XXV Congresso Brasileiro de Ciência e Tecnologia de Alimentos
Alimentação: a árvore que sustenta a vida
X CIGR Section IV International Technical Symposium
Food: the tree that sustains life
24 a 27 de outubro de 2016 • FAURGS • GRAMADO/RS

PHENOLIC COMPOSITION OF COMMERCIAL AÇAÍ PULPS

A.V. Carvalho[1], T.F.F Silveira[2], R.A. Mattietto1, H.T. Godoy[2]

1-Embrapa Amazônia Oriental – CEP: 66.095-903 – Belém – PA – Brasil, Telefone: 55 (91) 3204-1130 – Fax: 55 (91) 3276-9845 – e-mail: (ana-vania.carvalho@embrapa.br; rafaella.mattietto@embrapa.br)
2- Departament of Food Science, Faculty of Food Engineering, University of Campinas (UNICAMP), Monteiro Lobato Street, n. 80 - CEP 13083-862 – Campinas – SP – Brazil – e-mail: (ferreira.tayse@gmail.com)

RESUMO – Este estudo teve como objetivo determinar a composição fenólica de três polpas de açaí comerciais, provenientes de Belém, Pará, Brasil. As antocianinas e os compostos não-antociânicos foram determinados por cromatografia líquida de alta eficiência acoplada a um detector de arranjo de diodos. A antocianina 3-rutinosídeo foi a principal antocianina presente em amostras de polpa de açaí liofilizados. A amostra comercial C apresentou a maior quantidade de cianidina 3-glicosídeo e cianidina 3-rutinosídeo (18.942 μg g^{-1} e 34.397 μg g^{-1} de amostra liofilizada, respectivamente). O conteúdo de compostos fenólicos variou significativamente entre as amostras comerciais e o ácido vanílico apresentou a maior concentração nas amostras estudadas.

ABSTRACT – This study aims to determine the phenolic composition of three commercial açaí pulps, from Belém, state of Pará, Brazil. Anthocyanins and non-anthocyanin compounds were determinated by high performance liquid chromatography coupled to a diode array detector. Anthocyanin 3-rutinoside was the major anthocyanin present in freeze-dried açaí pulp samples. The commercial sample C showed the greatest amounts of cyanidin 3-glucoside and cyanidin 3-rutinoside (18,942 μg g^{-1} and 34,397 μg g^{-1} in freeze-dried sample, respectively). The content of phenolic compounds varied significantly among the commercial samples, and the vanillic acid was found in the highest concentration in the samples studied.

PALAVRAS-CHAVE: *Euterpe oleracea*; compostos fenólicos; antocianinas.

KEYWORDS: *Euterpe oleracea*; phenolic compounds; anthocyanins.

1. INTRODUCTION

Açaí pulp has received much attention in recent years as one of the new ‘‘superfruits’’. The consumption of açaí from the Amazon region has been increasing, mainly due to the benefits reported in the scientific literature. The *Euterpe* species has a high economic potential since it is used to prepare açaí beverages which are exported all over the world as an energetic drink (Yamaguchi et al., 2015). The main açaí by-product is the beverage obtained by the mechanical separation of the edible endocarp from the fibrous seeds and the addition of water.

Açaí is known for its high concentrations of bioactive compounds. Anthocyanins are the major phenolic compounds in this fruit, with predominance of cyanidin-3-glucoside and cyanidin-3-rutinoside (De Rosso et al., 2008; Pacheco-Palencia et al., 2009; Yamaguchi et al., 2015). Other phenolic compounds, such as rutin, orientin, homoorientin, catechin, epicatechin, ferulic acid, vanillic acid, gallic acid, *p*-hydroxibenzoic acid, and syringic acid have also been reported (Gordon et al., 2012; Pacheco-Palencia et al., 2008; Schauss et al., 2006; Yamaguchi et al., 2015). The presence

of these compounds is associated with free radical scavenging activity and inhibition of liposome oxidation, reduction of oxidative damage and inflammation in brain cells, potential antiproliferative and anti-inflammatory effects, atheroprotective effect, and protective effect against carcinogenesis among others (Fragoso et al., 2013; Kang et al., 2012; Noratto et al., 2012; Pacheco-Palencia et al., 2008; Poulose et al., 2014; Schauss et al., 2006).

Therefore, this study aimed to determine the composition of anthocyanin and non-anthocyanin phenolic compounds of three commercial pulps, from Belém, state of Pará, the largest açaí producer in Brazil.

2. MATERIALS AND METHODS

2.1 Sample Preparation

Three commercial samples of açaí pulp, denominated 'A', 'B', and 'C', were purchased from local shops in Belém and transported to the Food Analysis Laboratory at Embrapa Eastern Amazonia. The commercial pulps were then freeze-dried for 48 h.

2.2 Phenolic Compounds

Extraction of anthocyanins: the anthocyanins were exhaustively extracted from 0.05 g of lyophilized pulp samples using 1% HCl in methanol, according to Zanatta et al. (2005). The solution was then filtered, vacuum-concentrated and stored at -18 ºC until HPLC analysis.

Extraction of non-anthocyanic compounds: in order to obtain a fraction free of anthocyanins, the method described by Gordon et al. (2012). To eliminate the solvent fraction, the samples were vacuum-evaporated. The aqueous fraction remaining was partitioned with diethyl ether and of ethyl acetate. (Pozo-Baýon et al., 2003). Finally, the ether and ethyl acetate phase, rich in nonanthocyanic phenolics, was vacuum-dried, resuspended in aqueous solution of formic acid:acetonitrile, and injected into the HPLC.

2.3 Cromatographic Conditions

Anthocyanins were determinated by high performance liquid chromatography (Agilent 1260). The system was equipped with a quaternary pump, automatic injector, column oven, and diode array detector, based on the method described by De Rosso et al. (2008). Chromatograms were recorded at absorbance of 520 nm, and data acquisition was performed using the Chemistation software (Agilent, Santa Clara, CA, USA). Anthocyanin identification was performed by comparison of retention times and visible spectrum of the peaks of known standards with the peaks present in the samples. Quantification was performed by external standard curve calibration, using the linear range of concentration for every compound.

Non-anthocyanic phenolic compounds were determined by high performance liquid chromatography (Agilent 1100), according to Pacheco-Palencia et al. (2009). In order to detect all phenolics compounds studied and quantify them as close as possible to the wavelength of their most intention absorption, detection was performed at 280 nm (hydroxybenzoic acids), 325 nm (hydroxy cinnamic acids), and 350 nm (flavonoids).

Standard curves were constructed for each compound using a wide range of concentration encompassing the content expected in each sample, between 0.1 and 7 ppm. The data were subjected to analysis of variance and lack of fit test; it was apparent that the curves were linear ($p<0.05$) over the concentration range studied, and there was no evidence of lack of fit ($p>0.05$).

2.4 Statistics

The results were subjected to analysis of variance and Tukey's test to evaluate the differences between the samples (p<0.05).

3. RESULTS AND DISCUSSION

3.1 Phenolic Composition of Commercial Açaí Pulp

Table 1 presents the content of anthocyanic and non-anthocyanic phenolic compounds in the acaí samples analyzed. There was significant difference in the content of phenolic compounds and anthocyanins quantified (p<0.05). The commercial sample C showed the highest concentration of cyanidin 3-glucoside and cyanidin 3-rutinoside (1,8942 μg g^{-1} and 34,397 μg g^{-1}, respectively). In agreement with the values found in the literature, it was found that anthocyanin 3-rutinoside was the major anthocyanin present in freeze-dried açaí pulp samples. Schauss et al. (2006) found 1,930 μg g^{-1} of cyanidin 3-rutinoside and 1,170 μg g^{-1} of cyanidin 3-glucoside in freeze-dried açaí pulp; these values are higher than those obtained in the present study, except for the C sample. On the other hand, Gordon et al. (2012) found 179 and 49.4 μg g^{-1} DW of cyanidin 3-rutinoside and cyanidin 3-glucoside, respectively, and these values are lower than those observed in the present study.

Table 1. Anthocyanin (μg g^{-1}) and non-anthocyanic (μg g^{-1}) compounds presents in commercial açaí pulps.

Compound	Sample		
	A	B	C
Cyanidin 3-glucoside	469±39.18 ^{b}	613±64.87^{b}	18,942±22.96^{a}
Cyanidin 3-rutinoside	932±60.44^{b}	1,329±96.20^{b}	34,397±45.53^{a}
3,4-dihydroxibenzoic acid	13.08±0.99^{b}	17.31±0.63^{a}	9.73±0.01^{c}
4-hydroxibenzoic acid	9.69±0.80^{b}	10.78±2.52^{ab}	14.45±0.02^{a}
Vanilic acid	27.94±4.06 ^{ab}	30.29±2.48^{a}	23.88±0.2^{b}
Caffeic acid	1.36±0.15^{a}	1.44±0.10^{a}	1.78±0.03^{a}
Syringic acid	11.18±1.64^{a}	11.75±1.18^{a}	12.05±0.00^{a}
p-coumaric acid	2.90±0.37^{a}	3.08±0.35^{a}	3.28±0.01^{a}
Isoorientin	1.95±0.81^{b}	1.66±0.06^{b}	12.56±0.00^{a}
Orientin	1.40±0.68^{b}	1.11±0.07^{b}	7.04±0.08^{a}
Ferulic acid	6.27±0.36^{a}	7.60±0.62^{a}	6.42±0.00^{a}

Freeze-dried sample.
Equal letter in the same line represent samples that do not differ at a 95% confidence level.

With regard to the non-anthocyanic compounds, it was found that the phenolic profile of the samples evaluated is in agreement with previous studies reported (Gordon et al., 2012; Pacheco-Palencia et al., 2009; Schauss et al., 2006). It was observed that the content of phenolic compounds varied significantly between the commercial samples. Vanillic acid was the major compound present in all of the samples studied, while caffeic acid had the lowest concentration. Gordon et al. (2012) reported that vanillic acid was the non-anthocyanic phenolic compound with the highest concentrations of freeze-dried açaí pulp, made from ripe açaí; this value is higher than that found in the present study. These authors also found higher concentrations of flavonoid orientin (112 μg g^{-1}) and similar amounts of syringic acid (11.0 μg g^{-1}). Schulz et al. (2015) found similar values of *p*coumaric acid (1.9 μg g^{-1}) in juçara (*Euterpe edulis* Martius) extracts.

The content of phytochemicals in the açaí pulp may vary significantly due to the different procedures used to prepare this product, such as the amount of water added to the fruit pulp.

Additionally, climatic conditions, variety, harvest, and ripening stage are known to influence the phytochemical contents in foods (De Rosso et al., 2008; Gordon et al., 2012).

4. CONCLUSION

The commercial samples evaluated had high levels of anthocyanins and non-anthocyanin compounds. The anthocyanin 3-rutinoside was the major anthocyanin present in freeze-dried açaí pulp samples. With regard to the non-anthocyanic compounds, it was observed that the vanillic acid was the major compound present in all of the samples studied, while caffeic acid had the lowest concentration.

5. REFERENCES

De Rosso, V. V., De Hillebrand, S., Cuevas, E., Bobbio, F. O., Winterhalter, P. & Mercadante, A. Z. (2008). Determination of anthocyanins from acerola (*Malpighia emarginata* DC.) and açai (*Euterpe oleracea* Mart.) by HPLC-PDA-MS/MS. *Journal of Food Composition and Analysis*, 21, 291-299.

Fragoso, M. F., Romualdo, G. R., Ribeiro, D. A. & Barbisan, L. F. (2013). Açai (*Euterpe oleracea* Mart.) feeding attenuates dimethylhydrazine-induced rat colon carcinogenesis. *Food Chemistry Toxicology*, 58, 68-76.

Gordon, A., Cruz, A. P. G., Cabral, L. M. C., Freitas, S. C., Taxi, C. D., Donangelo, C. M., Mattietto, R. A., Friedrich, M., Matta, V.M., Marx, F. (2012). Chemical characterization and evaluation of antioxidant properties of açaí frutis (*Euterpe oleraceae* Mart.) during ripening. *Food Chemistry*, 133, 256-263.

Kang, J., Thakali, K. M., Xie, C., Kondo, M., Tong, Y., Ou, B., Jensen, G., Medina, M. B., Schauss, A. G. & Wu, X. (2012). Bioactivities of açaí (*Euterpe precatoria* Mart.) fruit pulp, superior antioxidant and anti-inflammatory properties to *Euterpe oleracea* Mart. *Food Chemistry*, 133, 671-677.

Noratto, G. D., Angel-Morales, G., Talcott, S. T. & Mertens-Talcott, S. U. (2011). Polyphenolics from açaí (*Euterpe oleracea* Mart.) and red muscadine grape (*Vitis rotundifolia*) protect human umbilical vascular endothelial cells (HUVEC) from glucose- and lipopolysaccharide (LPS)-induced inflammation and target microrna-126. *Journal of Agricultural and Food Chemistry*, 59, 7999-8012.

Pacheco-Palencia, L. A., Talcott, S. T., Safe, S. & Talcott, S. M. (2008). Absorption and biological activity of phytochemical-rich extracts from açai (*Euterpe oleracea* Mart.) pulp and oil in vitro. *Journal of Agricultural and Food Chemistry*, 56, 3593-3600.

Pacheco-Palencia, L. A., Duncan, C. E. & Talcott, S. T. (2009). Phytochemical composition and thermal stability of two commercial acai species, *Euterpe oleracea* and *Euterpe precatoria*. *Food Chemistry*, 115, 1199-1205.

Poulose, S. M., Fisher, D. R., Bielinski, D. F., Gomes, S. M., Rimando, A. M., & Schauss, A. G. (2014). Restoration of stressor-induced calcium dysregulation and autophagy inhibition by polyphenolics-rich acai (*Euterpe* spp.) fruit pulp extracts in rodent brain cells in vitro. *Nutrition*, 30, 853-862.

Pozo-Baýon, M. A., Hernández, T. M., Alvarés-Martin, P. J. & Carmen Polo, M. (2003). Study of low molecular weight phenolic compounds during the aging of sparkling wines manufactured with red and white grape varieties. *Journal of Agricultural and Food Chemistry*, 51, 2089-2095.

Schauss, A. G., Wu, X., Prior, R. L., Ou, B., Huang, D., Owens, J., Agarwal, A., Jensen, G. S., Hart, N. A. & Shanbrom, E. (2006). Antioxidant capacity and other bioactivities of the freeze-dried Amazonian palm berry, *Euterpe oleracea* Mart. (acai). *Journal of Agricultural and Food Chemistry*, 54, 8604-8610.

Schulz, M., Borges, G. S. C., Gonzaga, L. V., Katia, S., Seragilo, T., Olivo, I. S., Azevedo, M. S., Nehring, P., Gois, J. S., Almeida, T. S., Vitali, L., Spudeit, D. A., Micke, G. A., Borges, D. L. & Fett,

R. (2015). Chemical composition, bioactive compounds and antioxidant capacity of juçara fruit (*Euterpe edulis* Martius) during ripening. *Food Research International*, **77**, 125-131.
Yamaguchi, K. K. L., Pereira, L. F. R., Lamarão, C. V., Lima, E. S. & Veiga-Junior, V. F. (2015). Amazon acai: Chemistry and biological activities: a review. *Food Chemistry*, 179, 137-151.
Zanatta, C. F., Cuevas, E., Bobbio, F. O., Winterhalter, P., Mercadante, A. Z. (2005). Determination of anthocyanins from camu-camu (*Myrciaria dubia*) by HPLC-PDA, HPLC-MS and NMR. *Journal of Agricultural and Food Chemiestry,* 53, 9531-9535.