$8.9\pm0.0^{\rm b}$	7.42
	Medium	1.4 ± 0.0^{a}	$8.9\pm0.0^{\rm b}$	6.36
	Small	1.3 ± 0.0^{ab}	10.3 ± 0.0^{a}	7.92
Lima	Large	$0.2\pm0.0^{\mathrm{b}}$	$8.00\pm0.0^{\rm b}$	40.00
	Medium	$0.3\pm0.0^{\mathrm{b}}$	$8.30 \pm 0.0^{\circ}$	27.67
	Small	$0.5\pm0.0^{\mathrm{a}}$	15.10 ± 0.0^{a}	30.20
Natal	Large	1.6 ± 0.0^{a}	10.1 ± 0.0^{a}	6.31
	Medium	$1.4\pm0.0^{\mathrm{b}}$	$10.0 \pm 0.0^{\text{a}}$	7.14
	Small	1.7 ± 0.0^{a}	10.0 ± 0.0^{a}	5.88
Bahia	Large	$2.4\pm0.0^{\mathrm{a}}$	$7.00 \pm 0.0^{\circ}$	2.92
	Medium	$2.4\pm0.0^{\mathrm{a}}$	$8.80\pm0.0^{\rm b}$	3.67
	Small	$2.2\pm0.0^{\mathrm{b}}$	11.60 ± 0.0^{a}	5.27
Ponkan	Large	$1.1\pm0.0^{\rm b}$	$9.10\pm0.0^{\rm b}$	8.27
	Medium	$1.1\pm0.0^{\rm b}$	11.00 ± 0.0^{a}	10.0
	Small	$2.5\pm0.0^{\text{a}}$	$9.10\pm0.0^{\rm b}$	3.64
Murcote	Large	$1.0 \pm 0.0^{\rm b}$	$13.40\pm0.0^{\circ}$	13.40
	Medium	$1.0\pm0.0^{\mathrm{b}}$	$16.30\pm0.0^{\text{a}}$	16.30
	Small	$1.6 \pm 0.,0^{a}$	$14.10\pm0.0^{\rm b}$	8.81

¹Means of three repetitions \pm standart deviation. ²Different letters in vertical indicam differença estatística ($p \le 0.05$) between sizes (large, medium and small) in the same variety.

extraction, it was similar to 'Pêra' orange. The highest stability of ascorbic acid for 'Bahia' orange occurred because of the higher titratable acidity (Table 4), which preserved the ascorbic acid oxidation (BURDURLU; KOCA; KARADENIZ, 2006). All samples showed a decrease in the ascorbic acid amount ($p \le 0.05$) after storage at room temperature and at 4 °C, but only 'Ponkan' tangerine presented a significant difference ($p \le 0.05$) between the two storage temperatures.

'Bahia' orange presented higher ascorbic acid amount, with an average of 70.10 mg.100 g⁻¹, while tangerines presented lower amounts: 37.26 mg.100 g⁻¹ for 'Murcote' and 38.99 mg.100 g⁻¹ for 'Ponkan'. Tangerines presented lower losses during storage, too.

Ascorbic acid degradation in packaged fruit juices depends mainly on the following: storage temperature, dissolved oxygen level, residual H_2O_2 remnant after packaging material sterilization, and metal ions traces (ÖZKAN; KIRCA; CEMEROGLU, 2004).

Ascorbic acid is one of the substances that contribute to the antioxidant capacity in juices. It contributes to 56 to 77% of the antioxidant capacity of orange juice, 46% of the tangerine juice and 66 to 77% of grapefruit juice (VINSON et al., 2002).

Oranges have antioxidants (RAPISARDA et al., 1999) in greater quantities for protection against ascorbic acid oxidation. One of them is the flavonoids group, as presented by Miller and Rice Evans (1997), who studied the effect of polyphenols in the protection of vitamin C in juices. They protect the ascorbic acid against oxidation (DAUCHET et al., 2008; GHASEMI; GHASEMI, EBRAHINZADEH, 2009; XU et al., 2008)

Other important factor in the ascorbic acid stabilization in solution is the quantity of oxygen dissolved (KISHIDA et al., 2004), but this factor was constant for the analyzed juice.

Observing Table 7, small tangerines in storage at 4 °C presented good conservation of ascorbic acid, and did not differ

Varieties	Ascorbic acid immediatily	Ascorbic acid after	% lost	Ascorbic acid after	% lost
	after extraction	24 hours at room temperature		24 hours at 4 °C	
Pêra	60.63 ± 4.3^{abA}	$51.16 \pm 5.3^{\mathrm{bB}}$	15.62	$51.47 \pm 6.2^{\text{bB}}$	15.10
Valência	42.35 ± 1.8^{cA}	36.76 ± 2.8^{cB}	13.20	$37.65 \pm 2.2^{\text{cB}}$	11.11
Lima	$56.42 \pm 4.8^{\mathrm{bA}}$	$48.68 \pm 5.3^{\text{bB}}$	13.72	$51.42\pm3.9^{\rm bAB}$	8.86
Natal	55.40 ± 3.4^{bA}	$48.66 \pm 3.8^{\text{bB}}$	12.18	$51.47 \pm 3.0^{\text{bB}}$	7.11
Bahia	70.10 ± 1.6^{aA}	62.53 ± 2.8^{aB}	10.81	$63.79\pm1.4^{a^B}$	9.01
Ponkan	38.99 ± 3.8^{cA}	$28.20 \pm 1.4^{\rm cC}$	27.67	34.84 ± 3.3^{cB}	10.64
Murcote	37.26 ± 3.8^{cA}	28.74 ± 3.9^{cB}	22.88	$30.32 \pm 2.8^{\text{cB}}$	18.63

Table 6. Ascorbic acid (mg.100 g⁻¹)^{1,2,3} and porcetage of lost^{1,2,3} after storage at room temperature and 4 °C in juices by variety.

¹Average of the three sizes (small, medium and large) \pm standard deviation. ²Values within a column with different lowercase superscripts are significantly different at p \leq 0.05 by tukey test for varieties, in each item. ³Values within a line with different uppercase superscripts are significantly different at p \leq 0.05 by tukey test for storage temperatures.

			e	*	, ,	
	Varieties	Ascorbic acid immediatily after extraction	Ascorbic acid after 24 hours at room temperature	% lost	Ascorbic acid after 24 hours at 4 °C	% lost
Pêra	Large	$55.89 \pm 3.3^{\text{bA}}$	$50.21 \pm 1.6^{\text{bAB}}$	10.16	$45.47 \pm 2.8^{\mathrm{bB}}$	18.64
	Medium	64.42 ± 1.6^{aA}	$46.42 \pm 3.3^{\text{bB}}$	27.94	$51.16 \pm 2.8^{\mathrm{bB}}$	20.58
	Small	$61.58\pm1.6^{a^A}$	$56.84\pm0.0^{\rm aB}$	7.70	$57.79\pm1.6^{a^B}$	6.15
Valência	Large	44.12 ± 0.0^{aA}	37.94 ± 0.9^{aB}	14.01	37.94 ± 0.9^{aB}	14.01
	Medium	$40.59\pm0.0^{\rm cA}$	$33.53\pm0.0^{\rm bC}$	17.39	$35.29\pm0.0^{\rm bB}$	13.06
	Small	42.35 ± 0.0^{bA}	$38.82\pm0.0^{\rm aB}$	8.34	$39.71\pm0.9^{a^B}$	6.23
Lima	Large	$51.16 \pm 0.0^{\text{cA}}$	$42.63\pm0.0^{\rm bC}$	16.67	$48.32\pm0.0^{\rm bB}$	5.55
	Medium	57.48 ± 0.0^{bA}	$52.26\pm0.0^{\mathrm{aC}}$	9.08	55.74 ± 0.0^{aB}	3.03
	Small	60.63 ± 1.6^{aA}	51.16 ± 5.7^{aAB}	15.62	$50.21 \pm 3.3^{\text{bB}}$	17.19
Natal	Large	52.31 ± 0.0^{cA}	$44.72\pm0.8^{\rm cC}$	14.51	$48.09\pm0.8^{\rm cB}$	8.07
	Medium	59.06 ± 0.0^{aA}	$48.94\pm0.0^{\rm bC}$	17.14	54.00 ± 0.0^{aB}	8.57
	Small	$54.84\pm0.8^{\rm bA}$	$52.31\pm0.0^{\mathrm{aB}}$	4.61	$52.31\pm0.0^{\rm bB}$	4.61
Bahia	Large	71.05 ± 2.8^{aA}	$62.53\pm0.0^{\rm bB}$	11.99	$62.53 \pm 0.0^{\mathrm{bB}}$	11.99
	Medium	68.21 ± 0.0^{aA}	$59.68 \pm 0.0^{\circ C}$	12.51	63.47 ± 1.6^{abB}	6.95
	Small	71.05 ± 0.0^{aA}	$65.37\pm0.0^{\rm aB}$	7.99	$65.37\pm0.0^{\mathrm{aB}}$	7.99
Ponkan	Large	$42.30\pm0.0^{\mathrm{aA}}$	$27.37\pm0.0^{\rm aC}$	35.30	$37.33\pm0.0^{\mathrm{aB}}$	11.75
	Medium	$34.84\pm0.0^{\rm cA}$	$29.86\pm0.0^{\mathrm{aB}}$	14.29	$31.11\pm0.0^{\rm bB}$	10.71
	Small	39.82 ± 0.0^{bA}	$27.37 \pm 2.5^{a^B}$	31.27	$36.08\pm1.2^{\mathtt{a}^{A}}$	9.39
Murcote	Large	$41.68 \pm 1.6^{\mathrm{aA}}$	25.58 ± 2.8^{aB}	38.63	30.32 ± 3.3^{aB}	27.26
	Medium	$35.05 \pm 1.6^{\text{bA}}$	27.47 ± 3.3^{aB}	21.63	$27.47 \pm 1.6^{\mathrm{aB}}$	21.63
	Small	$35.05 \pm 1.6^{\text{bA}}$	33.16 ± 4.3^{aA}	5.39	$33.16\pm4.3^{a^A}$	5.39

Table 7. Ascorbic acid (mg.100 g⁻¹)^{1,2,3} and percentage of lost^{1,2,3} after storage at room temperature and 4 °C in juices by sizes.

¹Average of the three repitition \pm standard deviation. ²Values within a column with different lowercase superscripts are significantly different at p \leq 0.05 by tukey test for sizes, in each variety. ³Values within a line with different uppercase superscripts are significantly different at p \leq 0.05 by tukey test for sizes, in each variety.

significantly from control (p \leq 0.05). For 'Murcote' tangerine, small sized fruits did not present significant difference after 24 hours. Considering percentage loss, in general, small fruits lost less, except 'Lima' and 'Bahia' at 4 °C storage, and 'Lima' and 'Ponkan' at room temperature storage. Storage, at room temperature or at 4 °C, interferes in the loss of ascorbic acid, all varieties and sizes had some loss. All varieties and sizes showed a decrease in the amount of ascorbic acid, regardless the size, only 'Murcote' tangor did not present differences between sizes (p \leq 0.05). The highest loss percentage was observed in large sized 'Murcote' tangor at room temperature.

Table 8 shows the albedo as the highest pectin level part. The second highest value was found in the peel of the oranges, and in the pulp of the tangerines. The 'Natal' and 'Valência' oranges presented the lowest values of total pectin in juice. 'Murcote' tangor pectin contents stood out both in solid parts as in juice.

The values showed in Table 8 are very close to those related by Mendez et al. (2001), but they are higher in 'Murcote' tangerine and lower in 'Lima' orange, maybe because they were cultured in different weather conditions in the second case. Mendez et al. (2001) did not analyze the fruits in parts or sizes, but the whole fruits.

Considering all the solid parts of the fruit (Table 9), the highest values for pectin were found in the small sized 'Pêra' and 'Lima' oranges and in the medium sized 'Ponkan' tangerine and 'Bahia' and 'Valência' oranges. In 'Natal' orange, the highest pectin content in albedo was found in the large sized oranges and in the small sized orange peel and pulp. In 'Murcote' tangor, the highest content was found in the large sized tangerine albedo and pulp and in the medium and small sized tangerine peel.

Table 10 shows pectin values (total and soluble) in juice. They do not have any relation to the fruits sizes. However, in

Table 8. Total and soluble	e pectin ^{1,2} amount in Citrus fruits (s	solids part g.100 g ⁻¹ a	nd juice mg.100 g^{-1}).
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Varieties	Peel – total pectin	Albedo – total pectin	Pulp – total pectin	Juice – total pectin	Juice – soluble pectin
Pêra	$0.38\pm0.1^{\text{ab}}$	0.55 ± 0.2^{ab}	0.29 ± 0.1^{ab}	$10.76 \pm 1.4^{\rm ab}$	$7.89 \pm 1.6^{\mathrm{ab}}$
Valência	$0.23\pm0.1^{\rm bc}$	0.60 ± 0.2^{ab}	$0.10\pm0.0^{\mathrm{bc}}$	$7.69 \pm 1.0^{\mathrm{b}}$	$3.46\pm0.8^{\mathrm{b}}$
Lima	$0.28\pm0.1^{\text{abc}}$	$0.37\pm0.1^{ m b}$	$0.21\pm0.1^{ m bc}$	8.61 ± 1.0^{ab}	8.21 ± 0.7^{ab}
Natal	$0.13\pm0.1^{\circ}$	$0.43\pm0.0^{\mathrm{b}}$	$0.07 \pm 0.0^{\circ}$	7.46 ± 2.3^{b}	$4.58 \pm 1.1^{\mathrm{ab}}$
Bahia	$0.34\pm0.1^{\text{ab}}$	$0.45\pm0.1^{ m b}$	$0.29\pm0.1^{\rm ab}$	10.23 ± 1.9^{ab}	$7.80\pm5.0^{\mathrm{ab}}$
Ponkan	$0.23\pm0.0^{\mathrm{bc}}$	$0.37\pm0.0^{\mathrm{b}}$	$0.25\pm0.0^{\mathrm{bc}}$	11.47 ± 1.3^{ab}	10.54 ± 2.4^{a}
Murcote	$0.43\pm0.0^{\mathrm{a}}$	0.76 ± 0.1^{a}	0.48 ± 0.3^{a}	12.26 ± 1.7^{a}	11.07 ± 2.2^{a}

¹Average of the three sizes (small, medium and large) \pm standard deviation. ²Different lowercase letters in a column indicate statistic differences (p \leq 0.05) between the varieties, for each item (peel, albedo, pulp, total pectin in juice and soluble pectin in juice).

Table 9. Total pectin ^{1,2} ar	nount in solids	part of fresh	Citrus fruits
$(g.100 g^{-1})$ by sizes.			

Varieties	Part		Sizes	
		Large	Medium	Small
Pêra	Peel	$0.34\pm0.0^{\rm b}$	$0.35\pm0.0^{\rm b}$	$0.45\pm0.0^{\text{a}}$
	Albedo	$0.40\pm0.0^{\circ}$	$0.48\pm00^{\mathrm{b}}$	$0.77\pm0.0^{\mathrm{a}}$
	Pulp	$0.22\pm0.0^{\circ}$	$0.26\pm0.0^{\rm b}$	$0.38\pm0.0^{\mathrm{a}}$
Valência	Peel	$0.14\pm0.0^{\rm c}$	$0.28\pm0.0^{\rm a}$	$0.26\pm0.0^{\rm b}$
	Albedo	$0.42\pm0.0^{\rm b}$	$0.68\pm0.0^{\mathrm{a}}$	$0.71 \pm 0.0^{\mathrm{a}}$
	Pulp	$0.08\pm0.0^{\rm b}$	$0.10\pm0.0^{\mathrm{a}}$	0.11 ± 0.0^{a}
Lima	Peel	$0.21\pm0.0^{\circ}$	$0.27\pm0.0^{\mathrm{b}}$	$0.35\pm0.0^{\rm a}$
	Albedo	$0.28\pm0.0^{\rm b}$	0.42 ± 0.0^{a}	$0.41\pm0.0^{\mathrm{a}}$
	Pulp	$0.17\pm0.0^{\rm b}$	$0.13\pm0.0^{\circ}$	$0.32\pm0.0^{\rm a}$
Natal	Peel	$0.10\pm0.0^{\rm b}$	$0.06\pm0.0^{\rm b}$	$0.23\pm0.0^{\rm a}$
	Albedo	$0.47\pm0.0^{\mathrm{a}}$	$0.42\pm0.0^{\rm b}$	$0.39\pm0.0^{\circ}$
	Pulp	$0.03\pm0.0^{\circ}$	$0.07\pm0.0^{\rm b}$	$0.09\pm0.0^{\rm a}$
Bahia	Peel	$0.28\pm0.0^{\rm b}$	$0.39\pm0.0^{\mathrm{a}}$	$0.36\pm0.0^{\rm a}$
	Albedo	$0.41\pm0.0^{\rm b}$	$0.52\pm0.0^{\mathrm{a}}$	$0.41\pm0.0^{\rm b}$
	Pulp	$0.25\pm0.0^{\circ}$	$0.36\pm0.0^{\rm a}$	$0.26\pm0.0^{\rm b}$
Ponkan	Peel	$0.22\pm0.0^{\circ}$	$0.24\pm0.0^{\mathrm{a}}$	$0.23\pm0.0^{\rm b}$
	Albedo	$0.34\pm0.0^{\circ}$	$0.39\pm0.0^{\rm a}$	$0.37\pm0.0^{\rm b}$
	Pulp	$0.21\pm0.0^{\circ}$	$0.29\pm0.0^{\rm a}$	$0.25\pm0.0^{\rm b}$
Murcote	Peel	$0.38\pm0.0^{\rm b}$	0.46 ± 0.0^{a}	$0.46\pm0.0^{\text{a}}$
	Albedo	$0.87\pm0.0^{\rm a}$	$0.72\pm0.0^{\mathrm{b}}$	$0.69\pm0.0^{\circ}$
	Pulp	$0.61\pm0.0^{\mathrm{a}}$	$0.34\pm0.0^{\circ}$	$0.50\pm0.0^{\rm b}$

¹Average of the three repitition \pm standard deviation. ²Different lowercase letters in a horizontal line indicate statistic differences ($p \le 0.05$) between the sizes (large, medium and small), for the same variety, for each item (peel, albedo and pulp).

Table 10. Total and soluble pectin amount (mg.100 g^{-1}) in juic	e by
different sizes.	

Varieties	Size	Pec	tin
		Soluble	Total
Pêra	Large	6.33 ± 0.2^{1c2}	$9.47 \pm 0.1^{\circ}$
	Medium	$7.79\pm0.1^{ m b}$	10.60 ± 0.1^{b}
	Small	9.56 ± 0.1^{a}	12.22 ± 0.1^{a}
Valência	Large	4.37 ± 0.1^{a}	8.71 ± 0.1^{a}
	Medium	$2.91\pm0.0^{\circ}$	$7.59\pm0.0^{\rm b}$
	Small	$3.10\pm0.1^{\mathrm{b}}$	$6.78 \pm 0.1^{\circ}$
Lima	Large	$7.40 \pm 0.3^{\mathrm{b}}$	$7.43\pm0.2^{\rm b}$
	Medium	8.50 ± 0.0^{a}	9.11 ± 0.0^{a}
	Small	8.73 ± 0.0^{a}	9.28 ± 0.0^{a}
Natal	Large	$4.04\pm0.0^{\rm b}$	8.82 ± 0.1^{a}
	Medium	5.87 ± 0.1^{a}	$8.73\pm0.4^{\rm a}$
	Small	$3.84\pm0.1^{\circ}$	$4.82\pm0.2^{\rm b}$
Bahia	Large	$2.06\pm0.0^{\circ}$	$8.17 \pm 0.0^{\circ}$
	Medium	11.38 ± 0.1^{a}	11.76 ± 0.1^{a}
	Small	$9.95\pm0.0^{\rm b}$	10.76 ± 0.0^{b}
Ponkan	Large	$7.82 \pm 0.1^{\circ}$	$10.19 \pm 0.2^{\circ}$
	Medium	$11.40\pm0.2^{\rm b}$	11.53 ± 0.1^{b}
	Small	12.41 ± 0.1^{a}	12.70 ± 0.2^{a}
Murcote	Large	$8.60 \pm 0.4^{\circ}$	$10.61 \pm 0.1^{\circ}$
	Medium	$11.94\pm0.1^{\rm b}$	$12.27\pm0.0^{\rm b}$
	Small	12.68 ± 0.1^{a}	13.91 ± 0.2^{a}

¹Average of the three repetition \pm standard deviation. ² different lowercase letters in a column indicate statistic differences (p \leq 0.05) between the sizes (large, medium and small), for the same variety, for each item (total and soluble pectin).

most samples, the highest pectin contents were observed in small sized fruits.

4 Conclusions

Although differences have been found between sizes, they were not uniform, in small amount or even inexistent.

The total soluble solids are higher in medium sized tangerine and smaller oranges.

Tangerines present lower quantity of ascorbic acid than oranges, except for the 'Valencia' variety.

Percentage of vitamin C loss in different varieties was independent of storage temperature, except for 'Ponkan' tangerine.

Albedo presented the highest content of pectin of all studied fruits.

In juice, the total and soluble pectin contents increased as fruits size decreased.

Different oranges and tangerines differ in the amount of pectin.

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