Food Research International 102 (2017) 32–42

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Dehydration of jambolan [*Syzygium cumini* (L.)] juice during foam mat drying: Quantitative and qualitative changes of the phenolic compounds

Tavares Iasnaia Maria de Carvalho[a], Tuany Yuri Kuboyama Nogueira[a], Maria Aparecida Mauro[a], Sergio Gómez-Alonso[b], Eleni Gomes[a], Roberto Da-Silva[a], Isidro Hermosín-Gutiérrez[b,*], Ellen Silva Lago-Vanzela[a]

[a] São Paulo State University (Unesp), Institute of Biosciences, Humanities and Exact Sciences (Ibilce), Cristovão Colombo, 2265, Jardim Nazareth, 15054-000, Campus São José do Rio Preto, São Paulo, Brazil

[b] Universidad de Castilla-La Mancha, Instituto Regional de Investigación Científica Aplicada, Avda. Camilo José Cela S/N, 13071 Ciudad Real, Spain

ARTICLE INFO

Keywords:
Jambolan
Juice
Foam mat drying
Phenolic compounds
Anthocyanins
Flavonols
Hydrolysable tannins
Antioxidant activity

ABSTRACT

Jambolan [*Syzygium cumini* (L.)] berries are a popular fruit in Brazil, renowned for their high phenolic compound (PC) content. These PCs have antioxidant, antibacterial, and other characteristics that may be beneficial to human health. The objective of the study was to evaluate the quantitative and qualitative changes of the main phenolic compounds (PCs) (anthocyanins, flavonols, and hydrolysable tannins) in the jambolan fruit, the produced fruit juice, and in the corresponding dehydrated powders obtained by foam mat drying (60, 70, and 80 °C) and lyophilization (control). The PCs were analyzed using high-performance liquid chromatography with a diode array detection coupled with an electrospray ionization mass spectrometry (HPLC-DAD-ESI-MS^n). Juice production resulted in a more pronounced degradation of anthocyanins than flavonols, and facilitated the extraction of hydrolysable tannins. Elevation of the dehydration temperature negatively impacted the anthocyanin content of the products; on the other hand, the flavonols and hydrolysable tannins were more sensitive to oxidation and heating time during dehydration, respectively, than dehydration temperature. In summary, it can be concluded that processing at 70 °C is most suitable, in light of the least loss of nutritional quality of the product with processing time. This study directly informs further investigations into preparation of high-quality jambolan fruit products.

Chemical compounds

Delphinidin 3,5-diglucoside (PubChem CID: 10100906)
Petunidin 3,5-diglucoside (PubChem CID: 10151874)
Malvidin 3,5-diglucoside (PubChem CID: 44256978)
Myricetin 3-glucoside (PubChem CID: 44259426)
Myricetin 3-rhamnoside (PubChem CID: 5281673)
Laricitrin 3-glucoside (PubChem CID: 44259475)
Syringetin 3-glucoside (PubChem CID: 44259492)
Gallic acid (PubChem CID: 370)
Ellagic acid (PubChem CID: 5281855)
Valoneic acid dilactone (PubChem CID: 10151874)

1. Introduction

Jambolan [*Syzygium cumini* (L.)] is a plant belonging to *Myrtaceae* family, originate in tropical Asia that covers 121 genuses and 3800 to 5800 species, and being widespread in all tropical and subtropical regions of the World. In Brazil, jabuticaba (*Myrciaria cauliflora* (Mart.) O. Berg) (Seraglio et al., 2017), cambuci (*Campomanesia phaea* (O. Berg.) Landrum), cagaita (*Eugenia dysenterica* DC), camu-camu (*Myrciaria dubia* Mc. Vaugh) (Balisteiro, de Araujo, Giacaglia, & Genovese, 2017)

Abbreviations: 3glc, 3-monoglucosylated; 35diglc, 3,5-diglucosylated; AA, antioxidant activity; ANOVA, analysis of variance; AOAC, association of official analytical chemists; cy, cyanidin; dp, delphinidin; DPPH, 2,2-diphenyl-1-picrylhydrazyl; FS, Fe_2SO_4 or ferric sulfate; FMD, foam mat drying; FRAP, ferric reducing antioxidant power; GA, gallic acid; GA-Me, methyl ester GA; HLPC-DAD-ESI-MS^n, high-performance liquid chromatography with diode array detection coupled with an electrospray ionization mass spectrometry; I, isorhamnetin; isoVA-Me, isomer of valoneic acid dilactone methyl ester; K, kaempferol; L, laricitrin; M, myricetin; M3glc, myricetin 3-glucoside; mv, malvidin; PC, phenolic compound; PCs, phenolic compounds; pn, peonidin; pt, petunidin; Q, quercetin; S, syringetin; TPC, total phenolic content; Trolox, 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid; TSS, total soluble solids; TA, titratable acidity; VA-Me, valoneic acid dilactone methyl ester; glcU, glucuronide; gal, galactoside; glc, glucoside; rhm, rhamnoside; pent, pentoside

* Corresponding author.
E-mail addresses: iasnaiamct@gmail.com (T. Iasnaia Maria de Carvalho), tuh.kuboyama@hotmail.com (T.Y.K. Nogueira), cidam@ibilce.unesp.br (M.A. Mauro), sergio.gomez@uclm.es (S. Gómez-Alonso), eleni@ibilce.unesp.br (E. Gomes), dasilva@ibilce.unesp.br (R. Da-Silva), isidro.hermosin@uclm.es (I. Hermosín-Gutiérrez), ellen@ibilce.unesp.br (E.S. Lago-Vanzela).

http://dx.doi.org/10.1016/j.foodres.2017.09.068
Received 15 June 2017; Received in revised form 10 September 2017; Accepted 24 September 2017
Available online 28 September 2017
0963-9969/

and pitanga (*Eugenia uniflora*) (Costa, Garcia-Diaz, Jimenez, & Silva, 2013) stand out among *Myrtaceae*. It bears fruit in the form of berries, 1.5 to 3.5 cm long. These berries are covered by a thin dark purple skin, have a colorless fleshy pulp, and a single seed (Singh et al., 2016). The fruit is edible and has a sweet but sharp taste (Jebitta & Allwin, 2016). The intense color of the skin is associated with a high anthocyanin content (Tavares et al., 2016), which is higher than that of other well-known Brazilian fruits, such as jaboticaba, camu-camu, and pitanga; its phenolic compound (PC) content is higher than in açaí (Costa et al., 2013).

Recent studies have highlighted the complex composition of PCs in jambolan; these include anthocyanins, flavonols, and hydrolysable and condensed tannins (Santhalakshmy, Don Bosco, Francis, & Sabeena, 2015; Tavares et al., 2016). According to Tavares et al. 2016, around 74 individual phenolic compounds, including 9 anthocyanins (mainly based on delphinidin, petunidin and malvidin), 9 flavonols (myricetin, laricitrin and syringetin glycosides), 19 flavanonols (dihexosides of dihydromyricetin and its methylated derivatives), 8 flavan-3-ol monomers (mainly gallocatechin), 13 gallotannins and 13 ellagitannins, together with some proanthocyanidins (highly galloylated prodelphinidins) and free gallic and ellagic acids were detected in the edible parts of jambolan. It has been suggested that these compounds possess various functional characteristics, i.e., antioxidant, antimutagenic, antimicrobial, antiglycemic, anticarcinogenic, and antiviral activities (Costa et al., 2013).

Given the possible health benefits associated with its PCs, jambolan has attracted considerable attention from the scientific community and industrialized food producers, as a potential raw material for the development of a variety of products. In the United States and European countries, jambolan is considered a delicacy, and is marketed in a dehydrated, seed-less form (Singh et al., 2016). It is also used for the preparation of pulp (Branco et al., 2016; Sheikh, Shahnawaz, Nizamani, Bhanger, & Ahmed, 2011), wine (Nuengchamnong & Ingkaninan, 2009), jelly (Lago-Vanzela, Santos, Lima, Gomes, & da Silva, 2011), and bread or “chapatti” (Kapoor, Ranote, & Sharma, 2015). Due to the seasonality and perishability of the fruit, various studies assessed the drying of jambolan fruit using different techniques, such as lyophilization (Sheikh et al., 2011), spray-drying (Santhalakshmy et al., 2015), warm air drying with a forced convection drier (Kapoor et al., 2015) and a spouted bed drier (Mussi, Guimarães, Ferreira, & Pereira, 2015; Sheikh et al., 2011).

Another promising technique for obtaining dehydrated fruit products aimed at retaining the bioactive compounds is foam mat drying (FMD). This technique involves mixing a pulp or juice of fruits and vegetables with stabilizing agent and/or foaming agent to produce stable foam spread on a tray, which undergoes air drying temperatures ranging from 50 to 80 °C, and then the dried product is further ground to produce a powdered product (Abbasi & Azizpour, 2016). Compared with more expensive techniques, such as spray-drying and freeze-drying, foam mat drying has the advantages of simplicity and low cost. In this technique, the drying rates during foam mat drying are quicker than during conventional drying with heated air circulation because of the greater exposed surface area; this contributes to reduce energy consumption and raises the quality of the product, which becomes more porous and with better rehydration capacity (Abbasi & Azizpour, 2016). However, the use of FMD poses a few disadvantages due to the surface area that is high due to incorporation of air to produce foam, which may require a larger surface area of drying. Moreover, because different countries take different approaches to ensuring food safety and health, the use of additives as foaming agents must to obey legislative aspects of the country or continent before to be used in this technology, i.e., each additive is assigned a unique number, termed as “E numbers”, which is used in Europe for all approved additives, similarly in the USA, the Food and Drug Administration (FDA) list these allowed items as “generally recognized as safe” (GRAS), and in Brazil, the allowed additives are listed by the Brazil National Health Surveillance Agency (ANVISA).

Despite the documented advantages of this technique, to the best of our knowledge, no studies on its employment for the production of jambolan powder have been published.

The objective of this study was to evaluate the quantitative and qualitative changes of jambolan fruit PCs (anthocyanins, flavonols, and hydrolysable tannins) in jambolan juice and in dehydrated products generated by foam mat drying at different temperatures (60, 70, and 80 °C), in comparison with lyophilization products (a control). The analysis was performed by high-performance liquid chromatography with a diode array detection coupled with an electrospray ionization mass spectrometry (HPLC-DAD-ESI-MS^n). The total content of PCs (TPC) and antioxidant activity (AA) of the products were also evaluated.

2. Materials and methods

2.1. Chemicals

All solvents were of chromatographic grade (> 99%); all chemical standards were of analytical grade (> 95%); ultrapure water (Milli-Q system) was used. Chemical standards malvidin (mv) 3-glucoside (3glc), mv 3,5-diglucoside (35diglc), peonidin (pn) 35diglc and quercetin (Q) 3-glucuronide were from Phytolab (Vestenbergsgreuth, Germany). The other chemical standards, cyanidin (cy) 3-glucoside, cy 35diglc, Q, kaempferol (K), isorhamnetin (I), myricetin (M), syringetin (S); the 3-glucosides of Q, K, I, and S; 3-galactosides of Q, K, and I; and ellagic and gallic acids, were from Extrasynthese (Genay, France). The commercially unavailable standard laricitrin (L) 3-glucoside was previously isolated from Petit Verdot grape skins (Castillo-Muñoz et al., 2009).

2.2. Jambolan fruit samples

Mature, healthy jambolan fruit [*S. cumini* (L.), vintage of 2014] was harvested in the city of São José do Rio Preto (São Paulo, Brazil), located at 20° 47′ 08″ S and 49° 21′ 36″ E, and 544 m above sea level (refer to WGS84 datum) (World Geodetic System, 1984). The species was identified by Dr. Regina Sampaio and a voucher specimen (number 32.214) was deposited in the herbarium SJRP in the IBILCE/UNESP, São José do Rio Preto. The pulp, skins and seeds yields of the fruit were determined and the results were expressed as a percentage (w/w). The physicochemical characteristics (moisture, pH, titratable acidity (TA), total soluble solids (TSS) and TSS/TA ratio) of the fruit were determined according to Association of Official Analytical Chemists (AOAC, 2005) in triplicate. The results were expressed in averages ± standard deviations.

2.3. Preparation of dehydrated jambolan products

All experiments were performed in triplicate. Fresh fruits (2 kg), hygienized and sanitized with chlorinated water, were used to prepare the juice by steam extraction in a stainless steel steamer pan (Suga Sucos, Bento Gonçalvez, Rio Grande do Sul, Brazil) at an average temperature of 85 °C, for 2.5 h. Immediately after extraction, the juice was packed in sterilized glass bottles with plastic screw lids. The bottled juice was cooled and stored (± 10 °C) until use, to ensure their quality in terms of microbial stability.

The percentage of juice yield (% w/w) was calculated as the difference between the initial mass of the fruit and the weight of the pellet after extraction of the juice divided by the initial mass of the fruit. The physicochemical characteristics (moisture, pH, TA, TSS and TSS/TA ratio) of the juice were determined according to AOAC (2005) in triplicate. The results were expressed in averages ± standard deviations.

To dehydrate the jambolan juice using the foam mat drying technique, the foams were first obtained as described by Tavares et al.

(2015) using 200 g of the following formulation: 10.0% (w/w) of Emustab® (Selecta, Jaguará do Sul, São Paulo, Brazil), 2.5% (w/w) of Super Liga Neutra® (Selecta, Brazil), 20.0% (w/w) of maltodextrin 10 DE (Ingredion, Mogi Guaçu, São Paulo, Brazil) and 67.5% (w/w) of juice. The foams were placed in stainless steel trays (150 mm radius, 5 mm height), dried in a hot-air dryer (0.42 m/s) at 60, 70, and 80 °C until equilibrium moistures were achieved, and immediately vacuum-packed, anaerobically and in the dark. This same foam formulation was also subjected to lyophilization (FR-Dying Digital Unit Model lyophilizer, Thermo Fisher, Waltham, Massachusetts, USA) for 24 h. The lyophilized products were also vacuum-packed in the dark. The average drying times of foams were determined in hours and the physicochemical characteristics (moisture, pH, TA) of the dehydrated products were determined according to AOAC (2005) in triplicate. The results were expressed in averages ± standard deviations.

2.4. Preparation of samples for the determination of PC content

For quantitative and qualitative determinations of anthocyanin, flavonol, and hydrolysable tannin profiles in the fruit, juice, and dehydrated products by lyophilization and foam-mat drying (at 60, 70, and 80 °C), firstly, the compounds of interest in each sample, were extracted in triplicate.

For the fruit analyses (ca. 100 g per sample), the edible parts (the skin and pulp) were separated from the seeds, and were then subjected to three repeat extractions for a complete recovery of PCs. The subsamples were immerged in 50 mL of a solvent mixture of methanol, water, and formic acid (50:48.5:1.5, v/v), subjected to an ultrasonic bar for 10 min, and were then centrifuged at 2.500*g*, 5 °C for 10 min. The separated supernatant and the procedure repeated two more times. The obtained supernatants were then combined into a single extract, rotoevaporated (Hei-Vap Advantage, Heidolph, Schwabach, Baviera, Germany) at 35 °C and lyophilized. For the fruit juice analysis, ca. 50 mL of each sample were lyophilized directly in amber glass bottles, cooled and stored (± 10 °C) until use. At the time of analysis using HPLC-DAD-ESI- MS^n, both samples were re-dissolved in 50 mL of 0.1 N HCl and immediately analyzed.

For the dehydrated juice analysis, ca. 0.5 g of each sample was homogenized in 5 mL of 0.1 N HCl, sonicated (10 min), and centrifuged (9400 × *g*, 5 °C, 10 min). The supernatants were collected and the pellets submitted to another extraction round, totaling two extractions. The obtained supernatants were combined into a single extract that was used in the analyses.

For the PCs (anthocyanins, flavonols, and hydrolysable tannins) analysis by HPLC-DAD-ESI- MS^n, additional steps were required. In the case of anthocyanins analyzes, aliquots of the prepared sample extracts were diluted with 0.1 N HCl (1:3, 1:3, and 1:0, v/v, for the fruit, juice, and powder extracts, respectively), filtered (0.20-μm polyester membrane, Chromafil PET 20/25, Germany) and injected directly on the chromatographic column (10 μL, fruit extracts, and 20 μL, juice and powder extracts).

For the analysis of flavonols and hydrolysable tannins (gallotannins and ellagitannins), aliquots of fruit (3 mL), juice (2 mL), and powder (5 mL) extracts were subjected to solid-phase extraction on Bond Elut Plexa PCX cartridges (Agilent; 6 cm^3, 500 mg of adsorbent) to remove interfering anthocyanins (Castillo-Muñoz et al., 2009).

For the analysis of flavonols, these anthocyanin-free extracts were filtered (0.20-μm polyester membrane, Chromafil PET 20/25) and injected directly on the chromatographic column (20 μL). The total concentrations of gallotannins and ellagitannins (hydrolysable tannins) were estimated after acidic hydrolysis of anthocyanin-free extracts. For the estimation of total hydrolysable tannins (Peng, Scalbert, & Monties, 1991), methanol (2100 μL), 37% HCl (600 μL) and a sample of 20% methanolic solution of the anthocyanin-free fraction of the extracts of jambolan (300 μL) were mixed in a sealed vial (10 mL). After heating in boiling water for 2 h, the vial was cooled (mixture of water and ice) and then 3 mL of water was added to the mixture. The hydrolyzed extracts were homogenized, filtered (0.20-μm polyester membrane, PET Chromafil 20/25) and injected directly on the chromatographic column (20 μL).

2.5. Determination of the qualitative and quantitative profiles of anthocyanins, flavonols, and hydrolysable tannins using HPLC-DAD-ESI-MS^n

Phenolic extracts of the fruit, juice, and dehydrated product samples were analyzed according to a previously described methodology (Tavares et al., 2016). PC HPLC separation, identification, and quantitation were carried out using an Agilent 1100 Series HPLC system (Agilent, Waldbronn, Germany) equipped with DAD (G1315B) and an LC/MSD Trap VL (G2445C VL) ESI-MS^n detectors, coupled to an Agilent ChemStation (version B.01.03) data-processing station. The mass spectra data were processed using the Agilent LC/MS Trap software (version 5.3). A Zorbax Eclipse XDB reversed-phase-C18 chromatographic column (2.1 × 150 mm, 3.5 μm particle, Agilent) was used and maintained at 40 °C, with a flow rate of 0.19 mL/min.

For the analysis of anthocyanins and flavonols, the solvents used were: solvent A (acetonitrile/water/formic acid, 3:88.5:8.5, v/v/v), solvent B (acetonitrile/water/formic acid, 50:41.5:8.5, v/v/v), and solvent C (methanol/water/formic acid, 90:1.5:8.5, v/v/v). The linear solvents gradient for anthocyanin and for flavonols were used according to a previously described methodology by Tavares et al. (2016). For PC identification, an ion trap ESI-MS/MS analyzer was used in positive (for anthocyanins) and negative (for flavonols) ion modes, as previously described (Tavares et al., 2016), setting the following parameters: dry gas, N_2, 8 L/min; drying temperature, 325 °C; nebulizer, N_2, 50 psi; scan range, 50–1200 *m/z*. The ionization and fragmentation parameters were optimized by a direct infusion of the appropriate standard solutions (malvidin 3,5-diglucoside, mv35diglc, in a positive ionization mode, and myricetin 3-glucoside, M3glc, in a negative ionization mode). The identification was mainly based on spectroscopic data (UV–Vis and MS/MS) for standards or data from previous reports (Castillo-Muñoz et al., 2009; Tavares et al., 2016).

Quantitative determination of PCs was accomplished by extraction of the DAD chromatograms at 520 nm (for anthocyanins) and 360 nm (for flavonols) and by the external standard (calibration curve) method. All calibration standard solutions were prepared by dilution of an appropriate aliquot of the stock solution of mv35diglc (from 1.5 to 125 mg/L) and mv3glc (from 5 to 120 mg/L) for anthocyanins, and of M3glc (from 5 to 100 mg/L) for flavonols. All calibration curves of components showed good linearity. The total concentrations of anthocyanins were expressed as mg of mv35diglc equivalents or as mg of M 3-glc equivalents, and of the flavonols were expressed as mg of M3glc equivalents, per 1 L or kg of sample.

The methodology for the analysis of gallotannins and ellagitannins (hydrolysable tannins) using HPLC was previously described by Peng et al. (1991) and modified to LC-MS equipment by Tavares et al. (2016). The identification of hydrolysable tannins was based on spectroscopic data (UV–Vis and MS/MS) for standards or on previously reported findings (Santos et al., 2011). For quantitation, DAD chromatograms were extracted at 280 nm and calibration curves of gallic (from 5 to 100 mg/L) and ellagic acids (from 5 to 40 mg/L) were prepared, as described for anthocyanins and flavonols. The total concentrations of gallotannins and ellagitannins were expressed in mg of gallic acid equivalents and in mg of ellagic acid equivalents, respectively, per 1 L or kg of sample.

To facilitate the interpretation of data, the total concentrations of the compounds in fruits and juices were expressed in terms of wet mass while those for the dehydrated products were expressed in terms of dry mass. The % gain or loss of compounds of interest following fruit processing into juice were calculated taking into account the quantitative values of the compounds present in the fruit and juice, and the average

Table 1
MS/MS spectral characteristics of anthocyanins identified in jambolan fruit, juice and juice dried powders (by lyophilization and foam mat drying at 60, 70 and 80 °C) by HPLC-DAD-ESI-MS/MS (positive ionization mode). Total concentration of anthocyanins were expressed as equivalents of malvidin-3,5-diglucoside. Each individual anthocyanin compound were expressed as percentage of molar ratio (%) regarding the total content. Given as mean value ± standard deviation (n = 3).

Anthocyanin	Molecular ion; product ions (m/z)	Molar ratio (%)					
		Fruit	Juice	Dried products			
				Lyophilization	Foam mat drying		
					60 °C	70 °C	80 °C
3,5-Diglucosylated anthocyanins							
dp35diglc	627;465, 303	30.36 ± 1.53 a	27.62 ± 1.35 a	27.28 ± 0.28 a	26.31 ± 0.91 a	25.76 ± 2.33 a	26.49 ± 2.46 a
cy35diglc	611;449, 287	3.71 ± 0.03 abc	3.59 ± 0.21 bc	3.37 ± 0.10 c	4.07 ± 0.21 ab	4.21 ± 0.10 a	4.17 ± 0.09 a
pt35diglc	641;479, 317	34.92 ± 0.51 c	36.31 ± 0.19 a	35.74 ± 0.30 abc	35.23 ± 0.07 bc	35.96 ± 0.25 ab	35.53 ± 0.33 abc
pn35diglc	625;463, 301	0.72 ± 0.05 c	1.01 ± 0.01 a	0.82 ± 0.02 bc	0.94 ± 0.02 ab	0.99 ± 0.04 a	0.94 ± 0.09 ab
mv35diglc	655;493, 331	28.29 ± 1.61 a	30.97 ± 1.65 a	32.37 ± 0.06 a	32.67 ± 1.51 a	32.37 ± 2.24a	32.24 ± 2.87 a
3-Monoglucosylated anthocyanins							
dp3glc	465;303	1.04 ± 0.41 a	0.28 ± 0.18 b	0.23 ± 0.05 b	0.42 ± 0.16 ab	0.40 ± 0.06 ab	0.31 ± 0.15 b
cy3glc	449;287	0.66 ± 0.19 a	0.10 ± 0.04 b	0.06 ± 0.01 b	0.12 ± 0.08 b	0.09 ± 0.03 b	0.10 ± 0.02 b
pt3glc	479;317	NQ	NQ	NQ	NQ	NQ	NQ
mv3glc	493;331	0.31 ± 0.02 a	0.14 ± 0.02 c	0.13 ± 0.00 bc	0.27 ± 0.06 ab	0.23 ± 0.01 abc	0.25 ± 0.08 abc
Total anthocyanins — wet basis (fruit, mg/kg; juice, mg/L)		1598.43 ± 93.80 A	853.48 ± 100.48 B				
Total anthocyanins — dry basis (powder, mg/kg)				2297.90 ± 145.62 A	2095.39 ± 183.35 A	2207.33 ± 174.27 A	1551.63 ± 35.88 B

Abbreviations: dp, delphinidin; cy, cyanidin; pt, petunidin; pn, peonidin; mv, malvidin; 35diglc, 3,5-diglucoside; 3glc, 3-glucoside; NQ, nonquantified, although its occurrence was detected by LC-MS as minor, coeluting compound. Different letters in the same line indicate significant differences by analysis of variance (ANOVA) and multiple comparison test of Tukey or Student t at $P < 0.05$.

juice yield. To evaluate the concentration and/or degradation of the phenolic compounds in dehydrated products, the amount of juice and the concentration of each compound in the foam prior to dehydration were taken into account.

2.6. Determination of TPC and AA parameters

The determination of TPC in the fruit, juice, and dehydrated product extracts was performed using the Folin-Ciocalteu spectrophotometric method (Ough & Amerine, 1988); TPCs were quantified using calibration curves prepared with gallic acid (GA). The results were expressed in mg of GA per g of fresh fruit or dehydrated product, or per mL of juice. The determination of AA in the samples was performed using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) method (Brand-Williams, Cuvelier, & Berset, 1995) and the ferric reducing antioxidant power (FRAP) method (Benzie & Strain, 1996). The measurements from DPPH and FRAP methods were based on calibration curves with 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox) (from 1.0 to 8.0 mM and from 0.5 to 2.0 mM, respectively). For the FRAP method, a ferric sulfate (Fe_2SO_4, FS) (from 0.5 to 2.0 mM) calibration curve was also constructed. The results were expressed as μmol of Trolox equivalents or FS per g of fresh fruit or dehydrated product, or per mL of juice.

2.7. Statistical analysis

Analysis of variance (ANOVA) was used for data interpretation. The means were compared using the Tukey test or t-test. In all the statistical tests, the significance level was set at 0.05, and the analyses were performed using the Minitab 17 Statistical Software (Minitab Inc., Torre Sul Paraíso, Brazil).

3. Results and discussion

The jambolan fruit presented on average 65.16 ± 0.59% of pulp, 11.76 ± 0.70% of skin, and 23.08 ± 0.22% of seeds, and the following results of the physicochemical characteristics were obtained: moisture, 85.52 ± 1.59%; pH, 3.87 ± 0.01; TA, 0.73 ± 0.01 g of tartaric acid per 100 g of fruit; TSS, 11.92 ± 1.36°Brix; and TSS/TA ratio of 16.43 ± 0.25.

The average yield of juice was 74.96 ± 3.13% (v/w) and the physicochemical characteristics of the juice were as follows: moisture, 90.42 ± 1.25%; pH, 3.87 ± 0.04; TA, 0.42 ± 0.03 g of tartaric acid per 100 mL of juice; TSS, 9.03 ± 0.79°Brix; and TSS/TA ratio of 21.84 ± 1.83.

The average drying times of foams at 60, 70, and 80 °C were 8.67 ± 1.02 h, 5.33 ± 0.23 h, and 4.17 ± 0.47 h, respectively. The physicochemical characteristics of the dehydrated products of foam mat drying and lyophilization, respectively, were as follows: moisture, 2.82 ± 0.54% and 5.14 ± 0.22%; pH, 4.36 ± 0.09 and 4.26 ± 0.09; and, TA, 1.06 ± 0.04 and 1.18 ± 0.02 of g tartaric acid per 100 g of powder.

The quantitative and qualitative changes undergone by the phenolic compounds (anthocyanins, flavonols, and hydrolysable tannins) present in the jambolan fruit after the processing are reporting below.

3.1. Anthocyanins

Nine anthocyanins were detected in the fruit, juice, and dehydrated product samples, namely: ones derived from 3-monoglucosylated (3glc) delphinidin (dp), cy, petunidin (pt), and mv; and 3,5-diglucosylated (35diglc) compounds derived from dp, cy, pt, mv, and pn, none of them were acylated. This profile was identical with what has been previously described for this fruit (Tavares et al., 2016). In the current study, the anthocyanins with high molar ratios in the jambolan fruit and its products were the 35diglc derivatives of the three anthocyanidins tri-substituted at ring B (dp, pt, and mv); they represented 93–95% of the total anthocyanin content. The same main anthocyanins were also identified by Santiago et al. (2015) in jambolan powder produced by dehydration of husks at 60 °C for 22 h in a convective dryer. However, the authors of that study found only six anthocyanins in the powder (35diglc derivatives of dp, cy, pt, pn, and mv, and 3glc of dp).

In the present study, statistically significant differences ($P < 0.05$) in the distribution (molar ratios) of some anthocyanins in the fruit, juice, and dehydrated products were observed (Table 1). The results strongly support the notion that the anthocyanin structure affects its

Table 2
MS/MS spectral characteristics of flavonols identified in jambolan fruit, juice and juice dried powders (by lyophilization and foam mat drying at 60, 70 and 80 °C) by HPLC-DAD-ESI-MS/MS (negative ionization mode). Total concentration of flavonols were expressed as equivalents of myricetin-3-glucoside. Each individual flavonol compound were expressed as percentage of molar ratio (%) regarding the total content. Given as mean value ± standard deviation (n = 3).

Flavonol	Molecular ion; product ions (m/z)	Molar ratio (%)					
		Fruit	Juice	Dried products			
				Lyophilization	Foam mat drying		
					60 °C	70 °C	80 °C
M3glcU	493;317	4.05 ± 0.29 a	2.47 ± 0.71 ab	1.08 ± 0.50 b	2.30 ± 0.67 ab	2.74 ± 0.75 ab	1.09 ± 0.42 b
M3gal	479;317	4.12 ± 0.73a	1.86 ± 0.89 b	1.68 ± 0.89 b	1.41 ± 0.24 b	1.58 ± 0.68 b	0.64 ± 0.29 b
M3glc	479;317	47.64 ± 2.38 a	45.20 ± 8.11 a	49.21 ± 4.08 a	45.55 ± 6.90 a	40.32 ± 8.47 a	33.44 ± 17.92 a
M3rhm	463;317	7.27 ± 0.60 a	6.20 ± 2.18 ab	7.35 ± 0.83 a	6.76 ± 0.85 a	6.13 ± 1.44 ab	2.16 ± 0.40 b
M3pent	449;317	6.61 ± 0.74 b	4.47 ± 1.39 bc	4.26 ± 0.19 bc	6.45 ± 4.15 ab	11.05 ± 2.23 a	0.00 ± 0.00 c
L3gal	493;331	2.26 ± 0.31 bc	1.76 ± 0.57 c	9.17 ± 0.89 ab	10.09 ± 0.79 ab	10.53 ± 3.47 a	10.55 ± 6.13 a
L3glc	493;331	5.04 ± 0.12 c	5.22 ± 0.54 c	18.28 ± 1.83 bc	16.88 ± 3.00 bc	19.73 ± 6.77 b	40.24 ± 13.81 a
S3gal	507;345	1.96 ± 0.14 b	1.75 ± 0.40 b	5.82 ± 0.61 a	4.78 ± 0.93 a	4.36 ± 0.59 a	5.38 ± 0.83 a
S3glc	507;345	1.43 ± 0.18 a	1.90 ± 0.51 a	1.16 ± 0.15 a	1.62 ± 0.41 a	1.21 ± 0.31 a	1.13 ± 0.52 a
Free M	317	19.22 ± 0.18 ab	27.62 ± 10.88 a	1.09 ± 0.06 b	1.47 ± 0.50 b	0.86 ± 0.09 b	1.76 ± 1.40 b
Free L	331	0.00 ± 0.00 b	0.92 ± 0.48 ab	0.59 ± 0.09 ab	1.52 ± 1.26 ab	0.85 ± 0.29 ab	2.51 ± 0.75 a
Free S	345	0.40 ± 0.04 a	0.62 ± 0.43 a	0.32 ± 0.11 a	1.16 ± 1.28 a	0.64 ± 0.11 a	1.09 ± 0.46 a
Total flavonols — wet basis (fruit, mg/kg; juice, mg/L)		43.25 ± 2.45 A	34.53 ± 2.30 B				
Total flavonols — dry basis (mg/kg)				62.58 ± 3.13 A	54.39 ± 11.71 A	58.10 ± 4.19 A	38.39 ± 13.92 A

Abbreviations: M, myricetin; L, laricitrin; S, syringetin; glcU, glucuronide, gal, galactoside; glc, glucoside; rhm, rhamnoside; pent, pentoside. Different letters in the same line indicate significant differences by analysis of variance (ANOVA) and multiple comparison Tukey test or Student t at $P < 0.05$. Lowercase letters are used for comparison between all samples and capital letters for comparison only between fruit and juice or between dried products obtained by lyophilization and warm air drying at 60, 70 and 80 °C.

stability: the 3glc anthocyanins were more unstable than the respective 35diglc derivatives, especially cy3glc, i.e., B-ring di-substituted non-methoxylated anthocyanins. After evaluating the stability of jambolan extract stored at 105 °C for 240 min, Sharma et al. (2016) observed different thermostabilities of diglucosylated anthocyanins: after 160 min of heating, pt- and mv-derived 35diglc anthocyanins were more resistant to degradation than dp-, cy-, and pn-derived 35diglc anthocyanins; the latter were considered less heat resistant under those conditions. Similarly, Torres et al. (2010) dried grape skins using two different methods, lyophilization and drying at 60 °C for 24 h, and observed that the 3glc anthocyanidins that were the least resistant to the processing were dp and cy derivatives.

In the jambolan fruit, the anthocyanin concentration, in mv35diglc equivalents, was ca. 1598 mg/kg of fresh fruit (Table 1). This was much higher than what has been reported in a previous study, i.e., 315 mg/kg of fresh fruit (Tavares et al., 2016). In the jambolan juice, the average anthocyanin concentration, in mv35diglc equivalents, was ca. 853 mg/L of juice (or 825 mg/kg of juice). Coelho et al. (2016) produced jambolan juice by pectin-aided extraction at 60 °C and reported an average anthocyanin concentration of 736 mg/kg of juice, as cy3glc equivalents (or 306 mg/kg of juice as mv35diglc).

In the current study, the total anthocyanin content in the extracted juice was only 40% that of the fruit (after conversion based on the juice yield). Studies of pasteurized jambolan pulp reported losses of ca. 8.5% (Branco et al., 2016) and 11% (Kapoor & Ranote, 2015), although in those cases the heating time was shorter than that achieved in the present study and no solid/liquid transference of anthocyanins occurred. The use of saturated steam to extract the juice has several advantages: it is easy to do and inexpensive; since the juice is obtained by hot processing, pasteurization is unnecessary if the bottling is done immediately after extraction; finally, only soluble substances are extracted, preventing precipitation issues (turbidity) commonly associated with extraction by milling. Nevertheless, exposure of fruit to saturated steam for a prolonged period of time (2.5 h) leads to pronounced anthocyanin degradation and incorporation of exogenous water into the product.

Anthocyanin concentration in the dehydrated products ranged from 1552 to 2298 mg/kg of powder, in mv35diglc equivalents (dry basis). Although the drying at 70 °C resulted in a reduction by 38% in processing time, compared with processing at 60 °C, no statistically significant differences ($P > 0.05$) of anthocyanin concentration were observed between the lyophilized and dehydrated products at these temperatures.

Compared with the drying time of the foam at 60 °C, the drying time at 80 °C decreased by 52%. Dehydration at 80 °C resulted in a 32% degradation of anthocyanins, compared with the lyophilized control. Kapoor, Ranote, and Sharma (2015) produced jambolan powder from the pulp by conventional drying (35–40 °C for 8 h) and lyophilization and, compared with the lyophilized powder, the conventionally dried powder presented 15% less total anthocyanins.

To date, to the best of our knowledge, no reports on dehydrated jambolan juice obtained by foam mat drying have been published. Abbasi and Azizpour (2016) produced dehydrated sour cherry juices by foam mat drying at 50, 65, and 80 °C, and observed the highest concentration of anthocyanins in the dry powder at intermediate temperature (65 °C). The results of the current study suggest that 70 °C is the optimal temperature for the preservation of this class of compounds during foam mat drying. Besides, more important is to get a product that is optimal in terms of hygiene and microbial stability, as this kind of drying is not susceptible to contamination of microorganism and insects from the environment and, this temperature is sufficient to eliminate the vegetative cells of occasional microorganisms present in the original raw material.

3.2. Flavonols

The distribution (molar ratios) of flavonols in the fruit, juice, and dehydrated products is shown in Table 2. No qualitative change was observed between the fruit and its derived products, similarly to anthocyanins. The flavonols identified in all samples included only the B-ring tri-substituted aglycones: myricetin (M), laricitrin (L), and syringetin (S). No flavonols derived from kaempferol, quercetin, or isorhamnetin were detected. All the analyzed samples contained 3-glucoside and 3-galactoside derivatives of myricetin, larycitrin, and syringetin. In addition, 3-glucuronide, 3-rhamnoside, and 3-pentoside derivatives of myricetin were identified; the myricetin-derived flavonols were the most common in all samples. The most important single flavonol in the samples was M3glc (molar ratios between 33 and 49%),

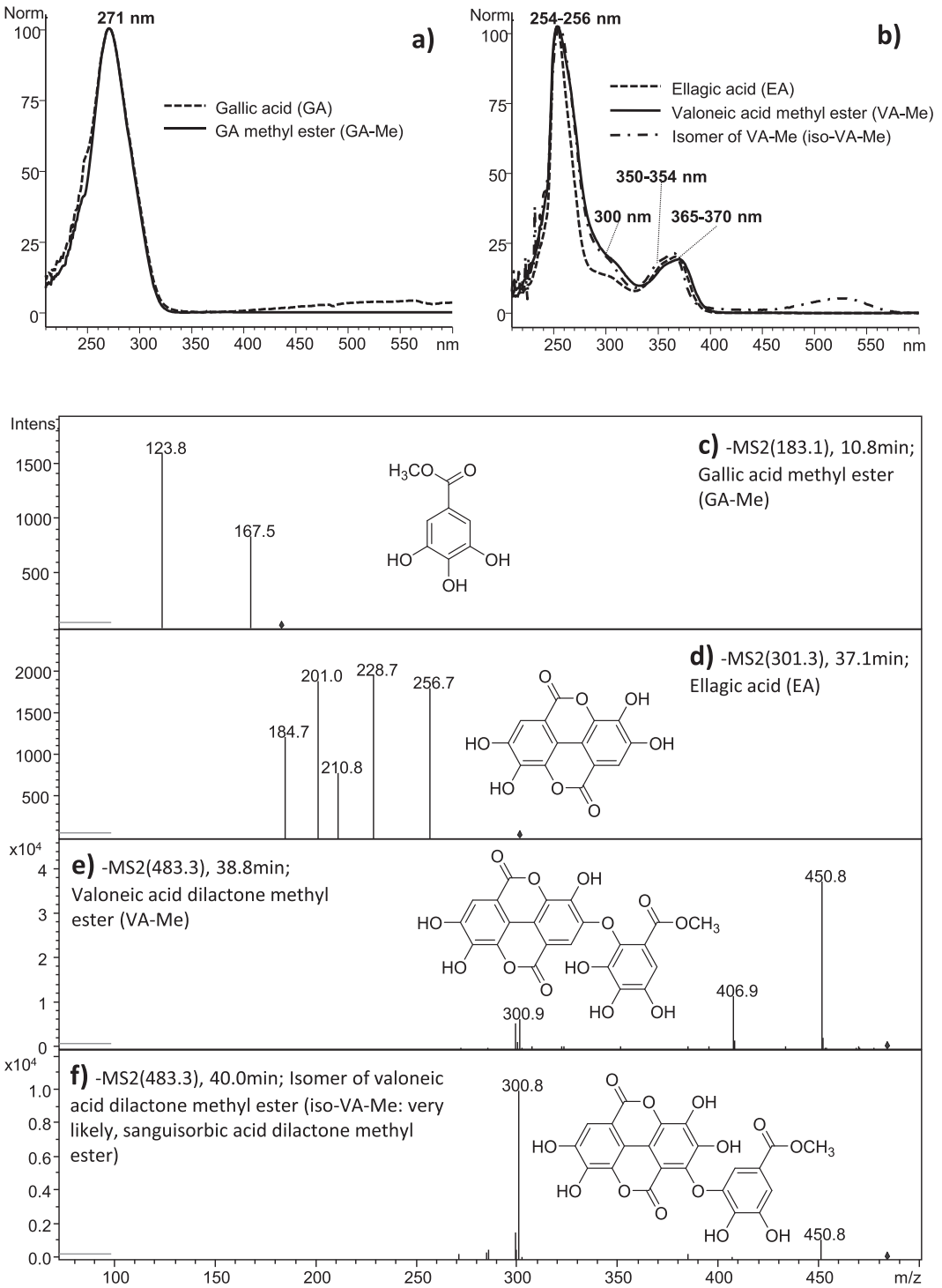

Fig. 1. Spectral data of compounds released after acidic hydrolysis of hydrolysables jambolan tannins. On-line DAD spectra: (a) gallic acid (GA) and its methyl ester (GA-Me); (b) ellagic acid (EA), and valoneic acid dilactone methyl ester (VA-Me) and its isomer (isoVA-Me). MS/MS spectra in negative ionization mode of: (c) gallic acid methyl ester (GA-Me); (d) ellagic acid (EA); (e) vanoleic acid dilactone methyl ester (VA-Me); (f) isomer of valoneic acid dilactone methyl ester (isoVA-Me; most probably a sanguisorbic acid dilactone methyl ester).

similarly to what has been reported by Tavares et al. (2016), who assessed different edible parts of jambolan (the peel and pulp).

Furthermore, in the present study, free myricetin and syringetin were detected in the fruit; free myricetin, laricitrin, and syringetin were detected in the juice and dehydrated products. Fruits usually only contain flavonol 3-glycosides and the occurrence of free aglycones is considered to be an artifact of the extraction method of the compounds of interest under acidic conditions (Hermosín-Gutiérrez, Castillo-Muñoz, Gómez-Alonso, & García-Romero, 2011). In the jambolan fruit and juice, myricetin was the biggest contributor to free aglycones. Similarly, Teleszko, Nowicka, and Wojdyło (2016) identified free aglycones in pasteurized strawberry juice. The authors attributed this finding to easy extraction and hydrolysis of flavonol glycosides, and also to the degradation of the plant cell wall, i.e., the release of aglycones by enzymatic hydrolysis during the heating of fruit for juice extraction. In addition to free aglycones, variations in the molar ratios of some flavonols were observed in the fruit and derived products. The levels of glucuronide, galactoside, and rhamnoside derivatives of

Table 3
Estimation of total hydrolysable tannins (as gallic acid for gallotannins; as ellagic acid for ellagitannins) after acidic hydrolysis in jambolan fruit, juice and juice dried powders (by lyophilization and foam mat drying at 60, 70 and 80 °C). Given as mean values ± standard deviation (n = 3).

Hydrolysable tannins	Concentration					
	Fruit	Juice	Dried products			
			Lyophilization	Foam mat drying		
				60 °C	70 °C	80 °C
Gallotannins						
Total gallotannins[a] — wet basis (fruit, mg/kg; juice, mg/L)	69.04 ± 11.83 B	147.33 ± 19.33 A				
Total gallotannins[a] — dry basis (mg/kg)			344.44 ± 85.73A	181.86 ± 27.89 B	196.23 ± 25.13 B	191.81 ± 33.96 B
Elagitannins						
Total ellagic acid — wet basis (fruit, mg/kg; juice, mg/L)	8.24 ± 2.80 B	60.15 ± 5.74 A				
Total ellagic acid — dry basis (mg/kg)			97.99 ± 18.74 A	43.43 ± 20.76 B	63.19 ± 10.66 AB	63.37 ± 8.48 AB
Total vanoleic acid[b] — wet basis (fruit, mg/kg; juice, mg/L)	5.07 ± 1.31 B	62.07 ± 8.48 A				
Total vanoleic acid[b] — dry basis (mg/kg)			66.31 ± 8.18 A	27.66 ± 16.30 A	41.93 ± 9.39 A	67.65 ± 20.54 A
Total ellagitannins — wet basis (fruit, mg/kg; juice, mg/L)	13.31 ± 4.11 B	122.22 ± 13.71 A				
Total ellagitannins acid — dry basis (mg/kg)			164.30 ± 10.56 A	71.09 ± 36.08 B	105.12 ± 20.05 AB	131.03 ± 28.95 AB

Different letters in the same line indicate significant differences by analysis of variance (ANOVA) and multiple comparison test of Tukey or Student t at $P < 0.05$. Lowercase letters used for comparison between samples of fruit and juices or comparison between dried foams by lyophilization and warm air drying at 60, 70 and 80 °C.

[a] Total sum of gallic acid (GA) and its methyl ester (GA-Me).

[b] Total sum of valoneic acid dilactone methyl ester (VA-Me) and its isomer (isoVA-Me).

myricetin showed the greatest reduction during fruit processing.

The molar ratios of free myricetin in the juice and dehydrated products (including lyophilized products) were compared; a pronounced reduction was noted in the latter. In addition, the comparison of molar ratios of dehydrated products revealed an increase in the proportions of laricitrin compounds in the foam mat dried at 80 °C. This was expected since M3glc was the most common compound in this class; they are also most unstable, mainly because of their susceptibility to oxidation, especially if the glycosides are first hydrolyzed and result in its free form. It may be inferred that, because myricetin contains three −OH groups, and laricitrin has two −OH groups and one OCH_3 group, the latter is responsible for an increased stability of the aglycone, especially during oxidation and thermal degradation. The increase in the proportion of laricitrin derivatives may have been influenced by the decrease in the myricetin derivative content. Similar results were obtained by Castillo-Muñoz et al. (2007) who analyzed flavonol profiles of different red wines. The authors reported that M3glc appeared to be more susceptible to acid hydrolysis that myricetin-3-glucuronide, and that the quantities of 3-glucosides of both laricitrin and syringetin were typically much higher than those of their corresponding free aglycones.

The concentration of flavonols in the jambolan fruit was about 43 mg/kg of fresh fruit, in M3glc equivalents (Table 2), lower than 75 mg/kg previously determined by Tavares et al. (2016). The average concentration in the jambolan juice was approximately 35 mg/L of juice in M3glc equivalents, i.e., a decrease of 40% when compared with the total content in the fruit (after conversion based on the juice yield); this decrease was lower than that determined for anthocyanins (60%). Branco et al. (2016) pasteurized jambolan pulp at 70 °C for only 5 min and reported a 33% decrease in the concentration of myricetin; even though in that experiment the heating time was shorter than that in the present study, no incorporation of exogenous water into the product and no solid/liquid transference of flavonols occurred.

The concentrations of flavonols (mg/kg in M3glc equivalents) in the dehydrated jambolan products, both from foam mat drying at temperatures of 60 °C (54.39), 70 °C (58.10) and 80 °C (38.39) and also in the lyophilized control (62.58), were not significantly different ($P > 0.05$; Table 2). This suggested that the temperature of the dehydration process did not affect the flavonol content, in contrast to the anthocyanin content. Michalska et al. (2016) produced plum powder using various drying methods (60 and 70 °C, and lyophilization) and similarly to our findings, found no significant differences between flavonol concentrations in the products; the concentrations of anthocyanins in powders produced at 60 and 70 °C were reduced by 86 and 93%, respectively, compared to the lyophilized powder.

During the drying of foams, the concentration of compounds changes because of the loss of water. The inclusion of coadjuvants in foam production (e.g., Emustab, Super Liga Neutra, and maltodextrin) partially compensates for this concentration effect, in conjunction with the expected degradation of flavonols upon exposure to temperature and oxygen. We compared the concentration of these compounds in the foams prior to the lyophilization (data not shown) with their concentration in lyophilized products, and the increase in anthocyanin concentration was more pronounced (3.85 times) than the increase of flavonols (2.59 times) in lyophilized products. These results allowed us to conclude that the incorporation of air during foam generation triggers an oxidative process that negatively affects the flavonols, especially free aglycones, more specifically free myricetin, with a consequent reduction of their total concentration.

3.3. Hydrolysable tannins

In the current study, as well as in several other studies reported in the literature, we commonly expressed the amount of hydrolysable tannins using the estimated total content of gallic and ellagic acids released after hydrolysis of these compounds. The identification of all the hydrolysis compounds was based on spectral data from the DAD-online UV–Vis spectra and MS/MS spectra (Fig. 1), and comparisons with data for standards (gallic and ellagic acid), and with previously reported data (Boulekbache-Makhlouf et al., 2010; Fracassetti, Costa, Moulay, & Tomás-Barberán, 2013; Tavares et al., 2016).

After hydrolysis of the fruit and juice samples, the total concentration of gallotannins (in mg gallic acid equivalents) was determined to be 69 mg/kg and 147 mg/L, respectively, which corresponded to the total sum of gallic acid methyl ester and residual unesterified gallic acid (Fig. 1a, Table 3). Comparison of these values (after conversion using the juice yield) revealed a 60% increase in the juice in relation to the

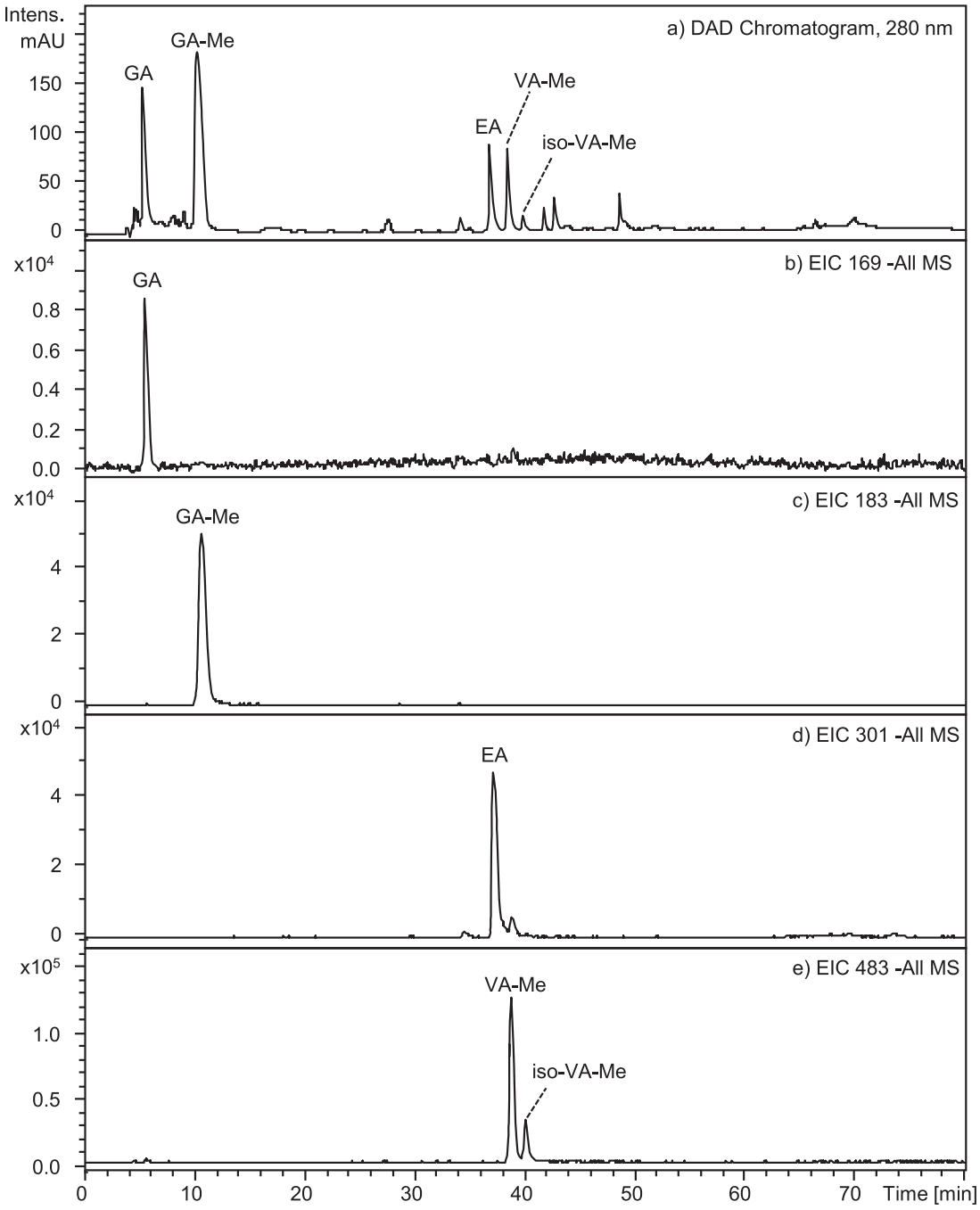

Fig. 2. DAD chromatogram and MS extracted ion chromatograms (EICs) of the acidic hydrolysis products of hydrolysable tannins from jambolan juice: (a) DAD chromatogram, extracted at 280 nm; (b) EIC of gallic acid (GA), extracted at m/z = 169; (c) EIC of gallic acid methyl ester (GA-Me), extracted at m/z = 183; (d) EIC of ellagic acid (EA), extracted at m/z = 301; (e) EIC of valoneic acid dilactone methyl ester (VA-Me) and its isomer (isoVA-Me), extracted at m/z = 483. Methyl ester derivatives predominate among the hydrolysis products because the reaction was carried out in a methanolic medium.

fruit. Similarly, in the study of Branco et al. (2016), jambolan pulp was produced and pasteurized at 60 °C for 5 min and, following pasteurization, the gallic acid concentration increased by 57%. According to these authors, this observation could be directly linked to the cleavage of covalent bonds of hydrolysable tannins in the pulp and the release of these molecules into the medium.

The total concentration of ellagitannins was determined by a sum of the total concentrations of ellagic acid and total valoneic acid (valoneic acid dilactone methyl ester and its isomer). An isomer of vanoleic acid dilactone methyl ester, very likely the sanguisorbic acid dilactone methyl ester (Fig. 1f), was identified (Boulekbache-Makhlouf et al., 2010; Fracassetti, Costa, et al., 2013) among the hydrolysis products in the course of estimating the hydrolysable tannin content (Fig. 2). This compound was present in all the samples analyzed, not only in the jambolan fruit and in the extracted juice, but also in the dried products.

In the fruit and juice, respectively, the concentration of ellagic acid was 8 mg/kg and 60 mg/L, and of vanoleic acid was 5 mg/kg and 62 mg/L (both in mg ellagic acid equivalents). The total ellagitannin content in the fruit and juice was, respectively, 13 mg/kg and 122 mg/L, which corresponded to a 489% increase in the juice compared with fruit (after conversion based on the juice yield).

The increase in the content of ellagitannins in the fruit compared to in the juice was much more pronounced than that of gallotannins, since the concentration of ellagitannins in the fruit was very low. Although

this increase was observed in the juice after extraction, the gallotannin content was higher than ellagitannin content, as observed by Tavares et al. (2016). This is probably because ellagitannin compounds are highly polar on account of the presence of many –OH groups (Nuengchamnong & Ingkaninan, 2009). Hence, during juice extraction, the ellagitannins are more easily extracted from the fruit and seeds, the sources of these compounds (Tavares et al., 2016). Further, in the current study, the seeds were discarded and only the edible parts (peel and pulp) were extracted for analysis while whole fruits (containing the seeds) were used for the elaboration of juices, which can explain the contribution of ellagitannins from the seeds to the extracted juice. Another explanation for the increase in ellagic acid content in the juice could be the release of this compound by hydrolysis from ellagitannins during the heat treatment. It is worth noting that the hydrolysis method provides only an estimate of the actual concentration of hydrolysable tannins because not all compounds of this class are hydrolyzed quantitatively, and various compounds can incorporate ellagic acid and gallic acid in the same molecule. A study of Fracassetti, Costa, et al. (2013) supports this hypothesis: the authors generated two powder products from the pulp and the waste (skin and seeds) of camu-camu, and reported that the heat treatment released ellagic acid from the ellagitannins.

In the dried jambolan products, the total average gallotannin concentrations (in mg gallic acid equivalents) ranged from 182 to 344 mg/kg. The concentrations were highest in the lyophilized products, and statistically differed ($P < 0.05$) from the concentrations in dryer-dehydrated powders but not among themselves. Compared with the lyophilized control, the total gallic acid concentration in the dehydrated powders was reduced by 43–47%.

Regarding ellagitannins, their average total concentration (in mg ellagic acid equivalents) in the dried jambolan products ranged from 71 to 164 mg/kg. In contrast with the gallotannin content, ellagitannins concentrations in the lyophilized product and products dried at 70 and 80 °C were not significantly different ($P > 0.05$), however, the product dried at 60 °C showed a significant reduction ($P < 0.05$), 56%. This suggested that ellagitannins are more sensitive to the heating time than to temperature, perhaps because of the oxidation during warm air exposure. Recently, it has been demonstrated that ellagitannins released from oak chips rapidly consume oxygen in a wine-like solution (Navarro et al., 2016). Among ellagitannins, the ellagic and valoneic acid average contents (in mg/kg of equivalents of ellagic acid) in the dried jambolan products were within 43–98 and 28–68 mg/kg, respectively. Based on the processing time and the results of the quantitative evaluation of the analyzed hydrolysable tannins, we suggest that the drying of the foams at 70 or 80 °C may be suitable for obtaining dried powders from jambolan juice. Furthermore, a comparison of the concentrations of these compounds in the foams prior to lyophilization (data not shown) and those in the lyophilized product revealed that gallotannin concentration increased to a greater extent (3.35 times) than ellagitannin concentration (1.92 times). This difference may be associated with the losses of ellagitannins by oxidation during foam generation.

3.4. Changes in TPC and AA

TPC and AA in the jambolan fruit, juice, and dried juice powders are presented in Table 4. After conversion based on the juice yield, we verified an increase of both TPC (9%) and AA (80% by FRAP) in the juice. Branco et al. (2016) observed an increase of both TPC (7%) and AA (56%) in pasteurized jambolan pulp produced at 60 °C for 5 min. Genova et al. (2016) pasteurized grape juice for 30 min at 78 °C and also observed an increase (0.6–9.9%) in TPC. It is noteworthy that the analysis of TPC performed by the Folin-Ciocalteu method suffers interference from at least 50 organic compounds (ascorbic acid, sugars as fructose and sucrose, aromatic amines, organic acids, and Fe^{++}) found naturally in fruits or incorporated due to the extraction methodology employed, which may interfere with the final values found (Prior, Wu, & Schaich, 2005). The AA values obtained by the FRAP method were higher than those obtained by the DPPH method, not only in the fruit but also in the juice and dehydrated products. The same was observed by Singh et al. (2016), who analyzed lyophilized jambolan extracts using the same methods. Rufino et al. (2010) determined the AA of jambolan using the ABTS (an approach involving the same methodology as DPPH) and FRAP methods; they reported values of 29.72 ± 0.3 μmol of Trolox/g of fresh fruit and 35.5 ± 0.3 in μmol of FS/g of fresh fruit, respectively, similarly to what was observed in the current study.

When comparing the drying processes, no statistical difference ($P > 0.05$) between the TPC and AA values for the dried products, including the lyophilized control, was noted although the analysis of individual compounds indicated different responses of the individual PCs. Mussi et al. (2015) dried the jambolan residue (mainly the seed, skin, and pulp waste) in a spouted bed at 60, 70, and 80 °C, to produce powder from the fruit; these authors observed a very small decrease of AA during drying (93–97% of the initial level was maintained). Jebitta and Allwin (2016) used different techniques to dry jambolan pulp, including lyophilization and conventional warm air drying (at 50, 60, and 70 °C), and reported TPC values of 8.43–13.99 mg of GA/g of powder; these values are close to ones in the current study (where fruit juice was used).

The AA values differed largely depending on the process, and those obtained by lyophilization were significantly higher ($P < 0.05$) than foam mat drying. Kapoor et al. (2015) dried jambolan pulp by lyophilization or by warm air (35–40 °C, 8 h), and reported that the TPC and AA of the lyophilized product were higher than those of the product obtained by conventional drying. The reported TPC values of products dehydrated by conventional drying and lyophilization were 3.67 ± 0.49 and 4.16 ± 0.28 g of GA/100 g in the product, respectively, i.e., lower than those determined in the current study.

The various classes of flavonoids differ in the level of oxidation and pattern of substitution of the C ring, which make individual compounds within a class differ in the pattern of stability regarding the exposition to temperatures. An accurate estimation of changes in each individual compounds is difficult, because of the wide varieties of available flavonoids and the extensive distribution in the matrix of used plants. The heat treatment can produce different and simultaneous reactions in vegetable matrix with different implication on antioxidant activity. For instance, it has demonstrated that under short time of heat treatments the food matrices reduces the total antioxidant activity due to the loss of natural antioxidants content, however extending this treatment, this loss is interrupted and even an enhanced antioxidant activity is observed due to the formation of Maillard reaction pro-oxidants. Besides that, it has been observed a reduction of total anthocyanin, despite of the maintenance of antiradical activity, and the authors believe this is probably due to the formation of antioxidant polymers, such as low molecular weight procyanidins, or the formation of degradation products of anthocyanin or phenolic acids, which show antioxidant activity as well (Nicoli, Anese, & Parpinel (1999). Moreover, jambolan berries are rich in sugars (glucose, fructose) and sugar browning as Maillard and caramelization reactions occur at high temperatures (i.e., 60–80 °C), the generated products (furanic derivatives as HMF and furfural) also increasing the total antioxidant activity (Fracassetti, Del Bó, et al., 2013). In view of the above described considerations, there could be a complex series of events implied in the resulting global antioxidant properties of processed foods, not only the changes in the initial phenolic composition.

4. Conclusions

Considering the qualitative and quantitative changes of individual PCs (anthocyanins, flavonols, hydrolysable tannins — gallotannins and ellagitannins) of the analyzed jambolan products, we conclude that

Table 4
Concentration of total phenolics and antioxidant activity of samples of fruit, its juice, lyophilized powder and foam mat powder dried at temperatures of 60 °C, 70 °C and 80 °C.

Samples	TPC (mg of GAE)/g or mL	Antioxidant activity		
		FRAP (μmol of FS/g or mL)	FRAP (μmol of Trolox/g or mL)	DPPH (μmol of Trolox/g or mL)
Fruit	1.22 ± 0.18 a	28.51 ± 3.11 b	8.02 ± 0.93 b	5.57 ± 0.13 b
Juice	1.63 ± 0.17 a	45.31 ± 7.00 a	21.26 ± 3.03 a	13.38 ± 2.64 a
Lyophilized	2.92 ± 0.08 A	55.99 ± 8.00 A	30.34 ± 0.05 A	11.71 ± 0.71 A
Dried at 60 °C	2.43 ± 0.41 A	58.28 ± 7.82 A	27.15 ± 3.40 A	12.82 ± 0.58 A
Dried at 70 °C	2.28 ± 0.41 A	52.72 ± 6.25 A	24.73 ± 2.71 A	13.93 ± 1.31 A
Dried at 80 °C	2.31 ± 0.31 A	58.90 ± 8.25 A	27.42 ± 3.57 A	13.79 ± 1.25 A

Abbreviations: TPC, total phenolic compounds, expressed as mg gallic acid equivalent (GAE)/g or mL. FS, ferric sulfate. The results for jambolan powders were expressed on a dry basis. Different letters in the same column indicate significant differences by analysis of variance (ANOVA) using multiple comparison test of Tukey at $P < 0.05$. Lower case letters used for comparison between fruit and the juice only, whereas capital letters used for comparison among the foams dehydrated by lyophilization and by drying at 60, 70 and 80 °C.

juice extraction leads to a more pronounced degradation of anthocyanins than flavonols, but the extraction of hydrolysable tannins is facilitated. In products dried using the foam mat drying method, elevation of the process temperature negatively affected the total anthocyanin content; the flavonols and hydrolysable tannins were more affected by oxidation and heating time, respectively, than by the drying temperature. Nevertheless, the obtained juice and dried jambolan products contained high concentrations of phenolic compounds, highlighting the potential to exploit this method to obtain dehydrated juice of great nutritional quality. In addition, the dehydration process employed provides greater microbial stability against deterioration and reduces the handling of products and the costs of packaging, transport and refrigeration during storage.

In summary, it can be concluded that processing at 70 °C is most suitable, in light of the least loss of nutritional quality of the product with processing time.

This work encourages the continuation of studies assessing the shelf life of dehydrated products as potential ingredients for the development of jambolan-based products, to enrich and improve the nutritional quality of products available to the consumer.

Acknowledgements

We thank EMBRAPA Grape and Wine (Jales, Brazil) for supplying the grape samples used in this work.

Funding

This work was supported by CAPES (grant number PDSE 99999.012757/2013-06); FAPESP (grant numbers 2013/19057-2 and 2014/11514-8); PROPE (grant number 0300/001/14-PROPe/CDC). The sponsors had no role in study design; in the collection, analysis and interpretation of data; in the writing of the report; and in the decision to submit the article for publication.

Conflict of interest

The authors declare no conflicts of interest.

Authors' contribution

All authors approved the final article.

References

Abbasi, E., & Azizpour, M. (2016). Evaluation of physicochemical properties of foam mat dried sour cherry powder. *LWT — Food Science and Technology, 68*, 105–110. http://dx.doi.org/10.1016/j.lwt.2015.12.004.

AOAC, Association of Official Analytical Chemists (2005). *Official methods of analysis of the Association Analytical Chemists* (18th ed.). Gaithersburg.

Balisteiro, D. M., de Araujo, R. L., Giacaglia, L. R., & Genovese, M. I. (2017). Effect of clarified Brazilian native fruit juices on postprandial glycemia in healthy subjects. Food Research International. https://doi.org/10.1016/j.foodres.2017.08.044.

Benzie, I. F., & Strain, J. J. (1996). The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": The FRAP assay. *Analytical Biochemistry, 239*(1), 70–76. http://dx.doi.org/10.1006/abio.1996.0292.

Boulekbache-Makhlouf, L., Meudec, E., Chibane, M., Mazauric, J. P., Slimani, S., Henry, M., ... Madani, K. (2010). Analysis by high-performance liquid chromatography diode array detection mass spectrometry of phenolic compounds in fruit of *Eucalyptus globulus* cultivated in Algeria. *Journal of Agricultural and Food Chemistry, 58*, 12615–12624. http://dx.doi.org/10.1021/jf1029509.

Branco, I. G., Moraes, I. C. F., Argandoña, E. J. S., Madrona, G. S., dos Santos, C., Ruiz, A. L. T. G., ... Haminiuk, C. W. I. (2016). Influence of pasteurization on antioxidant and in vitro anti-proliferative effects of jambolan (*Syzygium cumini* (L.) Skeels) fruit pulp. *Industrial Crops and Products, 89*, 225–230. http://dx.doi.org/10.1016/j.indcrop.2016.04.055.

Brand-Williams, W., Cuvelier, M. E., & Berset, C. (1995). Use of a free radical method to evaluate antioxidant activity. *LWT — Food Science and Technology, 28*(1), 25–30. http://dx.doi.org/10.1016/S0023-6438(95)80008-5.

Castillo-Muñoz, N., Gómez-Alonso, S., García-Romero, E., Gómez, M. V., Velders, A. H., & Hermosín-Gutiérrez, I. (2009). Flavonol 3-O-glycosides series of Cv. Petit Verdot red wine grapes. *Journal of Agricultural and Food Chemistry, 57*(1), 209–219. http://dx.doi.org/10.1021/jf802863g.

Castillo-Muñoz, N., Gómez-Alonso, S., García-Romero, E., & Hermosín-Gutiérrez, I. (2007). Flavonol profiles of *Vitis vinifera* red grapes and their single-cultivar wines. *Journal of Agricultural and Food Chemistry, 55*(3), 992–1002. http://dx.doi.org/10.1021/jf062800k.

Coelho, E. M., de Azevêdo, L. C., Corrêa, L. C., Bordignon-Luiz, M. T., & Lima, M. S. (2016). Phenolic profile, organic acids and antioxidant activity of frozen pulp and juice of the jambolan (*Syzygium cumini*). *Journal of Food Biochemistry, 40*(2), 211–219. http://dx.doi.org/10.1111/jfbc.12209.

Costa, A. G. V., Garcia-Diaz, D. F., Jimenez, P., & Silva, P. I. (2013). Bioactive compounds and health benefits of exotic tropical red–black berries. *Journal of Functional Foods, 5*(2), 539–549. http://dx.doi.org/10.1016/j.jff.2013.01.029.

Fracassetti, D., Costa, C., Moulay, L., & Tomás-Barberán, F. A. (2013). Ellagic acid derivatives, ellagitannins, proanthocyanidins and other phenolics, vitamin C and antioxidant capacity of two powder products from camu-camu fruit (*Myrciaria dubia*). *Food Chemistry, 139*(1–4), 578–588. http://dx.doi.org/10.1016/j.foodchem.2013.01.121.

Fracassetti, D., Del Bó, C., Simonetti, P., Gardana, C., Klimis-Zacas, D., & Ciappellano, S. (2013). Effect of time and storage temperature on anthocyanin decay and antioxidant activity in wild blueberry (*Vaccinium angustifolium*) powder. *Journal of Agricultural and Food Chemistry, 61*(12), 2999–3005. http://dx.doi.org/10.1021/jf3048884.

Genova, G., Tosetti, R., & Tonutti, P. (2016). Berry ripening, pre-processing and thermal treatments affect the phenolic composition and antioxidant capacity of grape (*Vitis vinifera* L.) juice. *Journal of the Science of Food and Agriculture, 96*(2), 664–671. http://dx.doi.org/10.1002/jsfa.7138.

Hermosín-Gutiérrez, I., Castillo-Muñoz, N., Gómez-Alonso, S., & García-Romero, E. (2011). Flavonol profiles for grape and wine authentication. In S. E. Ebeler, G. R. Takeoka, & P. Winterhalter (Eds.). *Washington, DC: ACS symposium series*. (pp. 113–129).

Jebitta, R. S., & Allwin, J. S. (2016). Antioxidant activity, total phenol, flavonoid, and anthocyanin contents of jamun (*Syzygium cumini*) pulp powder. *Asian Journal of Pharmaceutical and Clinical Research, 9*(2), 361–363.

Kapoor, S., & Ranote, P. S. (2015). Antioxidant potentials and quality of blended pear-jamun (*Syzygium cumini* L.) juice. *International Research Journal of Biological Sciences, 4*(4), 30–37.

Kapoor, S., Ranote, P. S., & Sharma, S. (2015). Bioactive components and quality assessment of jamun (*Syzygium cumini* L.) powder supplemented chapatti. *Indian Journal of Science and Technology, 8*(3), 287–295. http://dx.doi.org/10.17485/ijst/2015/v8i3/59863.

Lago-Vanzela, E. S., Santos, G. V., Lima, F. A., Gomes, E., & da Silva, R. (2011). Physical-chemical, caloric and sensory characterization of light jambolan (*Syzygium cumini* Lamarck) jelly. *Ciência e Tecnologia de Alimentos, 31*(3), 666–673. http://dx.doi.org/10.1590/S0101-20612011000300018.

Michalska, A., Wojdylo, A., Lech, K., Lysiak, G. P., & Figiel, A. (2016). Physicochemical properties of whole fruit plum powders obtained using different drying technologies. *Food Chemistry, 207*, 223–232. http://dx.doi.org/10.1016/j.foodchem.2016.03.075.

Mussi, L. P., Guimarães, A. O., Ferreira, K. S., & Pereira, N. R. (2015). Spouted bed drying of jambolão (*Syzygium cumini*) residue: Drying kinetics and effect on the antioxidant activity, anthocyanins and nutrients contents. *LWT — Food Science and Technology, 61*(1), 80–88. http://dx.doi.org/10.1016/j.lwt.2014.11.040.

Navarro, M., Kontoudakis, N., Giordanengo, T., Gómez-Alonso, S., García-Romero, E., Fort, F., ... Zamora, F. (2016). Oxygen consumption by oak chips in a model wine solution; influence of the botanical origin, toast level and ellagitannin content. *Food Chemistry, 199*, 822–827. http://dx.doi.org/10.1016/j.foodchem.2015.12.081.

Nicoli, M. C., Anese, M., & Parpinel, M. (1999). Influence of processing on the antioxidant properties of fruit and vegetables. *Trends in Food Science & Technology, 10*(3), 94–100. http://dx.doi.org/10.1016/S0924-2244(99)00023-0.

Nuengchamnong, N., & Ingkaninan, K. (2009). On-line characterization of phenolic antioxidants in fruit wines from family myrtaceae by liquid chromatography combined with electrospray ionization tandem mass spectrometry and radical scavenging detection. *LWT — Food Science and Technology, 42*(1), 297–302. http://dx.doi.org/10.1016/j.lwt.2008.04.012.

Ough, C. S., & Amerine, M. A. (1988). *Methods for analysis of musts and wines* (2nd ed.). New York: John Wiley & Sons.

Peng, S., Scalbert, A., & Monties, B. (1991). Insoluble ellagitannins in *Castanea sativa* and *Quercus petraea* woods. *Phytochemistry, 30*, 775–778. http://dx.doi.org/10.1016/0031-9422(91)85250-4.

Prior, R. L., Wu, X. L., & Schaich, K. (2005). Standardized methods for the determination of antioxidant capacity and phenolics in foods and dietary supplements. *Journal of Agricultural and Food Chemistry, 53*, 4290–4302.

Rufino, M. S. M., Alves, R. E., de Brito, E. S., Pérez-Jiménez, J., Saura-Calixto, F., & Mancini-Filho, J. (2010). Bioactive compounds and antioxidant capacities of 18 non-traditional tropical fruits from Brazil. *Food Chemistry, 121*(4), 996–1002. http://dx.doi.org/10.1016/j.foodchem.2010.01.037.

Santhalakshmy, S., Don Bosco, S. J., Francis, S., & Sabeena, M. (2015). Effect of inlet temperature on physicochemical properties of spray-dried jamun fruit juice powder. *Powder Technology, 274*, 37–43. http://dx.doi.org/10.1016/j.powtec.2015.01.016.

Santiago, M. C. P. A., Gouvêa, A. C. M. S., Peixoto, F. M., Borguini, R. G., Godoy, R. L., Pacheco, S., ... Nogueira, R. I. (2015). Characterization of jamelão (*Syzygium cumini* (L.) Skeels) fruit peel powder for use as natural colorant. *Fruits, 71*(1), 3–8. http://dx.doi.org/10.1051/fruits/2015041.

Santos, S. A. O., Freire, C. S. R., Domingues, M. R., Silvestre, A. J. D., & Neto, C. P. (2011). Characterization of phenolic components in polar extract of *Eucalyptus globulus* Labill, bark by High-Performance Liquid Chromatography-Mass Spectrometry. *Journal of Agricultural and Food Chemistry, 59*, 9386–9393. http://dx.doi.org/10.1021/jf201801q.

Seraglio, S. K. T., Schulz, M., Nehring, P., Betta, F. D., Valese, A. C., Daguer, H., ... Costa, A. C. O. (2017). Nutritional and bioactive potential of Myrtaceae fruits during ripening. *Food Chemistry, 239*, 649–656. http://dx.doi.org/10.1016/j.foodchem.2017.06.118.

Sharma, R. J., Gupta, R. C., Singh, S., Bansal, A. K., & Singh, I. P. (2016). Stability of anthocyanins- and anthocyanidins-enriched extracts, and formulations of fruit pulp of *Eugenia jambolana* ('jamun'). *Food Chemistry, 190*(1), 808–817. http://dx.doi.org/10.1016/j.foodchem.2015.06.029.

Sheikh, S. A., Shahnawaz, M., Nizamani, S. M., Bhanger, M. I., & Ahmed, E. (2011). Phenolic contents and antioxidants activities in jamman fruit (*Eugenia jambolana*) products. *Journal of Pharmacy and Nutrition Sciences, 1*(1), 41–47. http://dx.doi.org/10.6000/1927-5951.2011.01.01.08.

Singh, J. P., Kaur, A., Singh, N., Nim, L., Shevkani, K., Kaur, H., & Arora, D. S. (2016). In vitro antioxidant and antimicrobial properties of jambolan (*Syzygium cumini*) fruit polyphenols. *LWT — Food Science and Technology, 65*, 1025–1030. http://dx.doi.org/10.1016/j.lwt.2015.09.038.

Tavares, I. M. C., Lago-Vanzela, E. S., Rebello, L. P. G., Ramos, A. M., Gómez-Alonso, S., García-Romero, E., ... Hermosín-Gutiérrez, I. (2016). Comprehensive study of the phenolic composition of the edible parts of jambolan fruit (*Syzygium cumini* (L.) Skeels). *Food Research International, 82*, 771–779. http://dx.doi.org/10.1016/j.foodres.2016.01.014.

Tavares, I. M. C., Mauro, M. A., Da-Silva, R., Hermosín-Gutierrez, I., & Lago-Vanzela, E. S. (2015). Juice production BRS Violeta (*BRS rúbea* x iac 1398–21) and jambolan (*Syzygium cumini* (L.)) dehydrated by foam-mat drying: Foam testing and drying. *Journal of Fruits and Vegetables, 1*(2), 1–30. Retrieved from http://ebooks.cambridge.org/ref/id/CBO9781107415324A009.

Teleszko, M., Nowicka, P., & Wojdyło, A. (2016). Effect of cultivar and storage temperature on identification and stability of polyphenols in strawberry cloudy juices. *Journal of Food Composition and Analysis, 54*, 10–19. http://dx.doi.org/10.1016/j.jfca.2016.09.009.

Torres, C., Díaz-Maroto, M. C., Hermosín-Gutiérrez, I., & Pérez-Coello, M. S. (2010). Effect of freeze-drying and oven-drying on volatiles and phenolics composition of grape skin. *Analytica Chimica Acta, 660*(1–2), 177–182. http://dx.doi.org/10.1016/j.aca.2009.10.005.

World Geodetic System https://gis.icao.int/eganp/webpdf/REF08-Doc9674.pdfl >, Accessed date: March 2017.