Evaluation of biogenic amines and nitrate in raw and pickled jurubeba (*Solanum paniculatum* L.) fruit

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Revised: 18 March 2019 / Accepted: 4 April 2019 / Published online: 10 April 2019
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Abstract The presence of biogenic amines, such as histamine and tyramine, in pickled food can cause health problems, such as allergies. However, other bioactive amines may be present and can induce some diseases. Some biogenic amines can react with nitrate and form nitrosamines, compounds harmful to human health. In this research, we qualitatively and quantitatively evaluated some biogenic amines and nitrate content in jurubeba preserved in oil or vinegar. The fruits were obtained from cultivated plants, or wild plants, or they were purchased from market. Jurubeba fruit was analyzed raw and after cooking. After thermal processing, the fruits were preserved in soybean oil or vinegar and were evaluated after 1 h and at 30, 60 and 90 days of storage. Variations in the contents of biogenic amine were found depending on the place from which the fruits were obtained, as well as depending on the type of preservative and time of storage. The nitrate levels did not exceed the established limits, mainly when preserved in vinegar, which also showed the lowest levels of biogenic amines.

Keywords Cooking · Polyamines · Nitrate · Solanaceae · Shelf-life · UPLC

Introduction

Biogenic amines (BAs) are mono or polycationic molecules produced in plants and mammals after α -decarboxylation of free amino acids (Handa et al. 2018). In addition to their role as secondary messengers, these molecules are related to many biological functions, such as cell division, differentiation and the stabilization of membranes and nucleic acids, beyond acts as secondary messengers (Larqué et al. 2007). In humans, the body pool of BAs is maintained by three sources: (1) endogenous biosynthesis (de novo synthesis), (2) synthesis by gut microbiota, which are released into the intestinal lumen, and (3) dietary intake (Pegg 2016). Diet provides a greater daily number of BAs than endogenous biosynthesis since these molecules are completely absorbed from the ingested food (Handa et al. 2018). The concentration of BA can vary according to the cell type, but increased levels are generally found in tissues with high growth rate (Moinard et al. 2005). Low concentrations of BAs are not considered a health risk. However, when they are consumed excessively they can have toxic effects (Saaïd et al. 2009) such as fever, hypertension, vomiting, allergic processes (itching, rash), and breathing difficulties (Naila et al. 2010). More severe health problems have also been proposed, such as a possible relation between BAs and cancer development (Tassoni et al. 2000).

Jurubeba (*Solanum paniculatum* L.) is a non conventional vegetable, generally consumed after a cooking process. In Brazil, this vegetable is used in folk medicine for treatment of chronic hepatitis, jaundice and gastrointestinal

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disorders (Mesia-Vela et al. 2002). Even though studies investigating jurubeba production and quality have increased in recent years, little is known about its BA concentrations. Determining BAs in foods is of great interest, not only due to their possible toxicity but also because they can be used as indicators of freshness and deterioration.

Fresh fruits and juices are particularly rich in putrescine, while green vegetables are richer in spermidine (Valero et al. 2002). According to various authors, some processes using heat can influence the BAs' content (Silva et al. 2016). In addition, BAs' levels may be affected in canned or pickled foods as a result of microbial decarboxylation of amino acids during preparation or even during storage (Carelli et al. 2007). Some substances used as preservatives can inhibit the formation of BAs. For example, preservatives such as sodium nitrate (Kurt and Zorba 2010), ascorbic acid (Bozkurt and Erkmén 2004) and glycine (Mah and Hwang 2009), have shown efficiency in inhibiting the synthesis or interconversion of BAs. However, the effects of oil or vinegar as preservatives, and their relation with BAs, have not been clearly elucidated.

Putrescine and cadaverine are considered primary amines that cyclize after heating processes to form secondary amines, which react with nitrite to form nitrosamines. Vegetables naturally contain nitrate, which can be converted in nitrite in the oral cavity and/or the stomach (Duncan et al. 1997). Therefore, the formation of nitrosamine can be increased in foods with a high concentration of BAs, particularly in vegetables preserved at a low pH or with sodium chloride (Yurchenko and Mölder 2007). In processed food, the nitrosamine formation is a food safety problem. To verify the levels of BAs and nitrate, we quantified both classes of compounds in jurubeba fruit that had been pickled in oil or vinegar and stored up to 90 days.

Material and methods

Materials

The ingredients used in the pickled jurubeba were vinegar (Belmont© Lençóis Paulista, São Paulo, Brazil) and soybean oil (Cargill©, Brazil). All reagents used were of analytical grade or UPLC grade and purchased from Sigma Aldrich-Merck (St. Louis, MO, USA, and Darmstadt, Germany).

Samples

The set of samples consisted of jurubeba fruits harvested from wild and cultivated plants, and acquired in a local market. The fruits were harvested from cultivated adult

plants (of about 3 years) in full rural producer (Cáceres, Mato Grosso, Brazil, latitude 16°04'14"S and longitude 57°40'44"W, 118 m altitude). The soil of the cultivation area is Yellow Latosol with high fertility. The plants were fertilized with 40 kg ha⁻¹ of P₂O₅, 60 kg ha⁻¹ of K₂O and 60 kg ha⁻¹ of N, using as a source single superphosphate, potassium chloride and urea, divided into four annual applications. Fruit from wild plant was harvested in the same place and at the same time. Fruit from market was acquired in a municipal market in the same conditions. For standardization of samples, all fruits used in the study were harvested at full maturity stage, and samples acquired in the local market were carefully selected to avoid fruits with peel damage and to ensure the same appearance as the harvested fruits.

Thermal process and pickling preparation

Before the thermal process, 5 kg of each sample set of fruits were cleaned with tap water and later immersed for 10 min in chlorinated water (containing 20 mg of free chlorine per liter). Thereafter, one portion was kept raw, and the other (500 g of each sample) was cooked for 20 min in a stainless steel pan containing 1 L of boiling water (Silva et al. 2016). Samples were drained and cooled rapidly. The cooked fruit was pickled in 300 mL glass jars that had previously been sterilized for 30 min in a solution of boiling water containing 2 g of pure NaCl and 150 mL of commercial soybean oil or vinegar (with 4% acetic acid). The recipients were covered with Parafilm®, capped with plastic lids and stored on shelves at room temperature (25 ± 2 °C) and protected from light. Evaluations were later performed on the raw and pickled fruits after they had been stored for 1 h as well as after 30, 60 and 90 days.

Extraction and quantification of biogenic amines

Raw and processed jurubeba fruit were ground in a cryogenic mill (Spex Sample Prep 6770, MA, USA) for 5 min and stored at -80 °C, protected from light. The BAs (spermine, putrescine, cadaverine, spermidine, histamine, and tyramine) were extracted following the method described by Lima et al. (2008) and analyzed by ultra high pressure liquid chromatography (UPLC) according to Dadáková et al. (2009). Briefly, the jurubeba samples were homogenized in perchloric acid 5% v/v for 1 h and subsequently centrifuged for 10 min at 8000 g and 4 °C (MIKRO 220/220R—Hettich Lab Technology, USA). Two-hundred microliters of supernatant were mixed with buffer Na₂CO₃ (4.5 mol L⁻¹) and dansyl chloride (Sigma Aldrich, MO, USA) and kept in the dark (60 °C for 1 h). Then, 100 µL of proline solution (10% in ultrapure water) were added to the samples and incubated at room

temperature for 30 min. After incubation, all samples were homogenized and 1000 μL of toluene were added to the tubes to extract the dansylated PAs. Finally, the toluene fraction was collected, dried under gaseous nitrogen and resuspended in 1.5 mL of acetonitrile. The samples (20 μL) were injected into a UPLC system (Ultimate 3000 BioRS, Dionex-Thermo Fisher Scientific Inc., USA), equipped with a diode array detector (DAD-3000RS), and set at 225–300 nm. The flow rate was 0.7 mL min^{-1} , using an Ace 5 C18 (Advanced Chromatography Technologies, UK) column (5 μm , 250 $\times$ 4.6 mm). The mobile phase consisted of 100% acetonitrile (solvent A) and 50% acetonitrile (solvent B). A linear chromatographic gradient was set to the following parameters: 0–4 min, 40% A + 60% B; 4–8 min, 60% A + 40% B; 8–12 min, 65% A + 35% B; 12–15 min, 85% A + 15% B; 15–21 min, 95% A + 5% B; 21–22 min, 85% A + 15% B; 22 min, 75% A + 25% B. The biogenic amines were identified by comparing the retention time and the UV spectrum with commercial standards, and the quantification was done through standard curves of the respective commercial standards (Put— $y = 0.277x - 9.234$ $R^2 = 0.99$; Spd— $y = 0.241x - 8.560$ $R^2 = 0.99$; Spm— $y = 0.284x - 9.493$ $R^2 = 0.99$; Cad— $y = 0.270x - 9.307$ $R^2 = 0.99$; His— $y = 0.239x - 4.1818$ $R^2 = 0.99$ and Tyr— $y = 0.258x - 5.973$ $R^2 = 0.99$).

Determination of nitrate

The nitrate content was determined using a Nitrate Meter (C-141, Horiba-Cardy®) characterized by an interval of linearity of 0–9900 ppm and previously calibrated with patterns of known concentrations of nitrate (0, 500, 1000, 1500, 2000 and 2500 $\text{mg L}^{-1} \text{NO}_3^-$). The readings were performed directly in undiluted ground jurubeba fruits.

Statistical analysis

The results were expressed as mean $\pm$ standard deviation, $n = 3$. Differences among the samples were determined by one-way analysis of variance (ANOVA). A Tukey's post hoc test (HSD) was used to compare all the groups and to determine whether treatments were significant ($P < 0.05$). Statistical analyses were performed using Software Sisvar 5.6, Build 86 (DEX-UFLA, Brazil). Principal component analysis (PCA) was conducted on data to obtain an overview of correlations among variables (PCA, software XLSTAT—version 2017, Addinsoft, France).

Results and discussion

Biogenic amines

A list of identified BAs in jurubeba fruits is presented in Tables 1 and 2 and Fig. 1. Even though jurubeba is not consumed *in natura* (without cooking), the level of BA must be safe for consumption. The highest BAs values were found in fruits harvested from cultivated plants (64.9 $\text{mg}/100 \text{ g}$) and from fruits acquired in local market (52.6 $\text{mg}/100 \text{ g}$) (Table 1). Putrescine was the major compound in all groups of fruits (cultivated, wild, and marketed). Some studies have demonstrated that exogenous putrescine may contribute to the increased shelf life of fruit after harvest (Valero et al. 2002), and the higher content of this diamine in freshly harvested fruits of jurubeba could be indicative of shelf life. In addition, higher levels of putrescine have been related to maintaining firmness after harvesting in several species. The relationship of putrescine and fruit softening is attributed to the cross-linkage of this amine with the carboxyl group (COOH) of the pectic substances in the cell wall, contributing to the firmness of the fruits (Valero et al. 2002). Jurubeba is a fruit with hard pulp (that is, with great firmness) and the higher values of putrescine could be related to the hardness of the fruits at harvest time.

Throughout storage, variations occurred in the levels of putrescine and spermidine in pickled fruit (in either oil or vinegar) (Table 2). From all analyzed amines, putrescine was the major compound, and after 30 days of storage, this amine reached the highest content in the marketed fruit (86.48 $\text{mg}/100 \text{ g}$ in oil and 63.47 $\text{mg}/100 \text{ g}$ in vinegar). Lower cadaverine content at 30 days was found in fruit preserved in oil (0.56 $\text{mg}/100 \text{ g}$) or in vinegar (0.72 $\text{mg}/100 \text{ g}$) (Table 2).

Putrescine and cadaverine are thermostable amines, and their variable levels after cooking and storage reinforces the hypothesis that processing fruits may improve the BAs' extraction. These amines have been correlated with the spoilage of some foods, such as fish, meat and vegetables (Riebroy et al. 2004), although with no toxic effect for consumers. However, they do increase the adverse effects of other amines, such as histamine and tyramine by competing for the detoxifying enzymes (Landete et al. 2011) and by reacting with nitrite to produce carcinogenic nitrosamines (Yurchenko and Mölder 2007). There is evidence that putrescine could play a role in promoting the malignancy of adenomas in murine models (Ignatenko et al. 2006). However, putrescine, spermidine, cadaverine tyramine have a remarkable antioxidant activity (Papa-georgiou et al. 2018), contributing to the elimination of free radicals generated during the metabolic processes. There

Table 1 Individual quantities (mg 100 g⁻¹) and total biogenic amines in raw jurubeba fruits

Sample	Cadaverine	Putrescine	Spermidine	Spermine	Histamine	Tyramine	Total
Cultivated	6.77 ± 1.0 ^a	35.54 ± 2.1 ^b	13.0 ± 1.6 ^a	0.52 ± 0.1 ^a	5.26 ± 1.9 ^a	3.87 ± 1.3 ^a	64.9 ^a
Wild	0.20 ± 0.1 ^b	18.41 ± 0.8 ^c	5.09 ± 1.1 ^b	0.56 ± 0.9 ^a	0.13 ± 0.0 ^b	1.52 ± 0.3 ^a	25.9 ^c
Marketed	0.23 ± 0.1 ^b	44.63 ± 0.6 ^a	4.63 ± 0.6 ^b	0.47 ± 0.2 ^a	0.16 ± 0.0 ^b	2.52 ± 0.2 ^a	52.6 ^b

Each value is expressed as mean ± SD (n = 3). Means followed by the same lowercase letter in the column are not significantly different ($P > 0.05$)

Table 2 Individual quantities (mg 100 g⁻¹) and total biogenic amines in jurubeba fruit freshly cooked and pickled in two types of conservatives after 1 h and 30, 60 and 90 shelf days

Processing	Sample	Cadaverine	Putrescine	Spermidine	Spermine	Histamine	Tyramine	Total	
Freshly cooked	Cultivated	10.92 ± 0.58 ^b	32.62 ± 2.96 ^g	13.97 ± 1.23 ^c	0.64 ± 0.13 ^e	8.43 ± 1.70 ^a	4.95 ± 0.46 ^c	71.53 ^d	
	Wild	1.08 ± 0.19 ^f	46.63 ± 2.59 ^e	22.47 ± 0.85 ^b	0.60 ± 0.18 ^e	0.37 ± 0.09 ^d	7.77 ± 0.21 ^b	78.92 ^c	
	Marketed	0.56 ± 0.10 ^f	29.25 ± 1.85 ^h	8.85 ± 0.62 ^e	0.52 ± 0.33 ^e	0.24 ± 0.02 ^d	2.49 ± 0.94 ^d	41.92 ^g	
1 h	Oil	Cultivated	9.06 ± 1.00 ^c	36.70 ± 2.12 ^g	14.83 ± 1.09 ^c	0.57 ± 0.12 ^c	7.99 ± 0.58 ^a	4.80 ± 0.88 ^c	73.95 ^d
	Wild	0.94 ± 0.47 ^f	55.34 ± 1.77 ^d	22.61 ± 0.59 ^b	0.52 ± 0.21 ^c	0.76 ± 0.08 ^d	11.74 ± 0.17 ^a	91.92 ^b	
	Marketed	1.06 ± 0.12 ^f	40.93 ± 2.69 ^f	7.69 ± 0.83 ^e	0.60 ± 0.11 ^c	0.48 ± 0.02 ^d	2.55 ± 0.52 ^d	53.32 ^f	
Vinegar	Cultivated	8.99 ± 0.32 ^c	25.57 ± 2.91 ^h	13.22 ± 1.32 ^c	0.49 ± 0.19 ^e	7.53 ± 0.94 ^a	4.61 ± 0.47 ^c	60.42 ^e	
	Wild	1.62 ± 0.35 ^e	58.23 ± 0.56 ^d	32.32 ± 1.30 ^a	0.53 ± 0.02 ^c	0.85 ± 0.01 ^d	10.57 ± 2.59 ^a	104.14 ^a	
	Marketed	2.60 ± 0.08 ^e	34.68 ± 2.65 ^g	9.57 ± 1.16 ^e	0.68 ± 0.14 ^e	1.42 ± 0.26 ^c	3.39 ± 0.42 ^d	52.35 ^f	
30 days	Oil	Cultivated	6.76 ± 1.62 ^d	32.43 ± 1.61 ^g	11.87 ± 1.40 ^d	0.23 ± 0.09 ^e	7.57 ± 1.32 ^a	3.22 ± 0.83 ^d	62.75 ^e
	Wild	19.19 ± 0.10 ^a	35.66 ± 0.46 ^g	6.27 ± 0.29 ^f	2.93 ± 0.09 ^a	0.54 ± 0.14 ^d	9.73 ± 0.05 ^a	74.32 ^d	
	Marketed	0.56 ± 0.12 ^f	86.48 ± 1.55 ^a	4.78 ± 1.00 ^f	2.66 ± 0.94 ^b	2.45 ± 0.25 ^c	6.28 ± 1.23 ^c	103.04 ^a	
Vinegar	Cultivated	6.35 ± 0.24 ^d	27.37 ± 1.46 ^h	9.21 ± 1.04 ^e	0.38 ± 0.06 ^e	5.09 ± 0.54 ^b	3.22 ± 0.35 ^d	51.63 ^f	
	Wild	18.99 ± 0.09 ^a	23.70 ± 2.80 ⁱ	3.49 ± 1.17 ^g	1.46 ± 0.08 ^c	0.75 ± 0.11 ^d	10.13 ± 2.38 ^a	58.54 ^e	
	Marketed	0.72 ± 0.37 ^f	63.47 ± 4.36 ^c	4.74 ± 0.28 ^f	3.11 ± 0.33 ^a	1.93 ± 0.72 ^c	6.28 ± 1.23 ^c	80.27 ^c	
60 days	Oil	Cultivated	8.81 ± 1.32 ^c	34.89 ± 4.34 ^g	13.98 ± 0.85 ^c	0.38 ± 0.09 ^e	7.38 ± 1.31 ^a	4.68 ± 0.36 ^c	70.14 ^d
	Wild	19.02 ± 0.12 ^a	67.28 ± 2.48 ^c	3.50 ± 0.52 ^g	1.33 ± 0.26 ^d	1.00 ± 0.08 ^d	10.65 ± 0.65 ^a	103.00 ^a	
	Marketed	0.54 ± 0.16 ^f	56.62 ± 3.62 ^d	4.92 ± 1.70 ^f	2.46 ± 0.19 ^b	1.12 ± 0.05 ^d	4.47 ± 0.2 ^c	70.79 ^d	
Vinegar	Cultivated	6.48 ± 0.50 ^d	23.26 ± 1.44 ⁱ	9.60 ± 0.82 ^e	0.28 ± 0.08 ^e	5.64 ± 0.46 ^b	3.41 ± 0.28 ^d	48.68 ^f	
	Wild	19.07 ± 0.12 ^a	26.39 ± 1.19 ^h	3.08 ± 0.80 ^g	1.73 ± 0.85 ^c	1.42 ± 0.04 ^c	10.19 ± 2.9 ^a	61.89 ^e	
	Marketed	0.70 ± 0.10 ^f	82.18 ± 1.63 ^b	4.09 ± 0.46 ^g	2.33 ± 0.65 ^b	1.60 ± 0.17 ^c	4.47 ± 0.2 ^c	95.37 ^b	
90 days	Oil	Cultivated	8.29 ± 1.25 ^c	37.36 ± 2.45 ^g	11.14 ± 0.91 ^d	0.34 ± 0.05 ^e	7.89 ± 1.09 ^a	4.10 ± 0.36 ^c	69.13 ^d
	Wild	19.02 ± 0.04 ^a	56.93 ± 3.10 ^d	2.76 ± 0.35 ^g	1.23 ± 0.30 ^d	0.96 ± 0.21 ^d	10.03 ± 0.05 ^a	90.93 ^b	
	Marketed	0.57 ± 0.04 ^f	44.58 ± 2.03 ^e	3.15 ± 0.18 ^g	1.54 ± 0.42 ^c	0.87 ± 0.17 ^d	5.98 ± 0.12 ^c	55.65 ^f	
Vinegar	Cultivated	6.86 ± 0.69 ^d	27.65 ± 2.90 ^h	9.31 ± 0.80 ^e	0.41 ± 0.08 ^e	5.96 ± 0.5 ^b	3.23 ± 0.25 ^d	53.43 ^f	
	Wild	0.01 ± 0.0 ^f	20.83 ± 0.26 ⁱ	0.04 ± 0.01 ^h	0.02 ± 0.01 ^e	0.01 ± 0.00 ^d	0.16 ± 0.01 ^e	21.06 ^h	
	Marketed	0.39 ± 0.18 ^f	53.71 ± 2.92 ^d	3.95 ± 0.64 ^g	2.14 ± 0.35 ^c	0.84 ± 0.001 ^d	5.98 ± 0.12 ^c	67.02 ^d	

Each value is expressed as mean ± SD (n = 3). Means followed by the same lowercase letter in the column are not significantly different ($P > 0.05$)

was a lower concentration of putrescine in the fruit pickled in vinegar, compared to the fruit pickled in oil, except for the fruit purchased from the market and stored for 30 days.

This fruit, even in vinegar, could have already been in an advanced degree of senescence, because it was purchased detached from the peduncles and with an initial appearance

Fig. 1 The chromatogram of six biogenic amines in pickled jurubeba fruit (spermine, putrescine, cadaverine, spermidine, histamine and tyramine)

of oxidation. In a previous study, we also observed a lower content of putrescine in jurubeba fruit preserved in vinegar (Silva et al. 2016). It is well known that microbiological contamination is one of the main factors influencing the BAs levels in food, but the low pH induced by vinegar minimizes microbiological contamination. Nevertheless, the low pH of vinegar may have induced protonation of amine groups, improving its hydrophilicity and increasing the loss of these molecules to the pickle solution (vinegar).

The consumption of fruits obtained from the market and pickled, either in oil or in vinegar, can provide a higher content of putrescine, which can be harmful to the organism and cause allergic reactions in sensitive people. The accumulation of putrefactive amines as putrescine are presumably due to the storage time. Increased levels of putrescine in marketed jurubeba, raw or pickled, may be due to the time elapsed between harvest and acquisition in the market. Thus, it is recommended to use fresh harvested fruits for making pickled jurubeba fruit. Similar to

Fig. 2 Nitrate content (ppm) in jurubeba fruit cooked in water and pickled in two types of conservatives for 1 h and 30, 60 and 90 storage days

jurubeba, other vegetables from the Solanaceae family are consumed after being preserved, so a BAs' analysis would be useful for assessing the safety of such food.

In general, the highest spermidine contents was observed in jurubeba fruit raw (13.01 mg/100 g), cooked (13.97 mg/100 g), and after being pickled for one hour in oil (22.61 mg/100 g) or in vinegar (33.32 mg/100 g) (Table 2). As the shelf time increases, the spermidine levels tend to decrease, presenting the lowest contents at 90 days, mainly in the fruit harvested from wild plants and preserved in vinegar (0.04 mg/100 g). The method of obtaining the fruit also resulted in differences in spermine levels (Table 2). The BA level was the lowest between the amines analyzed and showed a tendency to increase in some samples after 60 and 90 days on the shelf. Spermidine and spermine are associated with cellular growth and development due to their ability to link and stabilize macromolecules, such as DNA, RNA and proteins (Kusano et al. 2008). The consumption of these polyamines is important for the cells; however, the excess might not be interesting due to its relation to carcinogenesis (Gugliucci 2004).

High BA level can cause nausea, headache, palpitations of the heart, changes in blood pressure and other physiological problems (Papageorgiou et al. 2018). The levels of putrescine, spermidine and spermine ingestion required to induce food poisoning are 2000, 600 and 600 mg kg⁻¹ of

body weight, respectively (Kalač and Krausová 2005). Considering that jurubeba consumption at each meal generally varies from 1 to 2 soup spoons (10 g), our results show that jurubeba does not contain toxic levels of these three amines. In addition, the type of preservative had little influence over the BAs content.

Histamine and tyramine are considered most toxic BAs and are related to food safety (Dong and Xiao 2017). Fruits from cultivated plants showed the highest histamine contents (5.0–8.43 mg/100 g), independently of the sample analyzed, while wild plants showed the lowest values (0.01–1.42 mg/100 g) (Table 2). This biogenic amine can cause toxicity in high levels, and the results of that toxicity could be confused with allergic processes (Ladero et al. 2012). The toxic histamine levels vary between 10 and 100 mg/100 g (Larqué et al. 2007), depending on an individual's sensitivity (Dong and Xiao 2017), and the effect of that toxicity can increase when there are high levels of putrescine and cadaverine. Others have found that the ingestion of 25 mg of histamine may cause symptoms of intoxication (Larqué et al. 2007). The histamine content found in 100 g of jurubeba is lower than the values known to cause health problems and the usual quantity consumed per person, around 10 g, is not enough to cause health problems, as allergic processes.

Tyramine was detected in all samples analyzed, ranging from 3.87 mg/100 g in the raw material of cultivated fruits

Fig. 3 Two-dimensional scores (a) and projection (b) after analysis of all raw and pickled samples. WC wild fruit cooked, WO wild fruit pickled in oil, WV wild fruit pickled in vinegar, MC marketed fruit cooked, MO marketed fruit pickled in oil, MV marketed fruit pickled in vinegar, CC cultivated fruit cooked, CO cultivated fruit pickled in oil and CV cultivated fruit pickled in vinegar. Abbreviations followed for number 1 refers to 1 h after cooking, and 30, 60 and 90 refers to the shelf time in days

(Table 1) to 11.74 mg/100 g in wild fruits after cooking and pickling for 1 h (Table 2). It is interesting to note that the tyramine content increased in almost all samples after processing (cooking and pickling). The most prominent exception was the wild fruit pickled for 90 days in vinegar, where the tyramine content was reduced to levels lower than those found in its raw fruit. Tyramine is a hazardous BA for human health, and ingestions of 10–100 mg can be toxic (Eerola et al. 1998). This amine is more toxic than histamine, and its toxic limit is around 300 mg kg⁻¹ (Linares et al. 2016). Tyramine can induce headaches and migraines, depending on how much of it is present in food

(Ladero et al. 2010). The tyramine analyses via UPLC in jurubeba showed that the content did not reach the toxic or limit level.

Cooked vegetables can show a decrease in BAs' content, due to lixiviation to the cooking water, decreasing the possible harmful effect to the consumer (Naila et al. 2010). These compounds are usually thermostable, and the cooking process or the exposition to heat does not eliminate its toxic effect (Gonzaga et al. 2009). Nevertheless, we found that in jurubeba the content of all dangerous amines (tyramine, histamine and cadaverine) were bellow levels considered toxic for consumers. In relation to health risks, despite limited legislations, low levels of BA are essential for several physiological functions in mammals, acting as hormones or neurotransmitters (Papageorgiou et al. 2018).

Nitrate content

Nitrate content in raw jurubeba ranged from 837.0 to 886.0 ppm (Fig. 2). After cooking and storage in vinegar for 1 h, the jurubeba fruit showed the lowest nitrate content (Fig. 2), while the highest values were observed in the fruit purchased from the market and stored for 90 days, both in oil or vinegar. The Joint Food and Agricultural Organization and World Health Organization have set the Acceptable Daily Intake (ADI) for the nitrate ion at 3.7 mg kg⁻¹ body weight (FAO/WHO 2013). Usually, in one meal, jurubeba consumption does not extrapolate 10 fruits, which weigh approximately 1 g. Therefore, at each meal, consumers may ingest 1 ppm of nitrate at most when consuming fruit acquired in the market and pickled up to 90 days (Fig. 2). Exposure to nitrate from jurubeba is unlikely to result in appreciable health risks if the nitrate content does not exceed the value suggested by FAO. Low levels of nitrate results in low nitrite formation since only 5–10% of the total nitrate ingested is converted in nitrite (NO²⁻) through oral saliva and the digestive system (Boink and Speijers 2001). When nitrate is reduced to nitrite, it can act as a precursor in the endogenous formation of carcinogenic nitrosamines. In addition, the presence of nitrate in foods with expressive BAs' content is related to the formation of nitrosamines after food consumption, as evidenced by an increased urinary nitrosamine secretion (Doyle et al. 1993).

The results obtained for BAs and nitrate were supported by the PCA (Fig. 3). The PC1 axis represents 34.89% of the total data variance, and PC2 21.81% of the total data. Fruits from cultivated plants, pickled and stored in oil or vinegar, were grouped in the PC1 negative quadrants and found to contain the highest values of histamine and spermidine. However, these fruits showed the lowest nitrate content. Higher levels of nitrate were observed in jurubeba fruits obtained in the market and stored for 30, 60

and 90 days (PC1 positive quadrants), which showed the higher content of putrescine and spermine (Fig. 3). Fruits obtained from the market and pickled in oil or vinegar must be consumed in the first hour after cooking and pickling since the nitrate levels increases in pickled fruit stored for more than 30 days. However, fruit preserved in vinegar tends to present lower levels of tyramine, putrescine and cadaverine, which can potentiate the histamine effect. Thus, jurubeba pickled in vinegar contains low BAs and nitrate levels, both of which are compounds responsible for allergies and the formation of nitrous compounds.

Conclusion

Cooked, pickled and stored jurubeba fruits had wide ranges of BAs and nitrate; however, the levels found does not represent a food problem for consumers. Fruits acquired in the market contain a higher contents of putrescine and cadaverine, probably due to an advanced stage of senescence. These results indicate that analyzing of BAs are important for estimating the intake levels and that such analyses should be performed in other fruits and vegetables from the Solanaceae family, when the intention is to consume them as preserves. In addition, it can be concluded that it is not necessary to establish limits of nitrate ingestion since jurubeba is usually consumed in small amounts.

Acknowledgements The authors gratefully acknowledge the financial support of São Paulo Research Foundation (FAPESP) for financial support of this work (Grant Nos. 2013/05644-3, 2016/22665-2) and National Council for Scientific and Technological Development (CNPq, Brazil) (Grant Nos. 478372/2013-2, 305177/2015-0).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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