Research, Society and Development, v. 9, n. 11, e44991110192, 2020
(CC BY 4.0) | ISSN 2525-3409 | DOI: http://dx.doi.org/10.33448/rsd-v9i11.10192

Bioactive compounds and antioxidant activity in tomatoes (*Lycopersicon esculentum* L.) cultivars *in natura* and after thermal processing

Compostos bioativos e atividade antioxidante em variedades de tomates (*Lycopersicon esculentum* L.) *in natura* e após processamento térmico

Compuestos bioactivos y actividad antioxidante en variedades de tomate (*Lycopersicon esculentum* L.) *in natura* y después del procesamiento térmico

Received: 11/12/2020 | Reviewed: 11/15/2020 | Accept: 11/17/2020 | Published: 11/21/2020

Angela Vacaro de Souza
ORCID: https://orcid.org/0000-0002-4647-2391
São Paulo State University, Brazil
E-mail: angela.souza@unesp.br
Jéssica Marques de Mello
ORCID: https://orcid.org/0000-0001-9965-7771
São Paulo State University, Brazil
E-mail: jessica.mello@unesp.br
Vitória Ferreira da Silva Favaro
ORCID: https://orcid.org/0000-0003-0688-3628
São Paulo State University, Brazil
E-mail: vitoria.favaro@unesp.br
Victória Farias da Silva
ORCID: https://orcid.org/0000-0002-5559-8877
São Paulo State University, Brazil
E-mail: victoria.farias@unesp.br
Diogo de Lucca Sartori
ORCID: https://orcid.org/0000-0002-4957-1408
São Paulo State University, Brazil
E-mail: diogo.sartori@unesp.br
Fernando Ferrari Putti
ORCID: https://orcid.org/0000-0002-0555-9271
São Paulo State University, Brazil
E-mail: fernando.putti@unesp.br

Abstract

The aim of the study was to evaluate the impact of processing by cooking in natura fruits on the content of bioactive compounds - vitamin C and ascorbic acid, phenolic compounds, flavonoids, carotenoids and anthocyanins, lycopene and β-carotene - and on antioxidant activity - DPPH and FRAP - of 9 varieties of commercial and non-commercial tomatoes. The fruits were harvested when they reached the point of physiological maturation, selected and evaluated in natura, and after grinding and cooking for 30 minutes. At the end of the experiment it was found that all bioactive compounds analyzed showed quantitative reductions when the fruits were processed, with cherry cultivars - 7, 8 and 9 - those that showed superior results compared to different bioactive compounds evaluated, proving to be interesting to be better explored. Regarding the antioxidant activities, the processed fruits of these cultivars showed less losses showing potential to be submitted to processing.

Keywords: Food processing; Carotenoids; Lycopene; Phenolic compounds; Flavonoids.

Resumo

O objetivo do estudo foi avaliar o impacto do processamento por cozimento em frutos in natura no conteúdo de compostos bioativos – vitamina C e ácido ascórbico, compostos fenólicos, flavonóides, carotenoides e antocianinas, licopeno e β-caroteno - e na atividade antioxidante – DPPH e FRAP - de 9 variedades de tomates comerciais e não comerciais. Os frutos foram colhidos quando atingiram o ponto de maturação fisiológica, sendo selecionados e avaliados in natura e após trituração e cozimento por 30 minutos. Ao final do experimento verificou-se que todos os compostos bioativos analisados apresentaram reduções quantitativas quando os frutos foram processados, sendo as cultivares cereja - 7, 8 e 9 - as que apresentaram resultados superiores em relação aos diferentes compostos bioativos avaliados mostrando-se interessantes para serem melhores exploradas. Já em relação às atividades antioxidantes, os frutos processados destas cultivares apresentaram menores perdas mostrando potencial para serem submetidas ao processamento.

Palavras-chave: Processamento de alimentos; Carotenoides; Licopeno; Compostos fenólicos; Flavonoides.

Resumen

El objetivo del estudio fue evaluar el impacto del procesamiento por cocción de frutas frescas sobre el contenido de compuestos bioactivos - vitamina C y ácido ascórbico, compuestos fenólicos, flavonoides, carotenoides y antocianinas, licopeno y β-caroteno - y sobre la actividad antioxidante - DPPH y FRAP - 9 variedades de tomates comerciales y no comerciales. Los frutos se recolectaron cuando alcanzaron el punto de maduración fisiológica, siendo seleccionados y evaluados in natura y luego de triturados y cocidos durante 30 minutos. Al finalizar el experimento se encontró que todos los compuestos bioactivos analizados mostraron reducciones cuantitativas cuando se procesaron los frutos, siendo los cultivares de cereza - 7, 8 y 9 - los que mostraron resultados superiores en relación a los diferentes compuestos bioactivos evaluados, mostrando ser de interés para mejor explorado. En cuanto a las actividades antioxidantes, los frutos procesados de estos cultivares presentaron menores pérdidas mostrando potencial para ser sometidos a procesamiento.

Palabras clave: Procesamiento de alimentos; Carotenoides; Licopeno; Compuestos fenólicos; Flavonoides.

1. Introduction

Tomato is an important agricultural product produced worldwide. Its affordable cost, availability throughout the year and pleasant taste contribute to its consumption by all social classes. In 2017, the world production was 182.3 million tons, with values in Brazil exceeding 4 million (Fao, 2019). In addition to in natura consumption, the fruit can be consumed processed in the form of sauces, ketchup, extract, puree and pulp, among others. (Ilahy et al., 2015).

The large consumption of tomatoes is not only because it is a versatile fruit, but also because it is known for its high antioxidant potential, due to the presence of compounds such as lycopene, phenolic compounds and vitamin C (Abreu, Barcelosa, 2012).

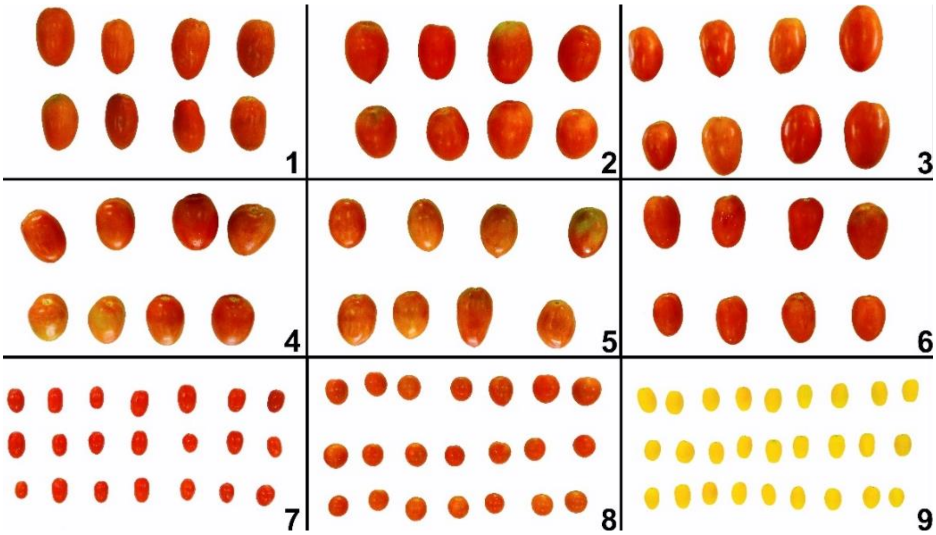
In a study by Kalogeropoulos et al., 2012, products from tomato processing together with in natura tomatoes were analyzed in a comparative study of several bioactive compounds. In this study, the authors found that sterols, tocopherols, carotenes, terpenes and total and simple polyphenols were detected in in natura tomatoes and were also present in products processed in significant quantities based on dry weight, leading to the conclusion that the bioactive compounds studied are capable of supporting industrial processing. This fact was confirmed in a study on the impact of industrial processing on the stability of tomato carotenoids, which indicated that the general nutritional quality of processed tomato products is satisfactorily preserved mainly during manufacture, except for vitamin C (Chanforan et al., 2012).

The thermal processing of tomatoes can cause important changes in their sensory characteristics and in the content of antioxidant compounds, changing the antioxidant potential of this fruit. The conditions of time and temperature are decisive for the increase or reduction of the antioxidant activity (AA) of the tomato (Takeoka et al., 2003) but results on the influence of the thermal processing of vegetables are still incipient and contradictory. Thus, the objective of this study was to evaluate the effect of thermal processing on the contents of bioactive compounds and antioxidant activity of nine tomato cultivars when compared to in natura fruits.

2. Materials And Methods

The fruits were purchased from producers in the city of Tupã/SP, Brazil (-21.9384, -50.514 21° 56’ 18” South, 50° 30’ 50” West). Figure 1 shows the tomato cultivars used in the experiment, so that the numbers represent the cultivars: 1 – ‘Katia’, 2 – ‘Paipai’, 3 – ‘Silvestre’, 4 – ‘Colibri’, 5 – ‘Milão’, 6 – ‘Glaziane’, 7 – ‘Cereja Heven’, 8 – ‘Cereja 15.916’ and 9 – ‘Cereja Aiko’ (Figure 1).

Figure 1. Tomato cultivars used for the experiment.



Source: Authors.

2.1 Sample preparation and processing

The fruits evaluated *in natura* were only cut, packed and frozen. The samples submitted to processing were crushed, cooked for 30 minutes and packaged. All samples – *in natura* and processed - were frozen in liquid N_2 for further analysis. The processing of tomato pulp includes several processing steps such as crushing, enzymatic inactivation, concentration and sterilization. These treatments reduce the water content and provide the product with a new appearance, texture and viscosity (Capanoglu et al., 2008).

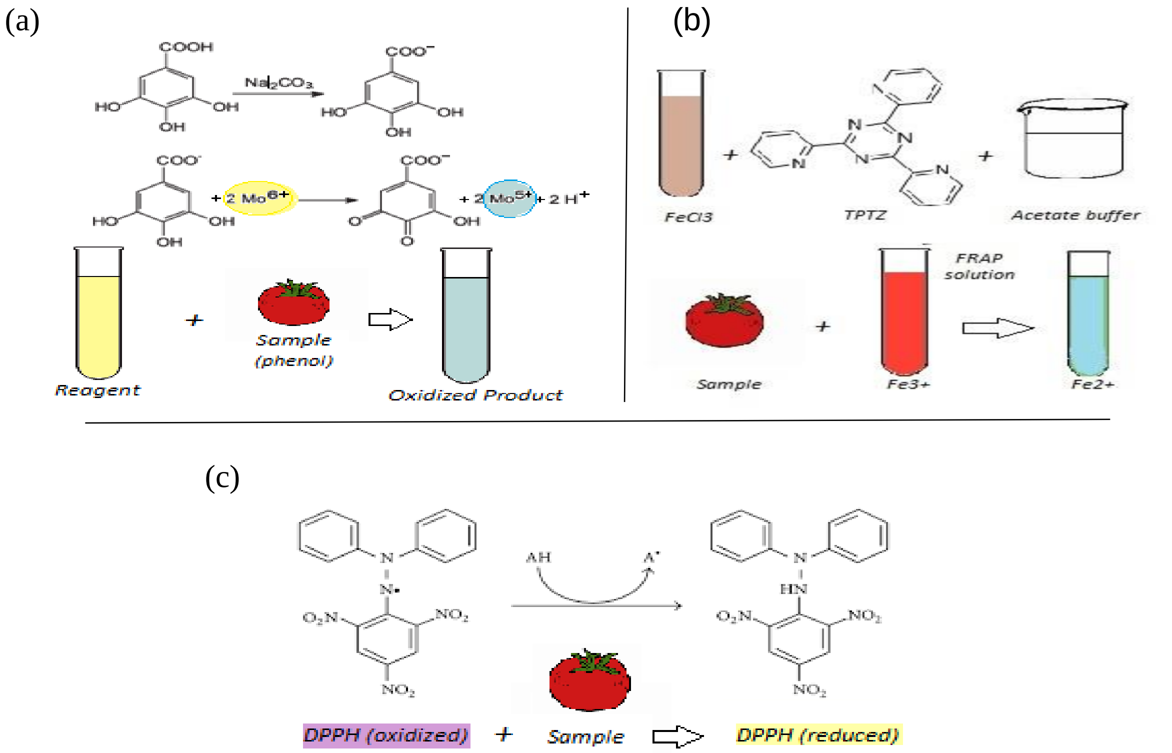
2.2 Laboratory analysis

The analyzes were carried out in the Biology and Chemistry Laboratory, belonging to the Faculty of Science and Engineering of Unesp at Tupã/SP. For all biochemical analyzes performed, the number of samples required, extractor and extractor concentration were standardized. All samples were homogenized with the Ultra Turrax T6 Basic from IKA. The ultrasonic bath used for some analyzes was the model 0335 D, version 1.0, from Quimis, and for the analyzes that required spectrophotometric reading, they were performed on the UV-1800 spectrophotometer, from SHIMADZU.

Analyzes were carried out to characterize the *in natura* and processed fruits as total sugars, according to the method described by Dubois et al. (1956) with results expressed in g $100g^{-1}$, soluble solids content (SS) in ºBRIX, pH, titratable acidity (TA) with results presented in g citric acid $100g^{-1}$, Maturation Index (SS/TA) and Content of Water, in g $100g^{-1}$ (I.A.L., 2008). Regarding bioactive compounds and antioxidant activity, the following analyzes were performed: vitamin C (Terada et al., 1978) and ascorbic acid (IAL, 2008), both with results expressed in $100mg^{-1}$ mg, total phenols (phenolic compounds) : analyzed according to the spectrophotometric method and using as reagent the reactive from Folin Ciocalteu (Singleton, Rossi Jr, 1965) with results expressed in mg of gallic acid equivalent per 100 g^{-1} of fresh weight (Figure 2a), total flavonoids: analyzed according to the method of Popova et al., 2004, with results expressed in rutin and quercetin curves (mg $100g^{-1}$) (Figure 3c), total carotenoids, anthocyanins, a and b chlorophylls: analyzed according to the method validated by Nagata and Yamashita (1992) with final values expressed in mg $100g^{-1}$ (Figure 3a), antioxidant activity - DPPH: determined against the free radical (DPPH) according to the method proposed by Brand-Williams et al. (1995) with results expressed as % of reduced DPPH (Figure 2c), antioxidant activity - FRAP: performed according to the method described by Benzie and Strain (1996) presented in mol g$FeSO_4$ (Figure 2b) and lycopene and β -carotene (Nagata M., Yamashita, 1992,) with final values expressed in mg $100mL^{-1}$ (Figure 3b).

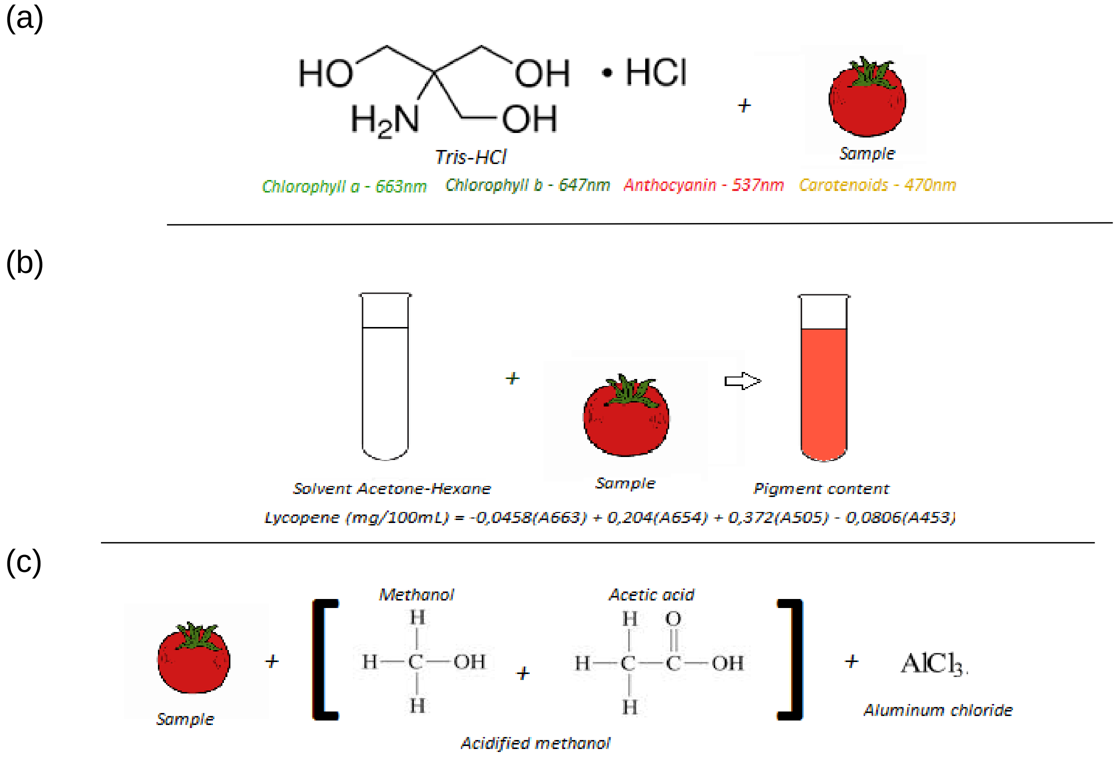
Figures 2 and 3 demonstrate in detail the methodologies used for the determination of bioactive compounds and antioxidant activities.

Figure 2. (a): Deprotonation of the phenolic compounds in standard gallic acid, in basic medium, generating the phenolate anion, in samples of tomatoes and sauces. Thereafter, an oxidation reaction occurs between the phenolate anion and the Folin-Ciocalteau reagent the molybdenum, a component of the Folin reagent, suffers a reduction and the reaction medium changes the color from yellow to blue, 2 (b): General scheme of the reaction of FRAP assay in samples of tomatoes and sauces, with details of the reduction of the TPTZ (2,4,6-tri (2-pyridyl) -1,3,5-triazine) complex with Fe^{3+} and 2 (c): General scheme of the reaction of DPPH assay in samples of tomatoes and sauces. The solution from DPPH radical, of purple color, is reduced by antioxidants contained in the plant extract, changing the color of the solution from purple to yellow.



Source: Authors.

Figure 3. (a): General scheme for pigment determination, 3 (b): General scheme of the reaction of lycopene determination and 3 (c): General scheme for determining the flavonoid content in *in natura* tomato and sauce samples.



Source: Authors.

2.3 Experimental design and statistical analysis

For better understanding, the results were submitted to analysis of variance comparing the cultivars studied and the types of treatment (*in natura* x thermal processing) using the *Scott-Knott* statistical test in order to detect very similar groups based on univariate groupings analyzes. The statistical analysis was performed with the support of the *Minitab* software. All analyzes were performed in 5 repetitions.

In order to establish a descriptive model of grouping samples based on the treatments used and laboratory analysis, multivariate analysis via principal components (Principal Component Analysis - PCA) was carried out in order to verify the grouping of the different responses of the cultivars' behavior regarding to thermal processing and thus simulate how it is the relationship among these variables (Vítolo et al., 2012). Principal component analysis is one of the simplest multivariate statistical methods.

For the analysis, the Statistica software was used, using the minimum absorption criterion of 80% in the first two principal components and thus simulating a possible relationship among the variables (Cruz et al., 2004, Souza et al., 2018).

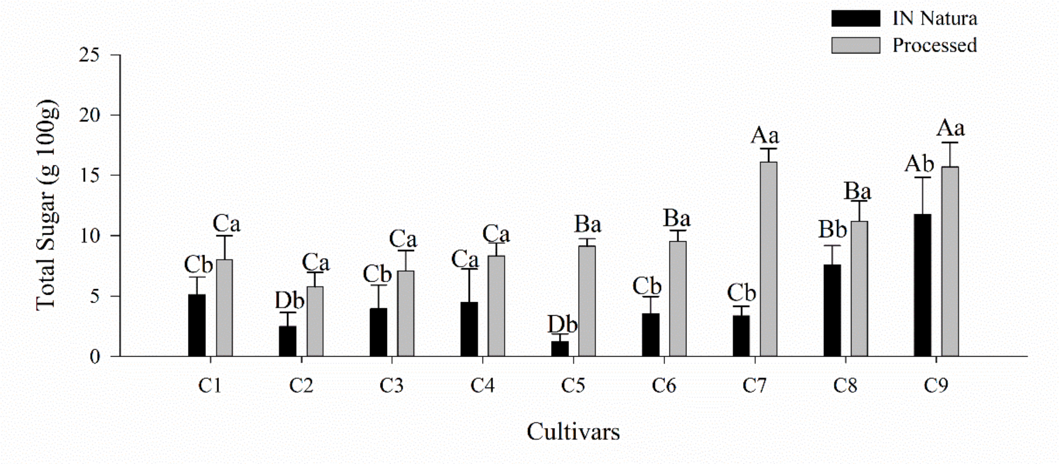
In a second approach, statistical multivariate analysis was applied to the data set and Pearson’s Correlation analysis was performed, in order to investigate the relationships among the study variables, which indicates the positive or negative existence between two variables, and α = 5% (coefficient of correlation) was adopted to verify significance. The analyzes were performed using the *Statistica* and *Sigmaplot* software.

3. Results And Discussion

3.1 Total sugars

Sugars are strongly related to fruit yield and quality, playing a critical role in production, growth, ripening and composition, an important parameter in determining agro-industrial quality and harvest point (Figure 4). All cultivars analyzed showed an increase in the total sugar content when submitted to processing, and increases greater than 3 times.

Figure 4. Total sugar content (g $100g^{-1}$), in the nine *in natura* and processed tomato cultivars.



Source: Authors.

3.2 Soluble Solids, pH, Titratable Acidity, Maturation Index and Water Content

The contents of soluble solids varied in *in natura* cultivars from 4.38 to 7.22ºBRIX. Similar results were found by Araújo et al., (2014) who found values ranging from 4 to 6ºBRIX studying 14 tomato cultivars. Industrial tomatoes must have contents of soluble solids of at least 5°BRIX (Cemeroglu et al., 2003). This content is directly associated with industrial yield, where each °BRIX increase in raw material has on average 10 to 20% increase in yield (Boiteux et al., 2012). Due to the processing, water loss occurs and with this increase in these contents, shown in Table 1.

Tomato fruits generally have sufficient acidity to maintain their pH below 4.6 and, for this reason, are considered acid food (Anthon & Barrett, 2012). The pH of *in natura* fruits varied from 4.09 to 4.22, similar to the values found in the study by Cemeroglu et al., 2003, and the authors found values that varied from 4.17 to 4.38. There was a statistically significant difference among cultivars when the fruits were submitted to processing.

There is an inverse relationship between titratable acidity and pH, in which the higher the acidity, the lower the pH (Anthon and Barrett, 2012) and vice versa, this behavior was observed in this study. The titratable acidity did not show significant statistical differences when comparing the averages of the processed and *in natura* fruits, with the averages in both treatments being 0.54 g of citric acid 100g^{-1}.

In the selection of genetic material for industrial tomatoes, titratable acidity and pH are important characteristics, and regarding to acidity, citric acid – the predominant acid in tomatoes - must be above 0.35 g 100g^{-1} and the pH below 4.3. Acidity contents maintained at these values allow for higher quality of the processed pulp, avoiding the proliferation of microorganisms such as *Clostridium pasteurianum* and *Clostridium butyricum* (Boiteux et al., 2012).

Regarding the maturation index, values were found that ranged from 6.21 to 12.99, with an average of 10.39 for the nine *in natura* cultivars and 10.24 to 23.22, with an average of 17.6 in the fruits submitted to processing. From these results it was found that the cultivars studied showed high quality compared to the balance between acidity and sugars present in the fruits, requirements to provide tomato products with adequate sensory characteristics, because a ratio greater than 10 demonstrates that the fruit has high quality (Vanzoonen, 1998).

In this study, the average water content found in cultivars for *in natura* fruits was 95.11 and 94.20 for fruits after thermal processing, similar to those found in TACO (2011) with 95% moisture for tomatoes. The cherry cultivars (7, 8 and 9) presented, on average, reduced water content and, consequently, higher contents of soluble solids. Water content is also important for determining and evaluating the durability and agro-industrial yield of agricultural products.

Table 1. Content of Soluble Solids, pH, Titratable Acidity, Maturation Index and Water Content, in the nine *in natura* and processed tomato cultivars.

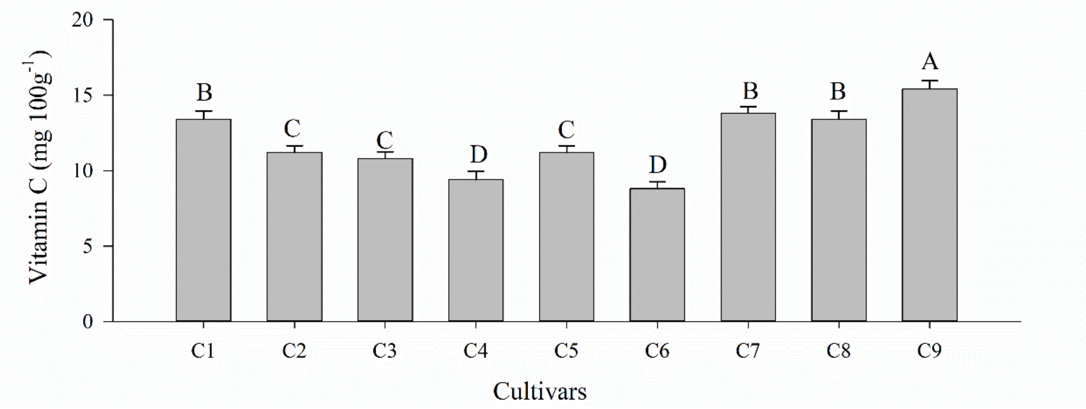
		Soluble Solids (ºBRIX)	**pH**	**Titratable Acidity (g Citric acid 100g^{-1})**	**Maturation Index**	**Water Content (%)**
Treatment	Processed	9.08a	4.15a	0.54a	17.60a	94.20b
	In natura	5.47b	4.10b	0.54a	10.39b	95.11a
Cultivar	C1	6.93d	4.23a	0.47c	15.27b	95.09a
	C2	6.40e	4.14c	0.78a	8.23d	95.33a
	C3	5.92f	4.12c	0.50c	11.84c	95.65a
	C4	6.85d	4.10c	0.40d	17.59a	95.34a
	C5	7.15c	4.17b	0.59b	12.15c	95.44a
	C6	7.24c	4.22a	0.46c	15.91a	95.47a
	C7	7.85b	4.13c	0.58b	13.61b	93.61b
	C8	7.91b	4.00d	0.54b	14.78b	93.60b
	C9	9.23a	4.00d	0.56b	16.61a	92.41ca
Processed	C1	8.80cA	4.26aA	0.46	19.92aA	94.67aA
	C2	8.10dA	4.11aB	0.80	10.24cA	95.20aA
	C3	7.46eA	4.11bA	0.50	14.92bA	95.11aB
	C4	8.72cA	4.09bA	0.38	23.22aA	94.77aB
	C5	9.08cA	4.17aA	0.60	15.27bA	95.08aB
	C6	9.04cA	4.22aA	0.46	19.86aA	95.19aB
	C7	9.54bA	4.19bA	0.58	16.55aA	92.65bB
	C8	9.74bA	4.11cA	0.54	18.21aA	92.95bB
	C9	11.24aA	4.10cA	0.56	20.24aA	92.18cB
In Natura	C1	5.06cB	4.20aB	0.48	10.62bB	95.50aB
	C2	4.70dB	4.17cA	0.76	6.21dB	95.45aA
	C3	4.38eB	4.13cA	0.50	8.76cB	96.18aA
	C4	4.98cB	4.10cA	0.42	11.96aB	95.91aA
	C5	5.22cB	4.18bA	0.58	9.03cB	95.80aA
	C6	5.44cB	4.22aA	0.46	11.96bB	95.75aA
	C7	6.16bB	4.08bB	0.58	10.67cB	94.56bA
	C8	6.08bB	3.89cB	0.54	11.35bB	94.24bA
	C9	7.22aB	3.90cB	0.56	12.99bB	92.64cA
	C.V.(%)	**4.01**	**1.02**	**9.81**	**13.78**	**0.45**

Source: Authors.

3.3 Vitamin C

The highest contents of vitamin C were found in cultivar 9 (Figure 5), with values of about 15 mg 100g^{-1}. These values were lower than those found by Borguini, 2002, since their values were between 18.9 and 21.9 mg 100g^{-1} of fresh weight in conventional and organic tomatoes from Carmen and Débora cultivars. In tomatoes samples submitted to thermal processing, the values were undetectable.

Figure 5. Vitamin C content (mg 100g^{-1}) in the nine *in natura* tomato cultivars.



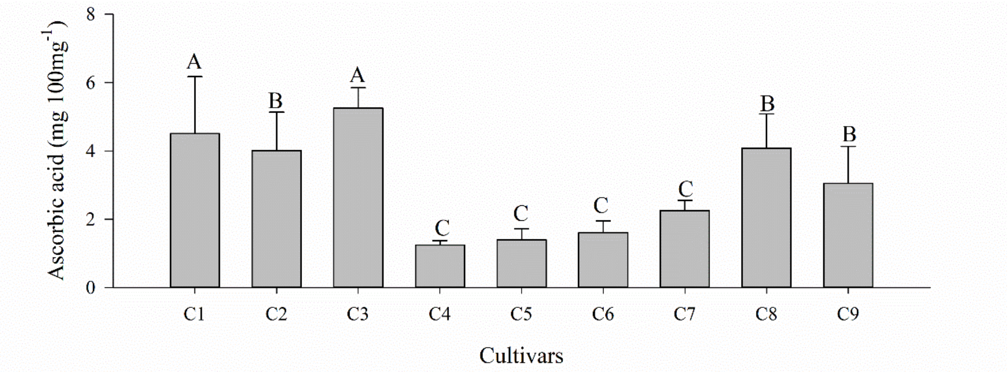
Source: Authors.

3.4 Ascorbic acid

The results for the analysis of ascorbic acid in *in natura* tomatoes are shown in Figure 7. Ascorbic acid decomposes with oxidation and heat treatments, especially at high temperatures. As this compound is very sensitive to several processes, the loss amount of ascorbic acid is used as a measure of the adverse effects on food processing (Boonpangrak et al., 2016), and this behavior is verified in the present study, since both the evaluation of vitamin C and ascorbic acid content were not detected in tomato samples submitted to processing since this vitamin is sensitive to thermal processing (Vieira, 2016).

Cultivars 1 and 3 showed the highest contents of ascorbic acid, this being 5.25 mg 100g^{-1} fresh weight, as shown in Figure 6. It was also possible to verify that cultivar 4 was the one with the lowest content among the cultivars studied, and their values were around 1.25 mg 100g^{-1}, a value 76.20% lower than cultivar 3, showing the variation that can be found in the contents of ascorbic acid in different cultivars.

Figure 6. Ascorbic acid content (mg 100g^{-1}) in the nine *in natura* tomato cultivars.



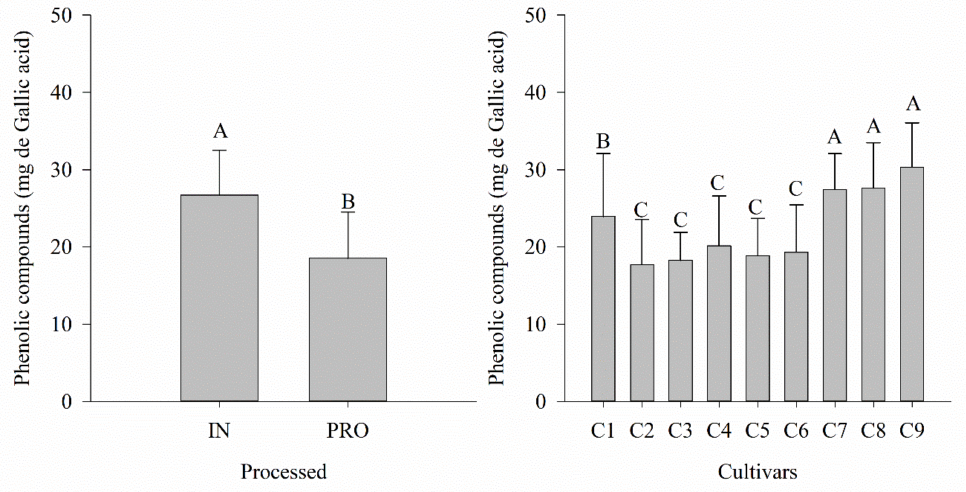
Source: Authors.

3.5 Total Phenols

The analysis of total phenols was performed for the nine *in natura* and processed tomato cultivars and the results are shown in Figures 7 (a) and (b). As can be seen in Figure 7 (a), the total polyphenol content decreased significantly during processing in all studied cultivars, varying from 11 to 46%. The results agree with those of Perez-Conesa et al. (2009), who also found a significant decrease in polyphenols due to cooking. However, the results found in this study are at disagreement with Abreu et al. (2012) who found values from 35 to 55 mg 100g^{-1} of phenolic compounds in tomato pulp and concluded that boiling increases polyphenols in tomatoes.

Thus, Figures 7 (a) and (b) show that for the contents of polyphenols, there was no interaction among the factors, only between the isolated factors, namely: cultivars and processing, respectively. Thus, it was possible to verify that the thermal processing had a negative influence on the polyphenols content, in all cultivars studied. It is worth mentioning that these biochemical parameters must be studied exhaustively because the results found in the literature present divergences.

Figure 7. Figure 7 (a) shows polyphenol content (mg Gallic acid 100g^{-1}) for *in natura* and processed tomato and Figure 7 (b) polyphenols content to nine tomato cultivars.



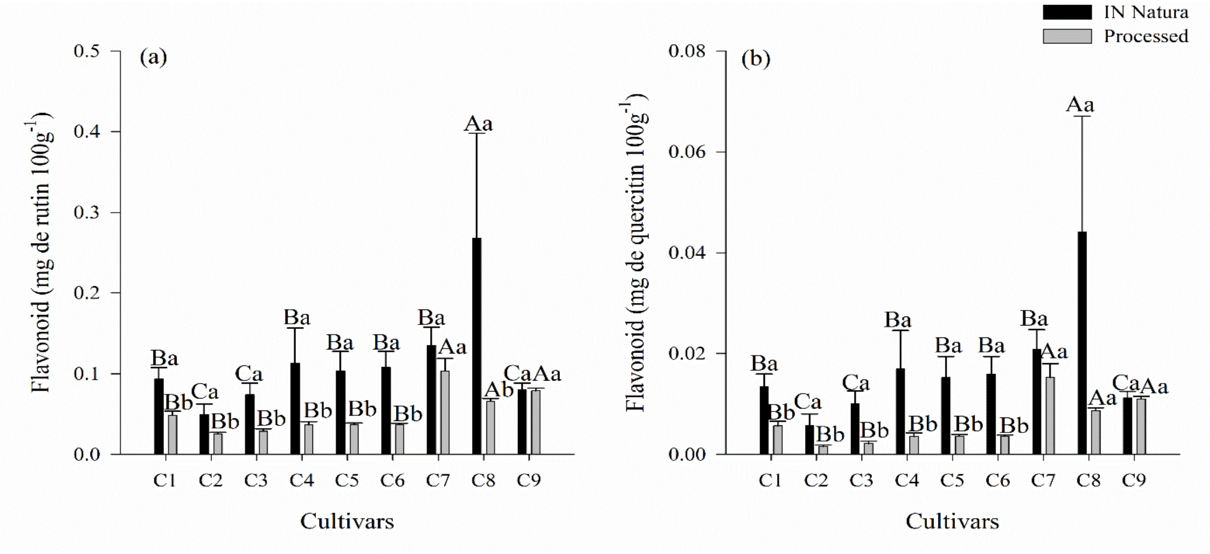
Source: Authors.

3.6 Flavonoids

The results regarding the evolution in the flavonoid content after processing can be seen in Figures 8 (a) and (b). Azzez et al., (2019) studying the kinetics of bioactive compounds in tomatoes subjected to different temperatures and drying time verified a tendency to reduce the flavonoid content with increasing temperature and drying time, this result was similar to that obtained for tomatoes by Dewanto et al. (2002) and Kamiloglu et al. (2014) who studied the effect of processing on the bioaccessibility of different compounds and Kamiloglu et al (2016) who studied the effect of drying on different vegetables. Studies such as those carried out by Raffo et al. (2006) showed that small tomatoes are rich in antioxidants, in particular carotenoids and flavonoids, and the cultivars studied showed from insignificant losses to considerable losses of flavonoids. In a study with two cherry tomato cultivars submitted to different irrigation systems, Pernice et al. (2010) found in *in natura* tomatoes and after processing that the amount of these compounds was similar or slightly lower compared to fresh fruits. In the present study, the highlight is given by the cherry cultivar 7, which presented the highest contents in *in natura* fruits, showing superior results in up to 3x the other cultivars studied. In the processed samples, the cherry cultivars presented the highest contents.

Figures 8 (a) and (b) show that all cultivars showed a quantitative decrease in the contents of flavonoids. For a better appreciation of the data, they are represented in the concentration curves in rutin and quercetin to express the results (Figures 8 (a) and (b), respectively).

Figure 8. Figure 8 (a) shows the flavonoids content (mg rutin $100g^{-1}$) and Figure 8 (b) shows the flavonoids contents (quercetin mg $100g^{-1}$), for the nine tomato cultivars.



Source: Authors.

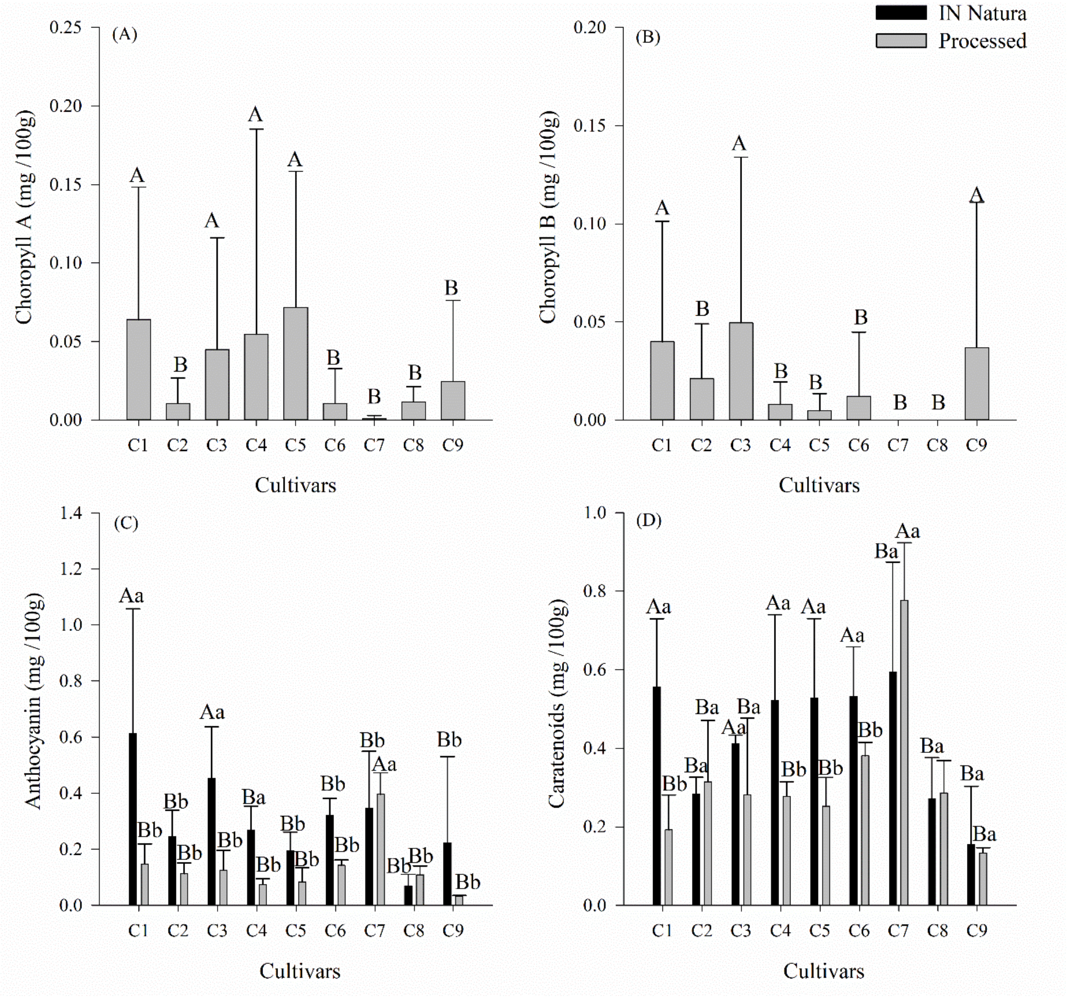
3.7 Carotenoids, anthocyanins and other pigments

Carotenoids are a family of fat-soluble pigments synthesized by plants and microorganisms, being responsible for the yellow, orange and red colors of many vegetables. The methodology used to determine the pigments: a and b chlorophyll, carotenoids and anthocyanin, was adapted from Sims and Gamon (2002). In this method, a spectrophotometric reading was performed and the results were expressed in mg 100g^{-1}fresh weight. The results for the pigment analysis are shown in Figures 9 (a) to (d). Looking at Figures 9 (a) and (b), it appears that the thermal processing did not interfere with the contents of chlorophyll (a) and (b), with a significant difference only among the cultivars, as for Figures 9 (c) and (d), thermal processing influenced the contents of anthocyanin and carotenoids.

Evaluating Figure 9 (a), it can be seen that cultivars 1, 3, 4 and 5 presented results superior to the others in the a chlorophyll indexes, while cultivar 7 presented one of the lowest contents, with its average being zero, for this component, while cultivar 5 presented 0.13 mg 100g^{-1}fresh weight. As for Figure 9 (b), it was found that cultivars 1, 3 and 9 showed little difference in the contents of b chlorophyll, with average values around 0.07 to 0.09 mg 100g^{-1} fresh weight, whereas cultivars 4, 5, 7 and 8, presented null values, or almost null, for this pigment.

As can be seen in Figure 9 (c), with the exception of cultivars 7 and 8, there was an increase of 14.13 and 58.21%, respectively, in the anthocyanin content, after thermal processing, whereas for the other cultivars there were reductions of 12.56 to 45.87% of the anthocyanin content after cooking. As for Figure 9 (d), cultivars 2, 7, and 8 showed an increase of 11.14%, 30.77% and 5.50%, respectively, in the contents of carotenoids after thermal processing, while for the other cultivars there were reductions from 34.57 to 85.90%. Heat treatment can reduce carotenoid contents via isomerization and/or oxidation of compounds (Cole and Kapur, 1957, Shi et al., 2000).

Figure 9. Figure 9 (a) shows the contents of a chlorophyll (mg $100g^{-1}$), 9 (b) b chlorophyll (mg $100g^{-1}$), 9 (c) anthocyanin (mg $100g^{-1}$) and 9 (d) carotenoids (mg $100g^{-1}$)), for *in natura* and processed tomatoes.



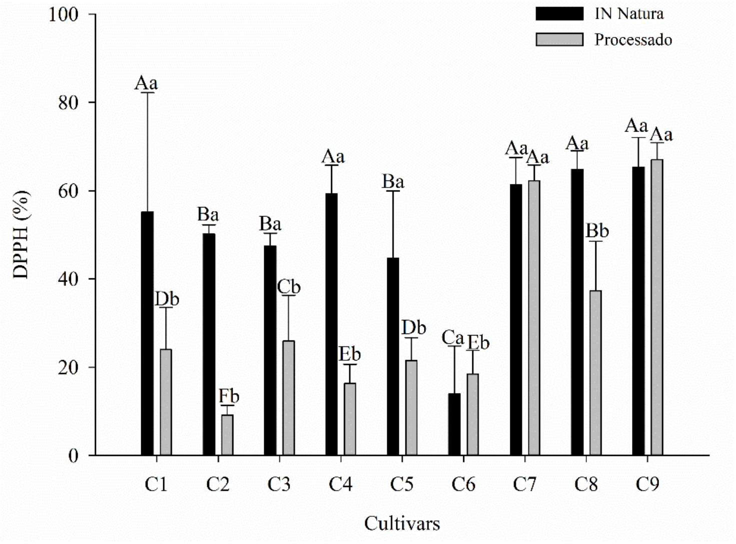
Source: Authors.

3.8 Total Antioxidant Activity

3.8.1 DPPH

As can be seen in Figure 10, thermal processing influenced the contents of antioxidant activity, with the exception of cultivars 6, 7 and 9, all the others showed decreases that ranged from 18.19 to 57.57% of antioxidant activity when evaluated by this method. Cultivars 6, 7 and 9 showed an increase in antioxidant activity by 32.34, 1.40 and 2.52%, respectively, agreeing with the result presented by Abreu et al. (2012) who found increased antioxidant activity after cooking. Significant reduction in antioxidant activity has been recorded for heat-processed tomatoes at different temperatures and cooking times compared to *in natura* tomatoes (Azzez et al., 2019).

Figure 10. Antioxidant activity content obtained by the DPPH method (%), in the nine *in natura* and processed tomato cultivars.



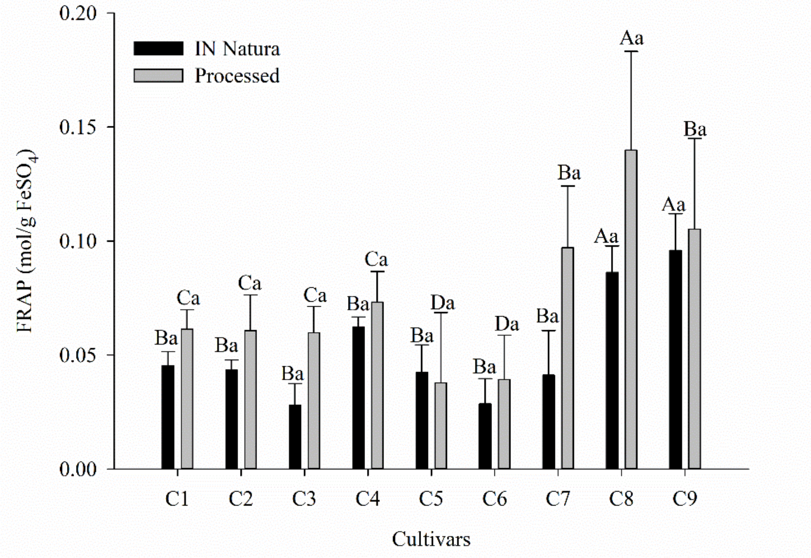
Source: Authors.

3.8.2 FRAP (Iron reduction capacity)

The results for the quantification of antioxidant activity by the FRAP method are shown in Figure 11. Analyzing Figure 11, it was possible to verify that cultivar 5 showed a 10.69% reduction in antioxidant activity after cooking, while the other studied cultivars showed an increase in antioxidant activity evaluated by this method, and the increase varied from 9.79 to 113.89%. The result is in agreement with Vieira, 2016 who also found increased antioxidant activity after subjecting the fruits to heat treatment using this method. Still evaluating Figure 12, it appears that the last three studied cultivars presented the highest values for the antioxidant activity evaluated by this method.

When comparing the antioxidant activity by the DPPH and FRAP method, it is noted that the cultivars that showed higher values related to the antioxidant activity were 7, 8 and 9, all of them cherry type.

Figure 11. Antioxidant activity content obtained by the FRAP method (mol g $FeSO_4$),), in the nine *in natura* and processed tomato cultivars.



Source: Authors.

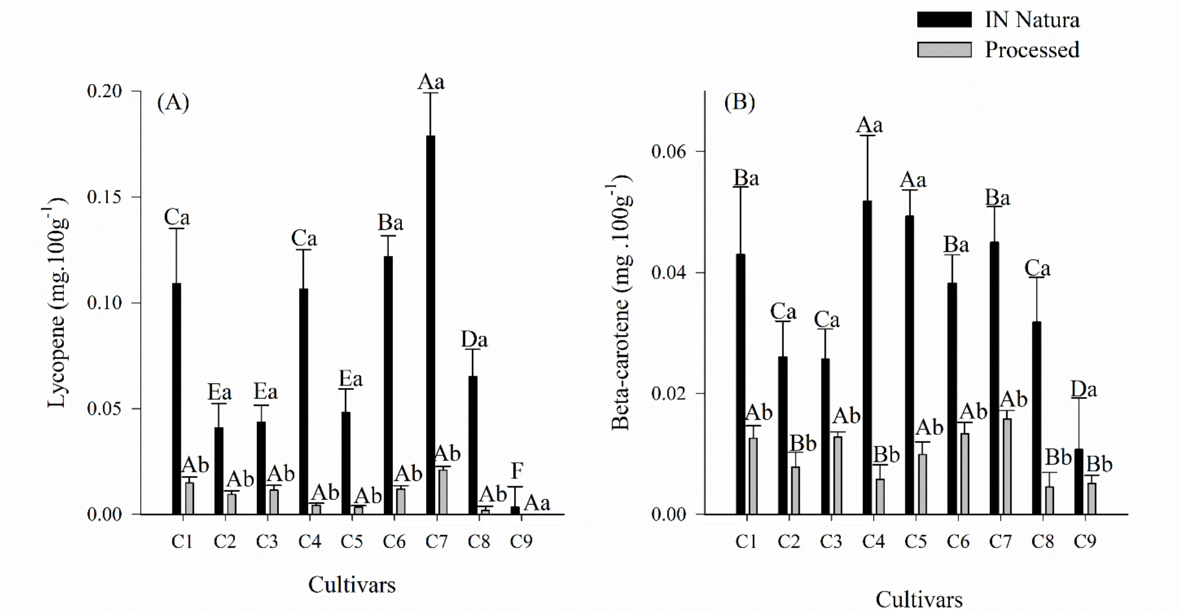
3.9 Lycopene and β- Carotene

The lycopene content of tomato products varies according to geographic location (Aherne et al., 2009), the cultivar, the stage of maturation, and the processing parameters and can vary from 879 to 4200 µg per 100 g in raw tomatoes, and the range may be greater in processed tomato products (Scalfi et al., 2000). In the present study, there were significant reductions compared to *in natura* tomatoes and after processing in the contents of lycopene and β-carotene.

One of the most important characteristics of lycopene is the efficient deactivation of a series of free radicals, such as hydrogen peroxide, nitrogen dioxide and thio and sulfonyl radicals, in addition to highly destructive hydroxyl radicals.

The antioxidant effects of lycopene can be increased by the presence of other bioactive compounds, such as carotenoids and vitamins, due to the synergistic antioxidant activity. This hypothesis has been the subject of numerous studies that confirm the positive correlation between the antioxidant properties of lycopene and the interactions with other bioactive compounds studied (Shi et al., 2004). The results regarding the quantification of lycopene and *beta*-carotene are shown in Figures 12 (a) and (b). Cultivar 7 was the one with the highest contents when compared to the other varieties (Figure 12 (a)). It is also possible to verify that all cultivars showed sharp losses when the tomatoes were submitted to processing.

Figure 12. Lycopene and *beta*-carotene contents (mg $100g^{-1}$), in the nine *in natura* and processed tomato cultivars.



Source: Authors.

β-carotene represents the second most abundant carotenoid, after lycopene, in industrial tomato residues, as confirmed by a recent study on bioactive compounds in industrial tomatoes and their processing by-products (Kalogeropoulos et al., 2012). In Figure 12 (b) it is possible to verify that cultivars 4 and 5 presented results superior to the others.

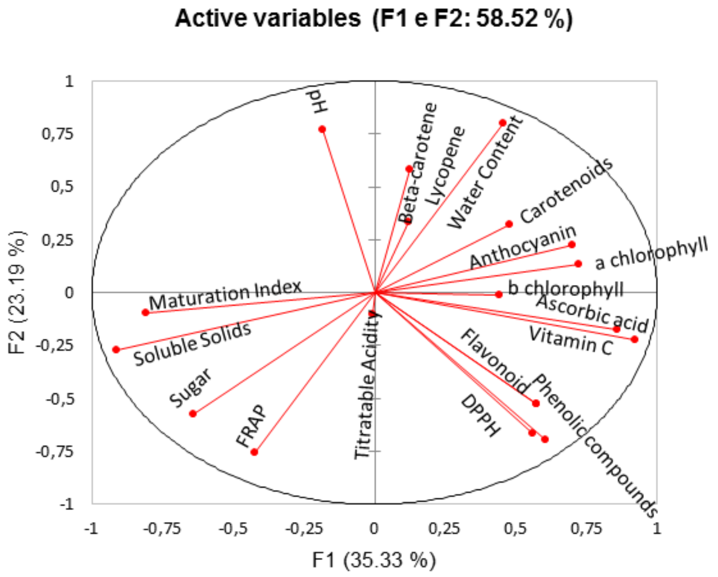
In a recent study it was found that the bioavailability of β-carotene increases as a consequence of moderate heating or enzymatic disruption of the structure of the plant cell wall (Singh & Goyal, 2008). In some cases, processing causes little or no change in the content and activity of naturally occurring antioxidants. In another study, in the case of some carotenoids, such as lycopene and β-carotene, these compounds proved to be very heat-stable, even after intense or prolonged heat treatments, such as those involved in sterilization, cooking and frying processes (Nicoli et al, 1999).

Principal component analysis

The multivariate analysis was performed to verify the grouping of the different responses and to obtain additional information about the influence of the analyzed variables regarding to the *in natura* and processed tomato samples analyzed. In this evaluation, it was found that components 1 and 2 (*in natura* and processed tomatoes, and laboratory analysis, respectively) explained 60.83% of the experiment variance (Figure 13).

When evaluating the results presented, it is possible to verify that according to the water content, the higher it appears, the lower the content of soluble solids and sugars in the samples, showing opposite behaviors as presented in Figure 13. The contents of vitamin C and ascorbic acid are similar with similar behavior as well as the contents of total sugar and soluble solids, DPPH and phenolic compounds, respectively.

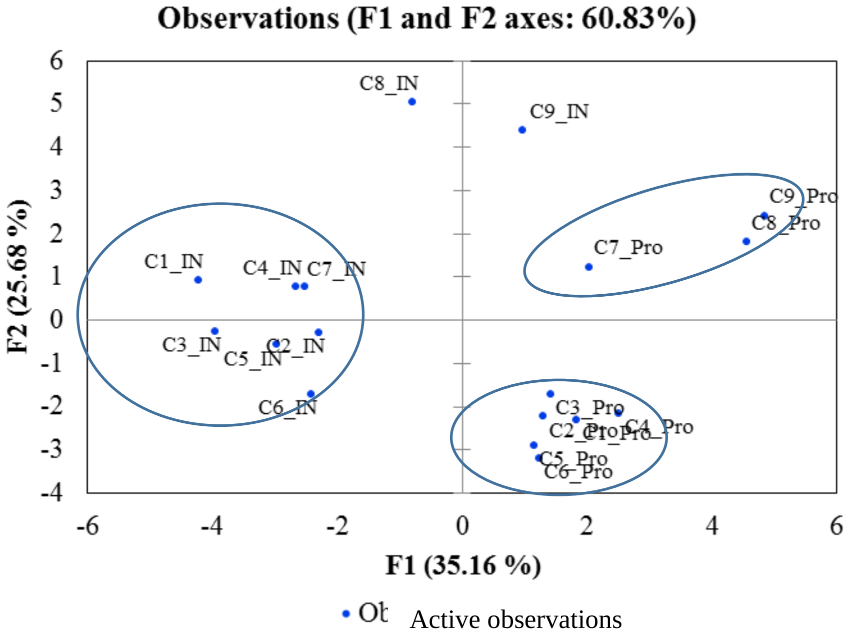
Figure 13. Two-dimensional projection (A) and scores (B) of the parameters analyzed in *in natura* and processed tomatoes.



Source: Authors.

Figure 14 shows a close approximation among them of the processed cultivars and in another quadrant the approximation of the *in natura* cultivars showing that these samples have similar performances compared to the analyzes performed. The behavior already shown on cultivars 7, 8 and 9, especially after processing, can be seen in Figure 14, which shows these cultivars approximated to each other, with similar behavior.

Figure 14. Principal Component Analysis of the obtained results (C = Cultivar, IN = *In natura* and Pro = Processed).



Source: Authors.

Tables 2 (a), (b) and (c) show the values of correlation between the variables of the parameters evaluated for the 9 *in natura* and processed tomato cultivars. In it, the following correlations can be highlighted: *beta*-carotene x lycopene, positive in 64%. As lycopene belongs to the carotenoids' family, the results presented explain this behavior, the antioxidant activity by the DPPH method showed a positive correlation regarding to the content of flavonoids, vitamin C, ascorbic acid and phenolic compounds, the latter having high antioxidant power and sugars x soluble solids with a correlation of 0.80.

Pearson's correlation analysis revealed that phenolic compounds followed by flavonoids were the compounds most strongly correlated with antioxidant activity by the DPPH method, with the first compound also showing a positive correlation when the method used to determine antioxidant activity was FRAP.

4. Conclusion

It was possible to verify from the data obtained that for most of the analyzed bioactive parameters that there are losses due to processing.

Another interesting conclusion was that the cherry cultivars (7, 8 and 9) had the highest contents for phenolic compounds, antioxidant activity by the DPPH and FRAP methods, soluble solids and sugar and, consequently, the lowest water content.

Regarding the antioxidant activity, these cultivars showed little or no loss when the evaluation method was based on DPPH and an increase in activity when the evaluation method was FRAP. This shows that these cultivars are interesting to be better explored and have great potential for processing.

Acknowledgments

The authors gratefully acknowledge the financial support of Sao Paulo Research Foundation (FAPESP) for financial support of this study (grant number 2019/00021-4) and for the scholarship provided to J. M. Mello (grant number 2019/00500-0) and T. G. F. Santos from National Council for Scientific and Technological Development (Pibic-CNPq, Brazil).

References

Abreu, W. C., & Barcelos, M. F. P. (2012). Atividade antioxidante total da polpa de tomate submetida ao processamento térmico doméstico em diferentes tempos. *Cient Ciênc Biol Saúde*, 14(2), 71-6.

Aherne, S. A., Jiwan, M. A., Daly, T., O’brien, N. M. (2009). Geographical location has greater impact on carotenoid content and bioaccessibility from tomatoes than variety. *Plant Foods Hum Nutr*, 64, (4), 250–256. https://doi.org/10.1007/s11130-009-0136-x

Anthon, G. E., Barrett, D. M. (2012). Pectin methylesterase activity and other factors affecting pH and titratable acidity in processing tomatoes. *Food Chemistry*, 132(2), 915-920. http://dx.doi.org/10.1016/j.

Araujo, J. C., Silva, P. P. M., Telhado, S. F. P., Sakai, R. H., Spoto, M. H. F., Melo, P. C. T. (2014). Physico-chemical and sensory parameters of tomato cultivares grown in organic systems. *Horticultura Brasileira*, 32(2), 205-209. https://dx.doi.org/10.1590/S0102-05362014000200015

Azeez, L., Segun, A. A., Oyedeji, A. O., Adetoro, R. O., Tijani, K. O. (2019). Bioactive compounds' contents, drying kinetics and mathematicalmodelling of tomato slices influenced by drying temperatures and time. *Journal of the Saudi Society of Agricultural Sciences*, 18, 120–126121. https://doi.org/10.1016/j.jssas.2017.03.002

Benzie, I. F. F. & Strain, J. J. (1996). The ferric reducing ability of plasma (FRAP) as a measure of antioxidant power: The FRAP assay. *Analytical Biochemistry* 239. 70–76. http://dx.doi.org/10.1006/abio.1996.0292

Boiteux, L. S., Fonseca, M. E. N., Giordano, L. B., Melo, P. C. T. (2012). Melhoramento genético. In F. M. V. T. Clemente & L. S. Boiteux (Ed.), *Produção de tomate para processamento industrial* (pp. 31-50). Brasília: Embrapa.

Boonpangrak, S., Lalitmanat, S., Suwanwong, Y. (2016). Analysis of Ascorbic Acid and Isoascorbic Acid in Orange and Guava Fruit Juices Distributed in Thailand by LC-IT-MS/MS. *Food Anal. Methods,* 9:1616. https://doi.org/10.1007/s12161-015-0337-x

Borguini, R. G. (2002). Tomate (Lycopersicon esculentum Mill.) orgânico: o conteúdo nutricional e a opinião do consumidor. 2002. 110 f. *Dissertação* (Mestrado em Agronomia)-Escola Superior de Agricultura Luiz de Queiroz, Universidade de São Paulo, Piracicaba.

Brand-Williams, W., Cuvelier, M. E., Berset, C. 1995. Use of free radical method to evaluate antioxidant activity. *Lebensmittel-Wissenschaft & Technologie,* 28, 25-30, https://doi.org/10.1016/S0023-6438(95)80008-5

Cemeroglu, B., Karadeniz, F., Ozkan, M. (2003). Meyve sebze isleme teknolojisi. *Gıda Teknolojisi Yayınları*, 28, 469-472.

Chanforan, C., Loonis, M., Mora, N. (2012). The impact of industrial processing on health-beneficial tomato microconstituents. *Food Chem.,* 134, 1786–1795. https://doi.org/10.1016/j.foodchem.2012.03.077

Cole, E., & Kapur, N. (1957). The stability of lycopene. I.-Degradation by oxygen. *Journal of the Science of Food and Agriculture*, 8:6, 360-365. https://doi.org/10.1002/jsfa.2740080610

Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., Smith, F. (1956). Colorimetric method for determination of sugars and related substances. *Analytical Chemistry*, 28, 3, 350-356. https://doi.org/10.1021/ac60111a017

Food and Agricultural Organization - FAO. (2019). *FAO Statistical Yearbook*. New York, Recuperado de www.fao.com.

Instituto Adolfo Lutz - IAL. (2005). *Métodos físico-químicos para análise de alimentos.* 4 ed. Brasília: ANVISA,

Ilahy, R, Hduder, C, Lenucci, M. S., Tlili, I, Dalessandro, G. (2011). Phytochemical composition and antioxidant activity of highlycopene tomato (Solanum lycopersicum L.) cultivares grown in Southern Italy. *Scientia Horticulturae*, 127:3, 255-261. https://doi.org/10.1016/j.scienta.2010.10.001

Kalogeropoulos, N., Chiou, A., Pyriochou, V. (2012). Bioactive phytochemicals in industrial tomatoes and their processing byproducts. LWT - *Food Sci Technol.*, 49, 213-216. https://doi.org/10.1016/j.lwt.2011.12.036

Nagata M., & Yamashita, I. (1992). Simple method for simultaneous determination of chlorophyll and carotenoids in tomato fruit. *Nippon Shokuhin Kogyo Gakkaish*, 39:10, 925-928. https://doi.org/10.3136/nskkk1962.39.925

Nicoli, M., Anese, M., Parpinel, M. (1999). Influence of processing on the antioxidant properties of fruit and vegetables. Trends *Food Sci Technol.*, 10, 94–100. https://doi.org/10.1016/S0924-2244(99)00023-0.

Perez-Conesa, D., Garcia-Alonso, J., Garcia-Valverde, V., Iniesta, M. D., Jacob, K., Sanchez-Siles, L. M. (2009). Changes in bioactive compounds and antioxidant activity during homogenization and thermal processing of tomato puree. Innovative. *Food Science and Emerging Technology*, 10:2, 179–188. https://doi.org/10.1016/j.ifset.2008.12.001

Pernice, R., Parisi, M., Giordano, I., Pentangelo, A., Graziani, J., Gallo, M., Fogliano, V., Ritieni, A. (2010). Antioxidants profile of small tomato fruits: Effect of irrigationand industrial process. *Scientia Horticulturae*, 126, 156–163. https://doi.org/10.1016/j.scienta.2010.06.021

Raffo, A., La Malfa, G., Fogliano, V., Maiani, G., Quaglia, G. (2006). Seasonal variations in antioxidant components of cherry tomatoes (*Lycopersicon esculentum* cv. Naomi F1). *Journal of Food Composition and Analysis*, 19, 11–19. https://doi.org/10.1016/j.jfca.2005.02.003

Resende, E. C. O. (2010). Enzimas antioxidantes em frutos com diferentes padrões de amadurecimento. Orientadora: BRON, I. U. Campinas: IAC, 2010. 67f. *Dissertação* (Mestrado) – Instituto Agronômico, Campinas, Recuperado de http://www.iac.sp.gov.br/areadoinstituto/posgraduacao/dissertacoes/Evellyn%20Couto%20Oliveira.pdf. Acesso em: 07 jan. 2020.

Scalfi, L., Fogliano, V., Pentangelo, A. (2000). Antioxidant activity and general fruit characteristics in different ecotypes of Corbarini small tomatoes. *J Agric Food Chem.*, 48:4, 1363–1366. https://doi.org/10.1021/jf990883h

Shi, J., Dai, Y., Kakuda, Y., Mittal, G., Xue, S. J. (2008). Effect of heating and exposure to light on the stability of lycopene in tomato purée. *Food Control*, 19:5, 514-520, https://doi.org/10.1016/j.foodcont.2007.06.002

Shi, J., Kakuda, Y., Yeung, D. 2004. Antioxidative properties of lycopene and other carotenoids from tomatoes: synergistic effects. *Biofactors*, 21, 203–210.

Sims, D. A., & Gamon, J. A. (2002). Relationships between leaf pigment content and spectral reflectance across a wide range of species, leaf structures and developmental stages. *Remote Sensing of Environment*, 81, 337-354. https://doi.org/10.1016/S0034-4257(02)00010-X

Singh, P., & Goyal, G. K. (2008). Dietary lycopene: its properties and anticarcinogenic effects. *Compr Rev Food Sci Food Saf*, 7, 255–270. https://doi.org/10.1111/j.1541-4337.2008.00044.x

Singleton, V. L., & Rossi Jr, J. A. (1965). Colorimetry of total phenolics with phosphomolybidic-phosphotungstic acid reagents. *American Journal of Enology and Viticulture*, 16, 144-158.

Singleton, V. L., Orthofer, R., Lamuela, R. M. 1999. Analysis of total phenol and other oxidation subtrates and antioxidants by means of Folin-Ciocauteau reagent. *Methods of Enzymology*, 299, 152-178. https://doi.org/10.1016/S0076-6879(99)99017-1

Souza, A. V., Vieira, M. R. S., Putti, F. F. (2018). Correlações entre compostos fenólicos e atividade antioxidante em casca e polpa de cultivares de uva de mesa. *Brazilian Journal of Food and Technology*, 21. https://doi.org/10.1590/1981-6723.10317

Szabo, K., Cătoi, A. F., Vodnar, D. C. (2018). Bioactive Compounds Extracted from Tomato Processing by-Products as a Source of Valuable Nutrients. *Plant Foods Hum Nutr.*, 73:268. https://doi.org/10.1007/s11130-018-0691-0

Takeoka, G. R., Dao, L., Flessa, S., Gillespie, D. M., Jewell, W. T., Huebner, B. (2003). Processing effects on lycopene content and antioxidant activity of tomatoes. *J Agric Food Chem.*,, 49, 3713-7. https://doi.org/10.1021/jf0102721

Terada, M, Watanabe, Y, Kunitoma, M, Hayashi, E. (1978). Diferential rapid analyses of ascobic acid and ascorbic acid 2-sulfate by dinitrophenil hydrazine method. *Am Biochem*., 84, 604-608. https://doi.org/10.1016/0003-2697(78)90083-0

Taco -Tabela Brasileira de Composição de Alimentos/Nepa. (4th ed.). Campinas: Nepa-Unicamp, 2011

Vanzoonen, P. (1996). Analytical methods for pesticide residues in foodstuffs. (6th ed.), Netherlands: Ministery of Public Health, Welfare and Sport.

Vieira, M. C. S. (2016). Investigação dos compostos bioativos em tomates (Lycopersicon esculentum L.) após processamento térmico. 59 f. *Dissertação* (Mestrado) - Curso de Mestre em Agronomia (horticultura), Faculdade de Ciências Agronômicas da Unesp – Campus de Botucatu, Universidade Estadual Paulista “Júlio de Mesquita Filho”, Botucatu.

Vítolo, H. F., Souza, G., M., Silveira, J. (2012). Cross-scale multivariate analysis of hysiological esponses to high temperature in two tropical crops with C3 and C4 metabolism. *Environmental and Experimental Botany*, 80:1. https://doi.org/10.1016/j.envexpbot.2012.02.002

Percentage of contribution of each author in the manuscript

Angela Vacaro de Souza – 30%
Jéssica Marques de Mello – 25%
Vitória Ferreira da Silva Favaro – 15%
Victória Farias da Silva – 10%
Diogo de Lucca Sartori - 10%
Fernando Ferrari Putti – 10%