

## Metabolic fingerprint of açai (*Euterpe oleracea*) berry pulp using $^1\text{H}$ NMR spectroscopy and chemometric analysis

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The açai fruit pulp (*Euterpe oleracea* Mart.) is an important food product widely consumed in all Northern region of Brazil and, more recently, in the Southeast and South regions and also abroad, in places such as the United States, Australia, Japan and Europe. It shows high nutritional value, being rich in lipids, proteins, vitamins (E, A, B1 e C), fibers,  $\alpha$ -tocopherol, anthocyanins, mineral salts and for showing medicinal activity such as antioxidant, anti-inflammatory and ant proliferative effects. The rapid degradation of the fruit is a major problem for its commercialization. Some other factors make it difficult to guarantee a product in the market with quality control and traceability because the fruits are collected in different periods of the year, from different regions and varieties of crops (dry and wet soil). Therefore, the objective of this work was to evaluate influence of different cultivars and seasonality of açai using the  $^1\text{H}$  NMR technique for fingerprinting profiling associated with chemometrics methods, obtained from genetically modified fruits (cultivated in agronomic control) and the commerce in Belem city. The açai berries genetically modified were collected at different season in the years 2014/2015, the fruits were sanitized, processed, freeze dried and stored at  $-20^\circ\text{C}$  in the same collection day. Frozen pulps of 10 commercial points were obtained in the same years. The methanolic extracts were obtained five times for each sample.  $^1\text{H}$  NMR spectra were acquired at 300 K in a Bruker AVANCE III 9.4 Tesla, using a 5 mm BBI probe head (with ATMA<sup>®</sup> and SampleXpress<sup>™</sup>). The NMR tubes with extracts were positioned at random in the automatic sampler. PCA was carried out in the  $^1\text{H}$  NMR data using AMIX<sup>®</sup> software. It was obtained  $^1\text{H}$  NMR spectra for 30 commercials and 39 genotypes samples. Some major compounds were identified through analysis of 1D and 2D NMR experiments, database and literature<sup>1-2</sup>. The study has showed that freeze-dried açai pulp of genotypes and commercials are strongly similar. It was possible to observe tendencies in the distribution of periods of fruits genotype collection and in the commercials açai pulp. However, some commercial samples showed higher concentration of unsaturated fatty acids as linoleic (omega 6), palmitoleic, vaccenic and oleic (omega 9) than genotype samples. Just a commercial point it wasn't possible to differentiate the periods of the year 2014/2015. Probably they buy açai fruit very often and do not keep stockpile. Of the 31 genetically modified açai palm trees, only five genotypes showed chemical different characteristics in the fruit and these fruits have higher concentration of amino acid (serine, leucine, threonine and glutamic acid), vitamin C and unsaturated lipids. The samples of 2014 had higher concentration of threonine, glutamic acid, glucose and fructose and at 2015, it was vitamin C and saturated fatty acids. Only two genetically modified açai palm trees showed higher concentration of phenolic compounds such as anthocyanins and other flavonoids in a period 2014.

[1] Le Gall, G., Colquhoun, I. J., Davis, A. L., Collins, G. J., Verhoeven, M. E., 2003. Metabolite profiling of tomato using  $^1\text{H}$  NMR spectroscopy as a tool to detect potential unintended effects following a genetic modification. *Journal of agricultural and food chemistry*. 51, pp. 2447-2456.

[2] Kang, K., Xie, C., Li, Z., Nagarajan, S., Schauss, A. G., 2011. Flavonoids from açai (*Euterpe oleracea* Mart.) pulp and their antioxidant and anti-inflammatory activities. *Food Chemistry*, 128, pp. 152-157.