Characterization of volatile compounds and bioactive compounds of pulp and jelly of cagaita by solid phase microextraction in the headspace mode and mass spectrometry by paper spray

Caracterização de compostos voláteis e compostos bioativos da polpa e geleia de cagaita por microextração em fase sólida no modo headspace e espectrometria de massa por paper spray

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Abstract
The cagaita (Eugenia dysenterica) belonging to the Myrtaceae family, is a tree native to the Brazilian Cerrado, its fruit is very fragile, with thin bark and juicy pulp, it is consumed in the processed form as a jelly to prolong its useful life. The present work had as objective to elaborate cagaita jelly and to evaluate the alteration of bioactive compounds and volatile compounds in relation to the pulp in natura. The analysis of mass spectrometry by paper spray in positive and negative modes allowed the identification of several substances, among them, organic acids, sugars, anthocyanins, hydroxycinnamic acids, hydroxybenzoic acids and flavonoids, indicating that the production of jelly can be a
technique for conservation of phenolic compounds with their respective sensory qualities such as color and flavor. In the analysis of volatiles by solid phase microextraction in headspace mode, monoterpenes, hydrocarbons and sesquiterpenes were detected, indicating that the production of jelly can preserve the characteristic aroma of the fruit. In the characterization of volatile compounds in cagaita pulp, 3-carene was the major monoterpen e found. While processing jelly there was production of furaldehyde, a product obtained as a natural consequence of heating.

**Keywords:** *Eugenia dysenterica*; Volatile compounds; Bioactive compounds; Mytaceae.

1. Introduction

The Cerrado constitute great natural fount of biological resources, extending itself per thirteen Brazilian states, with enormous biodiversity, occupying almost 25% of Brasil, and also some small areas in Bolivia and in Paraguay, but its entirety resides in Brazilian territory (Proença et al., 2000).

The study of native Cerrado fruits is a way of validate the exploration of the biome’s natural flora, it expresses species with properties beneficial to health and that are utilized as ways of treating diseases or symptoms by its local populations (Ramos et al., 2020; Santos et al., 2020). However, the area is mostly tapped for agricultural production which has as consequence the deterioration of the native vegetation and loss of exploration of these species (Klink & Machado, 2005; Oliveira, 2018).

Green and ripe cagaita fruits are rich in phenolic compounds such as: galic acid, caffeic acid, p-coumaric acid and quercetin, besides its mineral content, making the fruit a promising fount of bioactive compounds, with antioxidants, anti-obesity and nutritive action (Guedes et al., 2017; Bueno et al., 2017).

The uses of Cerrado fruits in culinary has been arising interest in diverse segments of society, among them stands out: food industry, cooperatives, search and university institutions. Because they are exotic fruits, with unknow flavors and aroma in many countries, the external market also can be conquered (Silva et al., 2001).
About the nutritional value, cagaita is considered a great font of vitamin C (24.53 mg/100 g), superior values are found in many conventionally grown fruits, such as banana (*Musa sp.*) (6.4 mg/100 g) and apple (*Malus domestica*) (5.9 mg/100 g) (Lemos-Filho, 2000).

The development of technological processes has driven a better utilization of the fruit. The frozen pulp production and the utilization of feedstock for jelly production compose an alternative to contour the cagaita market weak point, the deterioration of the product. This is a viable activity to add economical value, minimizing loss which can occur during the *in natura* fruit commercialization, beyond the extension of its post-harvest life (Damiani, 2009; Evangelista & Vieites, 2006).

Against the demand for less laborious and costly methods, many techniques of mass spectrometry (MS) with ambient ionization have been proposed. Among them MS with ionization by paper spray (PS) has taken greater attention in recent years for qualitative and quantitative analyses of bioactive compounds (Oliveira *et al*., 2020). Wang *et al* (2010) describe for the first time this technique, and, since then, has been widely spread due its great simplicity, efficiency and low cost in qualitative and quantitative analysis of bioactive substances in fruits and processed products.

The capillary action in the paper porous surface is the main processes responsible for the movement of the analytes which will be desolvated during the spray formation next to the mass spectrometer entrance (Yang *et al*., 2012). The production of ions by PS has the same principles of the electrospray ionization (ESI), in which a solution of the sample in acid or basic pH is subjected to an electrolytic spray under atmospheric pressure. A thin spray (aerosol) is formed (Taylor’s cone) in the presence of a high electrical field of +4000 volt (V) (or -4000 V). The ion is oxidized (or reduced) forming drops with excessive positive (or negative) charge.

The volatile compound identification resulted from the association of gas chromatography coupled with mass spectrometry (CGMS), introducing a useful tool in separation and identification of complex mixtures compounds. The mass spectrometers provide stability and sensibility for volatile compounds analyses (Thomazini & Franco, 2000).

The solid-phase microextraction in headspace mode (HS-SPME) is a technique which allows extraction with low cost, fast and without solvent utilization, besides providing affinity for countless analytes and being easily coupled with gas chromatography (Santos *et al*., 2020; Kataoka, Lord & Pawliszyn, 2000).

In view of the above and aiming to add value for the Cerrado fruits, through its post-harvest life, the objectives of this work was to study the bioactive compound profile and volatile compounds in cagaita pulp when subjected to freeze process and jelly elaboration.

2. Material and Methods

Ripped fruits of cagaita were collected from Sete Lagoas – MG (latitude 19° 28' 35.8'' and longitude 44° 11' 42.4'') in December of 2018. The cagaita were transported to the Organic Chemistry Lab in Universidade Federal de São João Del Rei of Sete Lagoas. The fruits were washed in current water, sanitized for 15 minutes using sodium hypochlorite (200 mgL⁻¹), washed again in current water and stored on a -20°C freezer. The pulp was produced before the beginning of the analysis, defreezing the fruits, eliminating the peel and seeds, then mixing the pulp for homogenization.

2.1 Jelly elaboration

The cagaita’s jelly was prepared with 60% pulp, 40% sucrose and 0.2% agar-agar. Initially sucrose was added to the pulp, then the mixture was subjected to cooking in domestic stove, with continuous manual agitation, for about 4 minutes. Then agar-agar was added to the mixture kept on low fire with continuous manual agitation for 2 minutes (Santos *et al* 2012). Posteriorly the jelly was bottled in glass flasks, previously sterilized. Then the flasks were sealed and stored in ambient temperature for 10 days.
2.2 Bioactive compound profile analysis

1.5 g of cagaita’s pulp and 1.5 g of cagaita’s jelly were weighted and putted on test tubes. 10 mL of methanol was added then the test tubes were homogenized and left in rest for 3 hours. Posteriorly 2 mL of the extract were transferred to eppendorfs and forwarded to the PSMS analyses carried out on the Mass Spectrometry Lab of the Chemistry Department in the Universidade Federal de Minas Gerais (Pereira et al., 2018).

The fixed compounds profile analysis was accomplished with a mass spectrometer (LCQ Fleet model, Thermo Scientific, San Jose, CA, USA), ion-trap type analyzer, coupled to a ionization fount by paper spray in positive and negative modes.

The analyses were carried out utilizing the following conditions: paper spray voltage of 4.0 kilovolts (kV) for positive mode and of 3.0 kV for negative mode, capillary voltage of 40 V, capillary temperature of 275°C and tube lens voltage of 120 V. The data acquisition was occurred in Full Scan mode with mass range of 100 to 1000 mass/charge (m/z) in positive and negative mode.

For the analyses accomplishment, 2.0 µL of sample were put on the edge of the equilateral triangle shaped chromatographic paper with 1.5 cm sides. This paper was fixated in the mass spectrometer entrance in a distance of 0.5 cm by a connector attached to a high tension fount. Posteriorly 40.0 µL of methanol were put on the edge of the chromatographic paper and the voltage fount was switched on for the data acquisition. The Thermo Scientific X Calibur software was used for the data acquirement and the compounds were identified according to its m/z and by comparison with literature data (Wang et al., 2010; Pereira et al., 2016; Carvalho et al., 2015; Silva et al., 2019).

2.3 Volatile compound analysis

In the volatile compound extraction was utilized the solid-phase microextraction method (SPME), in which was used semi-polar polymeric film, polydimethylsiloxane/divinylbenzene (PDMS/DVB). For the SPME analyses 2g of cagaita pulp and 2g of cagaita jelly were weighted which were put on 20 mL headspace flasks sealed with aluminum film and rubber septum. Posteriorly the flasks were placed on an aluminum bloc a heated to 60°C on a heating plate. After 5 minutes of preheating the SPME polymeric film was placed in a holder was exposed to the pulp and jelly samples for 20 minutes, then the holder with the polymeric film was withdraw and manually inserted on the gas chromatographer injector coupled to a mass spectrometer, exposing the polymeric film for 5 minutes for the extracted organic volatile compounds desorption (Garcia et al., 2019; Silva et al., 2019).

The samples were analyzed by a gas chromatography system (Trace GC Ultra) coupled to a mass spectrometer detector (Polaris Q model, Thermo Scientific, San Jose, CA, USA) with ion-trap type analyzer, on the Mass Spectrometry Lab in the Chemistry Department of Universidade Federal de Minas Gerais.

The samples analysis condition was: injector temperature of 250°C; splitless injection mode, desorption time of 5 minutes; injector temperature of 200°C; interface temperature of 275°C. The column heating temperature was programmed: beginning in 40°C for 2 minutes then with a temperature range of heating of 10°C/minute until 100°C for 2 minutes, of 15°C/minute until 180°C for 2 minutes and then for 15°C/minute until 245°C for 3 minutes. The detector was held on Full Scan mode (35 to 300 m/z), utilizing the electron impact (EI) ionization technique with 70 electron-volt (eV). The chromatographic column was a HP-5 MS capillary column (5% phenyl and 95% methylpolysiloxane) with the following dimensions: 30m of length, 0.25 mm internal diameter and 0.25 µm of film thickness (Agilent Technologies INC, Germany) (Garcia et al., 2019).
The detected volatile compounds identification was based on m/z relation correspondent to each peak generated by the full chromatogram of ions of each sample analyzed, being compared with the mass spectrum obtained by EI ionization which was used an 70 eV energy with a full scan range of 35 to 300 m/z (García et al., 2016).

The analytes mass spectrum found were compared with mass spectrum data obtained by the NIST library (National Institute of Standards and Technology) using literature data registry as volatile compounds presence confirmation within the cagaita pulp and jelly samples.

The RSI index consists in a comparison numeric factor between an unknown compound and a NITS library compound. The selected peak were the ones with a relation of signal/noise (S/N) greater than 50 decibels, considering a relative standard intensity level (RSI) superior to 700. The intensity peak values obtained and the S/N relation were withdrawn from X Calibur 1.4 of Thermo Electron Corporation and transferred to Microsoft Office Excel 2013 were the peak selection was made.

### 3. Results and Discussion

#### 3.1 Fixed compounds analysis

The analyses were carried out as triplicates for both ionization modes (positive and negative) and were obtained spectra on the paper spray mass spectrometry analysis (PSMS) from the cagaita pulp and jelly, which are shown and exemplified by Figures 1, 2, 3 and 4.

#### 3.1.1 Ion identification attempt PS-MS (+)

In general was possible to identify ions regarding amino acid, sugar, flavonoid and cumarine molecules in positive mode. Silva et al. (2019) in the cagaita ice cream analysis by PSMS (+) was identified 5 compounds of the flavone, anthocyanin and sugar classes in form of sodium and potassium adduct.

**Figure 1.** Cagaita pulp sample full-scan in positive mode and mirtiline molecule peak.

![Cagaita pulp sample full-scan in positive mode and mirtiline molecule peak](source: Authors (2020))
According to Silva et al. (2019) the m/z 175 ion refers to protonated L-arginine. This amino acid shows a different fragmentation pattern from other amino acids, not being characterized by the NH₃ loss. Its classification was confirmed by distinctive ions (m/z 70 and 129) obtained after the fragmentation reactions.

The m/z 206 ion refers to citroptene, a cumarine, which was observed by Ledesma-Escobar, Priego-Capote & Castro (2015) too when evaluating the cumarin identification parameters in lemon (Citrus limon) by liquid chromatography coupled to a mass spectrometer (LC-MS).

**Figure 2.** Cagaita jelly sample full-scan in positive mode and citroptene molecule peak.

Sucrose was identified in accordance to Ribeiro (2011) in cagaita pulp with peel. He identified fructose in 2,54g/100g, glucose in 1,75g/100g and sucrose in 0,59g/100g. During the cagaita jelly preparation the sucrose was added in the process.

The maltotriose compound was kept from the cagaita pulp, presenting itself in the jelly too. According to Lehninger, Nelson & Cox (2006) the maltotriose is a byproduct obtained by the fruit starch hydrolyses.
### Table 1. PSMS (+) ion identification from cagaita pulp and jelly.

| Nº | Identification attempt | CAS m/z | MS/MS | Cagaita Pulp | Cagaita Jelly | Reference |
|----|------------------------|--------|-------|--------------|--------------|-----------|
|    |                        |        |       |              |              |           |
| 1  | Mirtiline              | 50986-17-9 | 465   | 303          | +            | +        |
|    |                        |         |       |              |              | Flores et al. (2012); Silva et al. (2014) |
|    | Flavonoid              |         |       |              |              |           |
| 2  | L-arginine             | 74-79-3 | 175   | 70, 129      | +            | +        |
|    | Amino acid             |         |       |              |              | Gogichaeva et al. (2007); Ozcan et al (2006) |
|    | Coumarin               |         |       |              |              |           |
| 3  | Citropten              | 487-06-9 | 206   | 121          | +            | +        |
|    | Sugar                  |         |       |              |              | Ledesma-Escobar et al. (2015) |
| 4  | Sacarose or Hexose     | 42752-07-8 | 381   | 201, 219     | +            | +        |
|    |                        |         |       |              |              | Yuan et al. (2015); Asakawa and Hiraoka (2010) |
| 5  | Glucose                | 2280-44-6 | 219   | _            | +            | +        |
| 6  | Maltotriose            | 1109-28-0 | 543   | _            | +            | +        |

Source: Authors (2020).

#### 3.1.2 Ion identification attempt PSMS (-)

In general were identified organic acids, sugar, flavonoids and phenolic acids in cagaita pulp and jelly in the negative mode.

Hydroxycinnamic acid derivatives are phenolic acids. The p-coumaric, ferulic, caffeic and synaptic acids are the most common hydroxycinnamic acids in nature (Degáspari & Waszczynskyj, 2004).

Corroborating to this work, Guedes et al. (2017) detected the presence of p-coumaric acid in green and ripe cagaita fruits.

The m/z 115 and 133 showed m/z 71 and 89 as fragmentation ions, thus proposing malic acid as the signature compound. The m/z 191 ion was found as citric acid based in the post-fragmentation ions obtained (m/z 85 and 111) (Silva et al, 2019).
The m/z 133 was detected as a fragmentation ion from m/z 311, characteristic of caftaric acid which corresponds to a non-flavonoid phenolic compound originated from the caffeic and tartaric acid esterification. Previous studies shown its presence in a chinese medicinal plant (*Taraxacum formosanum*) and in wines (Silva et al., 2019).

The m/z 339 was assigned to caffeoyl-D-glucose. The m/z 683 substance can be identified as a caffeic acid 3-glucoside dimer. Guedes et al. (2017), using HPLC, characterized the cagaita’s fruit in different stages (green and ripe) and identified caffeic acid (0.28 and 1.57 mg/100g) and p-coumaric acid (2.79 and 20.92 mg/100g) in both stages, respectively.

The m/z 359 was detected as an syringic acid hexoside. This compound was previously reported by Guedes et al. (2017) in cagaita fruits (green and ripe) 1.66 and 2.50 mg/100g.

The m/z 477, 505 and 533 can be assigned as, respectively, quercetin-3-O-glucuronide, quercetin acetyl-hexoside and kaempferol-3-O-malonylglucoside. Guedes et al. (2017) reported a greater presence of quercetin in ripe cagaita fruits (22.10 mg/100g) than green fruits (14.97 mg/100g). Celli et al. (2011) identified quercetin-3-O-hexoside in two *Eugenia uniflora* varieties (purple and red fruits). Quercetin has garlic as its food source and kaempferol can be found in broccoli (Nijveldt et al., 2001; Beecher, 2003).
In comparison to the cagaita pulp the jelly processing showed disappearance of quercetin acetyl-hexoside (m/z 667). According to Bagetti (2009), the food preparation for consumption can sometimes result in phenolic compound loss, varying according to the food type and processing method.

Table 2. Ion identification PSMS (−) from cagaita pulp and jelly.

| Nº | Identification Attempt | CAS     | m/z  | MS/MS | Cagaita Pulp | Cagaita Jelly | References                      |
|----|-----------------------|---------|------|-------|--------------|--------------|---------------------------------|
| 1  | Malic acid            | 6915-15-7 | 133  | 89, 115 | +            | +            | Roesler et al. (2007)           |
| 2  | Citric acid           | 77-92-9 | 191  | 85, 111 | +            | +            | Wang et al. (2017)              |
| 3  | Malic acid            | 6915-15-7 | 115  | 71       | +            | +            | Wang et al. (2017)              |
| 4  | Caftaric acid         | 331-39-5 | 311  | 133      | +            | +            | Abu-Reidah et al. (2015)        |
| 5  | p-coumaric acid hexoside | –  | 325  | 119, 145 | +            | +            | Aaby et al. (2007); Kajdźanoska et al. (2010) |
| 6  | Caffeoyl-D-glucose    | –       | 339  | –       | +            | +            | –                               |
| 7  | Caffeic acid 3-glucoside dimer | – | 683  | 341      | +            | +            | Spinola et al. (2015)           |
### 3.2 Volatile compounds analysis

The analyses were performed in triplicates in the volatile compound extraction by the solid-phase microextraction method (SPME). Chromatograms from cagaita pulp and jelly were obtained, as it can be observed in Figure 5.
Figure 5. (A) Chromatogram of the cagaita pulp sample; (B) chromatogram of the cagaita jelly sample.

According to Table 3, which shows the identified compounds in both samples, the main chemical classes found in the samples were carboxylic acids, esters and terpenes.

Table 3. Volatile compounds found in cagaita pulp and cagaita jelly, obtained by CGMS analysis.

| Nº | Compounds        | Formula | CAS     | M/S              | PDMS/DVB fiber | Cagaita | Cagaita Jelly |
|----|------------------|---------|---------|------------------|----------------|---------|---------------|
| 1  | Ethyl butyrate   | C₆H₁₂O₂ | 105-54-4 | 43, 14, 55, 07, 71, 04, 87,99 | X              | X       |               |
| 2  | Methyl hexanoate | C₇H₁₄O₂ | 106-70-7 | 43, 01, 74, 05, 39, 14, 87,1 | X              | ND      |               |
| 3  | Butyl hexanoate  | C₁₀H₂₀O₂ | 626-82-4 | 173, 41, 11, 43,1 | X              | ND      |               |
| 4  | Pentyl decanoate | C₁₅H₃₁O₂ | 5933-87-9 | 173, 12, 55, 4, | X              | ND      |               |
| No. | Compound                      | Molecular Formula | PubChem CID | Retention Time* | Detection** | Monoterpene | Sesquiterpene | Others |
|-----|-------------------------------|------------------|-------------|----------------|-------------|-------------|--------------|--------|
| 5   | Prenyl caproate               | C_{11}H_{20}O_{2} | 76649-22-4  | 41, 15, 67, 15, 43, 15, 68, 11 | X           | ND          |              |        |
| 6   | Propyl dodecanoate            | C_{13}H_{30}O_{2} | 3681-78-5   | 201, 1, 157, 17, 55, 41, 73, 22 | X           | ND          |              |        |
| 7   | Ethyl trans-2-dodecanoate     | C_{12}H_{20}O_{2} | 7367-88-6   | 55, 26, 41, 19, 73, 23, 69, 63 | X           | ND          |              |        |
| 8   | Hexyl octanoate               | C_{14}H_{30}O_{2} | 1117-55-1   | 145, 14, 41, 21, 57, 38, 89, 41 | X           | ND          |              |        |
| 9   | Ethyl dodecanoate             | C_{14}H_{30}O_{2} | 106-33-2    | 157, 2, 73, 41, 55, 25, 185, 12 | X           | ND          |              |        |
| 10  | Tetrahydroionyl acetate       | C_{15}H_{30}O_{2} | 68555-59-9  | 97, 33, 57, 29, 123, 29          | X           | X           |              |        |
| 11  | Methyl-2-furoate              | C_{6}H_{10}O_{3}  | 611-13-2    | 95, 15, 96, 13, 39, 33, 125, 98 | ND          | X           |              |        |
| 12  | Ethyl octanoate               | C_{10}H_{20}O_{2} | 106-32-1    | 55, 43, 57, 45, 73, 23, 41, 19  | ND          | X           |              |        |
| 13  | Hexyl hexanoate               | C_{12}H_{30}O_{2} | 6378-65-0   | 41, 44, 117, 11, 43, 37, 56, 27 | ND          | X           |              |        |
| 14  | Ethyl dodecanoate             | C_{12}H_{30}O_{2} | 110-38-3    | 157, 1, 73, 45, 55, 21, 41, 2   | ND          | X           |              |        |

**Monoterpenes**

| No. | Compound                      | Molecular Formula | PubChem CID | Retention Time* | Detection** |
|-----|-------------------------------|------------------|-------------|----------------|-------------|
| 15  | 3-carene                      | C_{10}H_{16}     | 13466-78-9  | 93, 16, 79, 25 | X           |
| 16  | Nerol                         | C_{10}H_{18}O    | 106-25-2    | 41, 15, 43, 37, 67, 17, 69, 14 | X           |
| 17  | 2,6-Dimethyl-2,4,6-octatriene | C_{12}H_{16}     | 3016-19-1   | 121, 13, 105, 25, 136, 06 | X           |
| 18  | Linalyl acetate               | C_{12}H_{30}O_{2} | 115-95-7   | 93, 18, 43, 37, 55, 43, 91, 26 | ND          |
| 19  | 1,5,5-Trimethyl-6-methylene-cyclohexene | C_{16}H_{16}     | 514-95-4   | 121, 15, 105, 24, 136, 13, 43, 37 | ND          |

**Sesquiterpenes**

| No. | Compound                      | Molecular Formula | PubChem CID | Retention Time* | Detection** |
|-----|-------------------------------|------------------|-------------|----------------|-------------|
| 20  | Valencene                     | C_{12}H_{24}     | 4630-07-3   | 105, 29, 147, 27, 133, 24, 161, 19 | X           |
| 21  | 1,4-Methanoazulene-7(H)-one, octa-hydro-4,8,8,9-tetramethyl,(+)| C_{15}H_{32}O  | –           | 41, 28, 43, 38, 165, 19, 107, 24 | ND          |
| 22  | Geranyl isovalerate           | C_{15}H_{32}O_{2} | 109-20-6    | 41, 26, 71, 49, 57, 48, 43, 4 | ND          |
| 23  | Patchouli alcohol             | C_{15}H_{32}O_{2} | 5986-55-0   | 57, 51, 41, 42, 71, 35, 43, 41 | ND          |

**Others**
In the cagaita pulp volatile compound characterization, was detected 3-carene as a main compound which belongs to the terpene class. According to Dorman (1999), the terpenoids are the main compounds responsible for the medicinal, culinary and aromatic uses of plants, besides having insecticide activity. Terpenoids can be subdivided as: monoterpenes, sesquiterpenes and diterpenes (Tebaldi, 2008).

In the volatile compounds characterization numerous monoterpenes were detected such as: 3-carene; cis-geraniol; \((E, Z)\) 2,6-dimethyl-2,4,6-octatriene; hexanoic acid and butilic ester. Hydrocarbons as well were identified: decanoic acid; 3-methyl-2-butenilic ester; 2-decenico acid; ethylic ester; 3,8a-dimethyloctahydro-1(2H)-naftalenone; octanoic acid; hexilic ester; lauric acid. And sesquiterpenes: decanoic acid; pентilic ester; dodecanoic acid; propilic ester; eremophile-1(10),11-diene; tetrahydroionile acetate.

The results differ according to Santos (2015) studies with fruits collected from Universidade Federal de Goiás, between the volatile compounds identified in the frozen pulp the following sesquiterpenes were highlighted: \(\beta\)-caryophyllene; myrecene; \(\alpha\)-humulene; D germacrene; decahydro-1,1,4,7-tetramethyl-1H-cicloprop[E]azulene.

The different results found in this study can be explain by the low concentration of volatile compounds present in the cagaita fruits. Low concentration makes the compounds susceptible to a variety of conditions: agronomics (climatic conditions and ripening) and technological (harvest, post-harvest treatment, storage and processing conditioning) (Vendramini & Trugo, 2000; Botondi et al., 2003).

According to table 3 after the fruit processing some compounds remained in the jelly samples. In the cagaita jelly volatile compounds characterization 3-carene was still detected as a major compound. The jelly analysis show tetrahydroionile...

| No. | Compound Description                  | Chemical Formula | MW | Ranges | ND | X |
|-----|--------------------------------------|------------------|-----|--------|----|----|
| 24  | 3-Furaldehyde                        | C₄H₄O₂           | 60  | 498-60 | 2 | ND | X |
| 25  | 2-Acetylfuran                        | C₄H₆O₂           | 112 | 1192-62| 7 | ND | X |
| 26  | 3-Hydroxy-4-(2-hydroxyethyl) furan-2(5H)-one | C₄H₈O₄ | 1153 | 1145-53 | 9 | ND | X |
| 27  | Ethyl hexanoate                      | C₆H₁₀O₂          | 123 | 123-66 | 0 | ND | X |
| 28  | Octanoic acid                        | C₈H₁₆O₂          | 124 | 124-07 | 2 | ND | X |
| 29  | 5-Hydroxymethylfurfural             | C₆H₁₀O₃          | 67  | 67-47  | 0 | ND | X |
| 30  | 2'-Hydroxy-5'-methylacetophenone     | C₁₀H₁₆O₂         | 1450| 1450-72| 2 | ND | X |
| 31  | 3-(2,6,6-Trimethyl-1-cyclohexen-1-y)acrylaldehyde | C₁₂H₁₈O₂ | 5015 | 4951-40 | 0 | ND | X |
| 32  | 3-(1-Hydroxy-5-methyl-2-propan-2-y)cyclohexyl)prop-2-ynoic acid | C₁₃H₂₀O₃ | - | - | 41, 46, 191, 23, 57, 56, 43, 46 | ND | X |
| 33  | Hexanoic acid                        | C₆H₁₂O₂          | 142 | 142-62 | 1 | 60, 09, 39, 16, 73, 05, 41, 15 | X | X |
acetate having a major area percentual compared to the cagaita pulp. Furaldehyde was detected as the compound with the biggest relative area (14.09%).

The volatile compound are thermolabile substances, thus, subjected to rearrangements, cyclizations and oxidations when submitted to a temperature increase (Franco, 2003). The presence of different volatile compounds in the cagaita jelly can be a product of the temperature influence in the jelly production.

4. Conclusion

Exists a diversity in Cerrado native fruits of different climatic conditions that have not yet been explored by the scientific community. This diversity enables volatile and fixed compounds characterization researches which adds commercial and industrial value to the fruit as feedstock.

The PSMS analysis in positive and negative modes allowed to identify many substances of the organic acids, sugars, anthocyanins, hydroxycinnamic acids, hydroxybenzoic acids and flavonoids classes. In the jelly was not observed significant change in its composition compared to the cagaita pulp, showing that the jelly processing can be a technic for phenolic compound conservation.

In the cagaita pulp and jelly were detected monoterpenes, sesquiterpenes and hydrocarbons, proving that the jelly production can retain the fruit characteristic flavors. In its pulp volatile compound characterization were detected between the major identified compounds the monoterpe 3-carene which was present too in the jelly. However, in the later, furaldehyde was obtained as a product of the heating process.

References

Aaaby, K., Ekeberg, D. & Skrede, G. (2007). Characterization of phenolic compounds in strawberry (Fragaria x ananassa) fruits by different HPLC detectors and contribution of individual compounds to total antioxidant capacity. J. Agric. Food Chem., 55 (11), 4395-4406.

Abu-Reisdah, I. M., Ali-Shtayeh, M. S., Jamous, R. M., Arráezromán, D. & Segura-Carretero, A. (2015). Food Chem., 166, 179-191.

Asakawa, D., Hiraoka, K. (2010). Rapid Commun. Mass Spectrom. 24, 2431.

Bagetti, M. (2009). Caracterização físico-química e capacidade antioxidante de pitanga (Eugenia uniflora L.). Dissertação de mestrado, Centro de Ciências Rurais, Universidade Federal de Santa Maria, Santa Maria, RS, Brasil.

Barros, L., Dueñas, M., Carvalho, A. M., Ferreira, I. C. F. R. & Santos-Buelga, C. (2012). Characterization of phenolic compounds in flowers of wild medicinal plants from Northeastern Portugal. Food Chem. Toxicol., 50 (5), 1576-1582.

Beecher, G. R. (2003). Overview of dietary flavonoids: nomenclature, occurrence and intake. Journal of the Nutrition, 133 (10), 3248S-3254S.

Borges, K. C. (2015). Pitanga (Eugenia uniflora) desidratada por atomização e liofilização: Características físico-químicas, compostos bioativos e efeito sobre longevidade, estresse oxidativo e neurotoxicidade induzidas em modelos in vivo Caenorhabditis elegans. Tese de Doutorado, Universidade Federal do Rio Grande do Norte, Natal, RN, Brasil.

Botondi, R., Desantis, D., Belliconto, A., Vizovitis, K. & Mencarelli, F. (2003). Influence of ethylene inhibition by 1-methylcyclopropene on apricot quality, volatile production, and glycosidase activity of low-and high- aroma varieties of apricots. Journal of Agricultural and Food Chemistry, 51 (5), 1189-1200.

Bueno, G. H., Guedes, M. N. S., Souza, A. G., Madeira, A. P. C., Garcia, E. M., Taroco, H. A. & Melo, J. O. F. (2017). Caracterização física e físico-química de frutos de Eugenia Dysentérica DC, originados em reigião de clima tropical de altitude. Ver. Bras. Biom., 35 (3), 515-522.

Carvalho, A. R. F., Oliveira, J., Freitas, V. de, Mateus, N. & Melo, A. (2010). A theoretical interpretation of the color of two classes of pyrananthocyanins. Journal of Molecular Structure: Theoc hem., 948, 61-64.

Carvalho, T. C. (2015). Papersprary ionization: análise direta de licores do processo de etanol 2G por espectrometria de massas. Dissertação de mestrado, Universidade Federal de Goiás, Goiânia, GE, Brasil.

Celi, G. B., Pereira-Neto, A. B. & Beta, T. (2011). Comparative analysis of total phenolic contente, antioxidante activy, and flavonoids profile of fruits from two varieties of Brazilian cherry (Eugenia uniflora, L) throughout the fruit developmental stages. Food research international, 44 (8), 2442-2451.

Chen, H. J., Inbaraj, B. S. & Chen, B. H. (2012). Determination of phenolic acids and flavonoids in Taraxacum formosanum Kitam by liquid chromatography-tandem mass spectrometry coupled with a post-column derivatization technique. International Journal of Molecular Sciences, 13 (1), 260-285.
Psidium guineensis, R. E. (2017).

Proença, C. (2018). Cervejas. Disse Pereira, A. S.

Ozcan, S. & Senyuva, H. Z. (2006).

Oliveira, É. M. (2018). O significado do processo de modernização agrícola e os impactos ambientais em áreas de cerrado.

Araújo, R. L. B. (2020).

Oliveira, C. T. (2020). Caracterização e agregação de valor aos frutos do cerrado: Araçá (Psidium guineense Sw.) e Marolo (Annona Crassiflora Mart.). Tese de doutorado, Universidade Federal de Lavras, Lavras, MG, Brasil.

Degasperi, C. H. & Waszczyński, N. (2004). Propriedades antioxidantes de compostos fenólicos. Vião acadêmica, 5 (1), 33-40.

Dorman, H. J. D. (1999). Phytochemistry and bioactive properties of pant volatile oils: antibacterial, antifungal and antioxidant activities. Tese de doutorado, University of Strathclyde, Glasgow, UK.

Evangélista, R. M. & Vieites, R. L. (2006). Avaliação da Qualidade de Polpa de Goiaba Congelada, Comercializada na Cidade de São Paulo. Segurança Alimentar e Nutricional, 13 (2), 76-81.

Flores, G., Dastmalchi, K., Paulino, S., Whalen, K., Dabo, A. J., Reynertson, K. A., Foronjy, R. F., D’armiento, J. M. & Kennelly, E. J. (2012). Food Chem., 134 (3), 1256-1262.

Franco, M. R. B. (2003). Aroma e sabor de alimentos: temas atuais. Livraria Varela.

Garcia, Y. M., Guedes, M. N. S., Rufini, J. C. M., Souza, A. G., Augusti, R. & Melo, J. O. F. (2016). Volatile compounds identified in Barbados Cherry, BRS-366 Jaburú. Scientific Electronic Archives, 9(3), 67-73.

García, Y. M., Rufini, J. C. M., Campos, M. P., Guedes, M. N. S., Augusti, R. & Melo, J. O. F. (2019). SPME Fiber Evaluation for Volatile Organic Compounds Extraction from Acerola. Journal of the brazilian chemical society, 30 (2), 247-255.

Guedes, M. N., Rufini, J. C. M., Marques, T. R., Melo, J. O. F., Ramos, M. C. P. & Viol, R. E. (2017). Minerals and phenolic compounds of cagaita fruits at different maturation stages (Eugenia dysenterica). Rev. Bras. Frutic., 39 (1).

Gogichaeva, N. V., Williams, T. & Alterman, M. A. (2007). MALDI TOF/TOF tandem mass spectrometry as a new tool for amino acid analysis. J. Am. Soc. Mass Spectrom., 18 (2), 279-284.

Gordon, A., Jungfer, E., Silva, B. A., Maia, J. G. S. & Marx, F. (2011). Phenolic constituents and antioxidant capacity of four underutilized fruits from the Amazon region. J. Agric. Food Chem., 59 (14), 7688-7699.

Guo, Y., Gu, Z., Liu, X., Liu, J., Ma, M., Chen, B., Wang, L. (2017). Phytochem. Anal., 28, 344.

Kajdzanoska, M., Gjamovski, V. & Stefova, M. (2010). HPLC-DAD-ESI-MS Identification of phenolic compounds in cultivated strawberries from Macedonia. Maced. J. Chem. Chem. Eng., 29 (2), 181-194.

Kataoka, H., Lord, H. L. & Pawliszyn, J. (2000). Applications of solid-phase microextraction in food analysis. Journal of Chromatography A, 880 (1-2), 35-62.

Klink, C. A. & Machado, R. B. (2005). A conservação do cerrado brasileiro. Megadiversidade, 1 (1), 147-155.

Koolen, H. H. F., Silva, F. M. A., Gozzo, F. C., Souza, A. Q. L. & Souza, A. D. L. (2013). Antioxidant, antimicrobial activities and characterization of phenolic compounds from buriti (Mauritia flexuosa L. f.) by UPLC-ESI-MS/MS. Food Research International, 51 (2), 467-473.

Ledesma-Escobar, C. A., Prieo-Capote, F. & Castro, M. D. L. (2015). Characterization of lemon (Citrus limon) polar extract by liquid chromatography–tandem mass spectrometry in high resolution mode. Journal of Mass Spectrometry, 50 (11), 1196-1205.

Lehminger, A. L., Nelson, D. L. & Cox, M. M. (2006). Princípios de bioquímica (4a Ed). Sarvier.

Lemos-Filho, J. P. (2000). Fotoinibição em três espécies de cerrado (Annona crassifolia, Eugenia dysenterica e Campomanesia adamantum) na estação seca e na chuvosa. Rev Bras Bot., 23 (1), 45-50.

Nijveldt, R. J., Nood, E. V., Hoorn, D. E. V., Boelens, P. G., Norren, K. V. & Leeuwen, P. A. V. (2001). Flavonoids: a review of probable mechanisms of action and potential applications. American Journal of Clinical Nutrition., 74 (4), p. 418-425.

Oliveira, C. T., Ramos, A. L. C. C., Mendonça, H. O. P., Consenga, G. P., Silva, M. R., Fernandes, C., Augusti, R., Melo, J. O. F., Ferreira, A. V. M. & Araújo, R. L. B. (2020). Quantification of 6-gingerol, metabolomic analysis by paper spray mass spectrometry and determination of antioxidant activity of ginger rhizomes (Zingiber officinale). Research, Society and Development, 9 (8).

Oliveira, É. M. (2018). O significado do processo de modernização agrícola e os impactos ambientais em áreas de cerrado. Revista Cerrados, 16 (1), 40-58.

Ozcan, S. & Senyuva, H. Z. (2006). Improved and simplified liquid chromatography/atmospheric pressure chemical ionization mass spectrometry method for the analysis of underivatized free amino acids in various foods. J. Chromatogr. A, 1135 (2), 179-185.

Pereira, A. S., Dorlivete, M. S., Parreira, F. J., Shitsuaka, R. (2018). Metodologia da pesquisa científica. UAB/NTE/UFSM.

Pereira, H. V. (2016). Espectrometria de massas com ionização por paper spray combinada a métodos queirométricos para identificação de falsificações em cervejas. Dissertação de mestrado, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil.

Proença, C., Oliveira, R. S. & Silva, A. P. (2000). Flores e frutos do cerrado. UNB.

Ramos, A. L. C. C., Mendes, D. D., Silva, M. R., Augusti, R., Melo, J. O. F., Araújo, R. L. B. & Lacerda, I. C. A. (2020). Chemical profile of Eugenia brasiliensis (Grumixama) pulp by PS/MS paper spray and SPME-GC/MS solid-phase microextraction. Research, Society and Development, 9 (7).
Ribeiro, E. M. (2011). Atividade antioxidante e polifenóis totais do fruto de cagaita (Eugenia dysenterica DC) com e sem casca. Dissertação de mestrado, Universidade Federal do Rio de Janeiro, RJ, Brasil.

Roesler, R., Catharino, R. R., Malta, L. G., Eberlin, M. N. & Pastore, G. (2007). Antioxidant activity of Annona crassiflora: Characterization of major components by electrospray ionization mass spectrometry. Food Chem., 104 (3), 1048-1054.

Santos, M. N. G. (2015). Avaliação de Polpa de Cagaita (Eugenia dysenterica DC.) Submetida ao Congelamento e atomização. Dissertação de mestrado, Universidade Federal de Goiás, Goiânia, Brasil.

Santos, B. O., Augusti, R., Melo, J. O. F., Takahashi, J. A. & Araújo, R. L. B. (2020). Optimization of extraction conditions of volatile compounds from pequi peel (Caryocar brasiliense Camb.) using HS-SPME. Research, Society and Development, 9 (7).

Santos, P. R. G., Cardoso, L. D. M., Bedetti, S. D. F., Hamacek, F. R., Moreira, A. V. B., Martino, H. S. D. & Pinheiro-Santana, H. M. (2012). Geleia de cagaita (Eugenia dysenterica DC.): desenvolvimento, caracterização microbiológica, sensorial, química e estudo da estabilidade. Revista do Instituto Adolfo Lutz, 71 (2), 281-290.

Silva, D. B., Silva, J. A., Junqueira, N. T. V. & Andrade, L. R. M. (2001). Frutas do Cerrado. Brasília: Embrapa Informação Tecnológica.

Silva, M. R., Freitas, L. G., Souza, A. G., Araújo, R. L. B., Lacerda, I. C. A., Pereira, H. V., Augusti, R. & Melo, J. O. F. (2019). Antioxidant Activity and Metabolomic Analysis of Cagaitas (Eugenia dysenterica) using Paper Spray Mass Spectrometry. J. Braz. Chem. Soc., 30 (5), 1034-1044.

Silva, N. A., Rodrigues, E., Mercadante, A. Z. & Rosso, V. V. (2014). Phenolic compounds and carotenoids from four fruits native from the Brazilian Atlantic forest. J. Agric. Food Chem., 62 (22), 5072-5084.

Souza, E. R. B. D., Naves, R. V., Borges, J. D., Vera, R., Fernandes, E. P., Silva, L. B. & Trindade, M. D. G. (2008). Cagaita (Eugenia dysenterica DC.) phenology in Goiás State. Revista Brasileira de Fruticultura, 30 (4), 1009-1014.

Spínola, V., Pinto, J. & Castilho, P. C. (2015). Identification and quantification of phenolic compounds of selected fruits from Madeira Island by HPLC-DAD-ESI-MS(n) and screening for their antioxidant activity. Food Chem., 173, 14-30.

Teibaldi, V. M. R. (2008). Análise e potencial de uso de óleos essenciais no controle Pseudomonas sp. e na formação de biofilmes por Pseudomanos aeruginosa. Tese de doutorado, Universidade Federal de Lavras, Lavras, MG, Brasil.

Thomazini, M. & Franco, M. R. B. (2000). Metodologia para análise dos constituintes voláteis do sabor. Boletim SBCTA, 34 (1), 52-59.

Vendramini, A. L. & Trugo, L. C. (2000). Chemical composition of acerola fruit (Malpighia punicifolia L.) at three stages of maturity. Food Chemistry, 71 (2), 195-198.

Wang, H., Liu, J., Cooks, R. G. & Ouyang, Z. (2010). Paper spray for direct analysis of complex mixtures using mass spectrometry. Angewandte Chemie, 122 (5), 889-892.

Wang, J., Ia, Z., Zhang, Z., Wang, Y., Liu, X., Wang, L. & Lin, R. (2017). Analysis of chemical constituents of Melastoma dodecandrum Lour. By UPLC-ESI-Q-Exactive Focus-MS/MS. Molecules, 22 (3), 476-496.

Yang, Q., Wang, H., Maas, J. D., Chappell, W. J., Manicke, N. E., Cooks, R. G. & Ouyang, Z. (2012). Paper spray ionization devices for direct, biomedical analysis using mass spectrometry. International journal of mass spectrometry, 312 (15), 201-207.

Yuan, H., Wu, Y., Liu, W., Liu, Y., Gao, X., Lin, J., Zhao, Y. (2015). Carbohydr. Res., 407, 5.