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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

Caracterización de compuestos volátiles y compuestos bioactivos de pulpa y mermelada de cagaita por microextracción en fase sólida en modo headspace y espectrometría de masas por paper spray

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Abstract
The cagaiteira (*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 monoterpene 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.

Resumo

A cagaiteira (*Eugenia dysenterica*) pertencente à família *Myrtaceae*, é uma árvore nativa do Cerrado brasileiro, o seu fruto é muito frágil, apresentando casca fina e polpa suculenta, é consumido na forma processada como geleia para prolongar a vida útil. O presente trabalho teve como objetivo elaborar geleia de cagaita e avaliar a alteração de compostos bioativos e compostos voláteis em relação à polpa *in natura*. A análise de espectrometria de massa por *paper spray* nos modos positivos e negativos permitiu a identificação de 27 compostos, dentre elas, ácidos orgânicos, açúcares, antocianinas, ácidos hidroxicinâmicos, ácidos hidroxibenzóicos e flavonoides, indicando que a produção de geleia pode ser uma técnica para conservação de compostos fenólicos com suas respectivas qualidades sensoriais como cor e sabor. Na análise de voláteis por microextração em fase sólida no modo *headspace*, foram detectados no total de 33 compostos, principalmente das classes de monoterpenos, de sesquiterpenos e de ésteresindicando que a produção da geleia pode conservar o aroma característico do fruto. Na caracterização dos compostos voláteis da polpa de cagaita, o 3-careno foi o monoterpeno majoritário encontrado. Enquanto no processamento da geleia houve produção do furaldeído, produto obtido como consequência natural do aquecimento.
Palavras-chave: *Eugenia dysenterica*; Compostos voláteis; Compostos bioativos; Mytaceae.

Resumen

La cagaiteira (*Eugenia dysenterica*) perteneciente a la familia Myrtaceae, es un árbol originario del Cerrado brasileño, su fruto es muy frágil, con corteza delgada y pulpa jugosa, se consume en forma procesada como mermelada para prolongar su vida útil. El presente trabajo tuvo como objetivo elaborar mermelada de cagaita y evaluar la alteración de compuestos bioactivos y compuestos volátiles en relación con la pulpa fresca. El análisis de la espectrometría de masas por *paper spray* en modos positivo y negativo permitió la identificación de varias sustancias, entre ellas, ácidos orgánicos, azúcares, antocianinas, ácidos hidroxicinámicos, ácidos hidroxibenzoicos y flavonoides, lo que indica que la producción de gelatina puede ser una técnica para conservación de compuestos fenólicos con sus respectivas cualidades sensoriales como el color y el sabor. En el análisis de volátiles por microextracción en fase sólida en modo *headspace*, se detectaron monoterpenos, hidrocarburos y sesquiterpenos, lo que indica que la producción de la mermelada puede preservar el aroma característico de la fruta. En la caracterización de compuestos volátiles en la pulpa de cagaita, el 3-careno fue el principal monoterpeno encontrado. Mientras se procesaba la mermelada, se produjo furaldehído, un producto obtenido como consecuencia natural del calentamiento.
Palabras clave: *Eugenia dysenterica;* Compuestos volátiles*;* Compuestos bioactivos; 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 fount 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

Riped 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 metanol 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 metanol 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 capillar 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 (Garcia *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

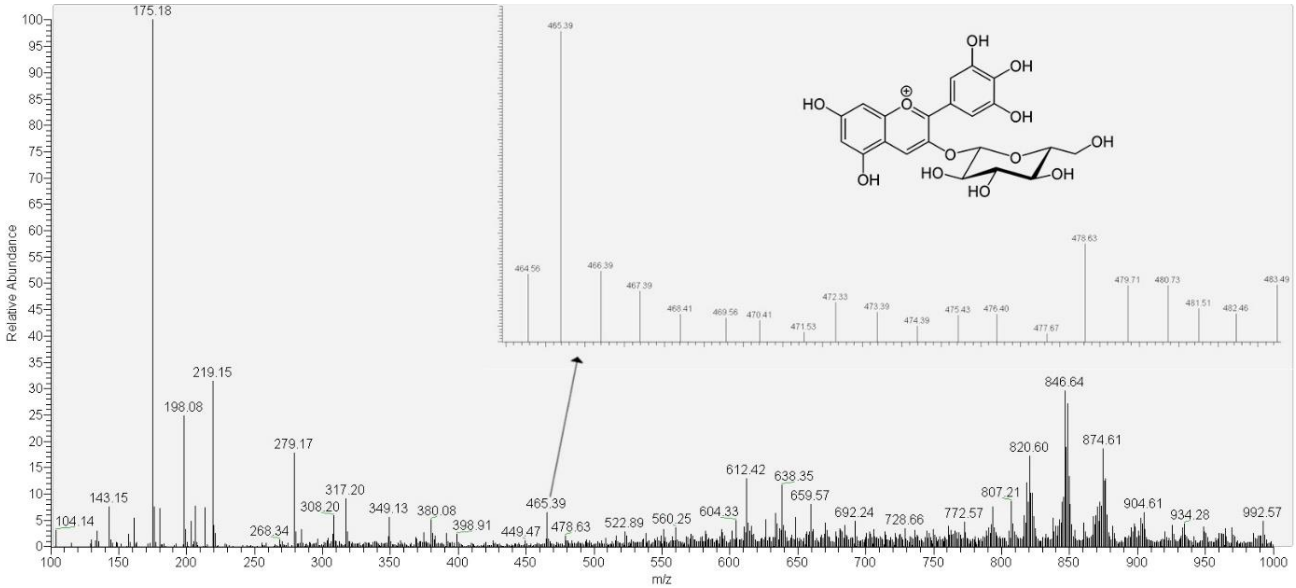
3.1 Fixed compounds analysis

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.

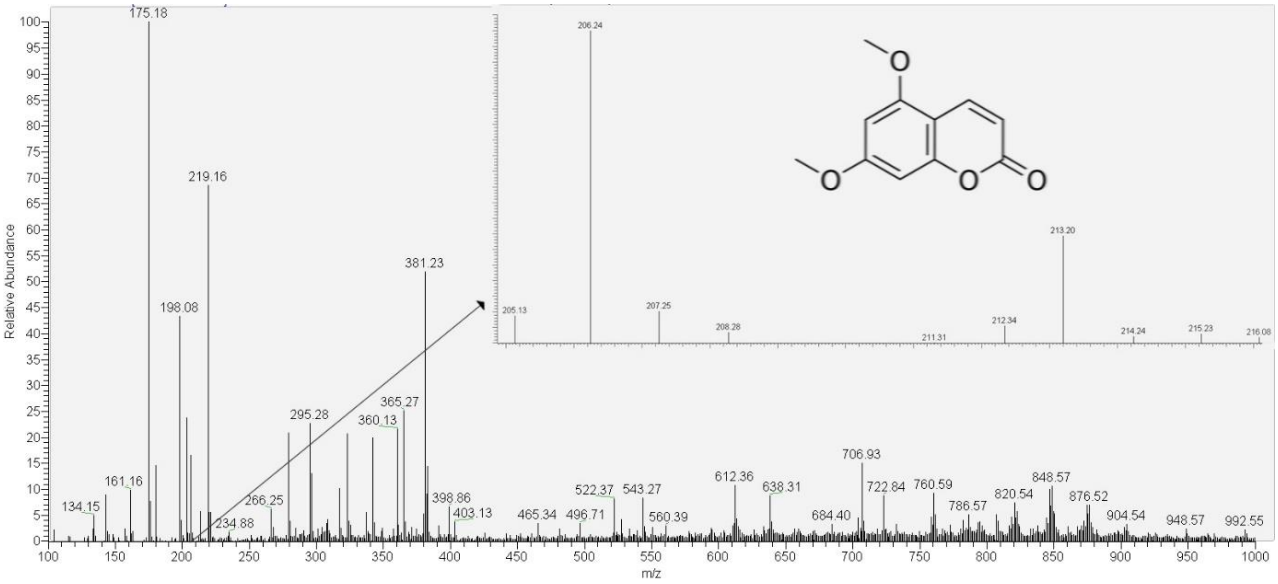


Source: Authors (2020)

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 NH_3 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.



Source: Authors (2020)

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
			Flavonoid				
1	Mirtiline	50986-17-9	465	303	+	+	Flores *et al*. (2012); Silva *et al*.(2014)
			Amino acid				
2	L-arginine	74-79-3	175	70, 129	+	+	Gogichaeva *et al*. (2007); Ozcan *et al* (2006)
			Coumarin				
3	Citropten	487-06-9	206	121	+	+	Ledesma-Escobar *et al.* (2015)
			Sugar				
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 (-)

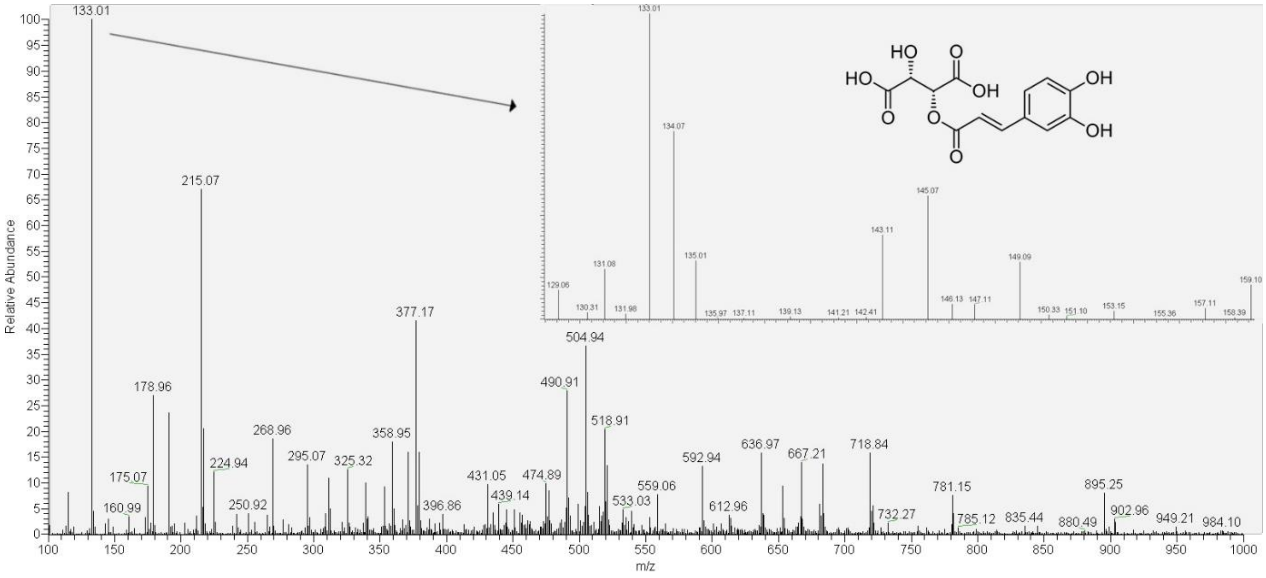
In general were identified organic acids, sugar, flavonoids and phenolic acids in cagaita pulp and jelly in the negative mode.

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).

Figure 3. Full-scan of cagaita jelly sample in negative mode and caftaric acid molecule peak.



Source: Authors (2020)

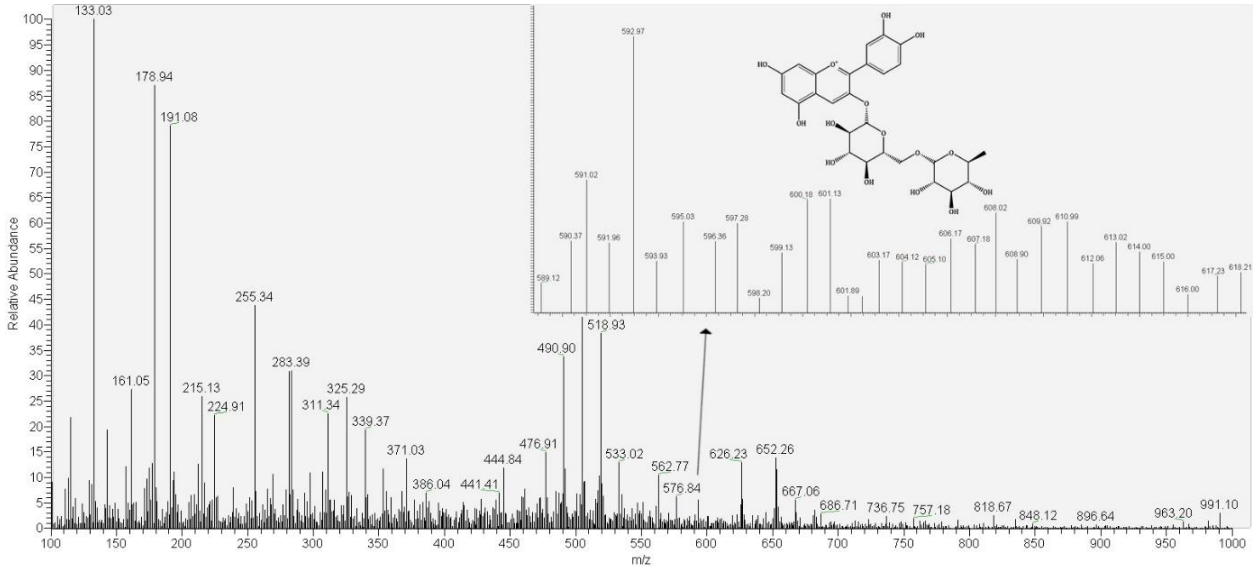
The m/z 133 was detected as a fragmentation ion from m/z 311, characteristic of caftaric acid which corresponds to a non-flavonoid phenolic compound originated from the caffeic and tartaric acid esterification. Previous studies shown its presence in a chinese medicinal plant (*Taraxacum formosanum*) 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).

Figure 4. Full-scan of cagaita pulp sample in negative mode and cyanidin-3-O-rutinoside molecule peak.



Source: Authors (2020)

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
			Phenolic compounds				
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); Kajdžanoska *et al*. (2010)
6	Caffeoyl-D-glucose	–	339	–	+	+	–
7	Caffeic acid 3-glucoside dimer	–	683	341	+	+	Spínola *et al*. (2015)

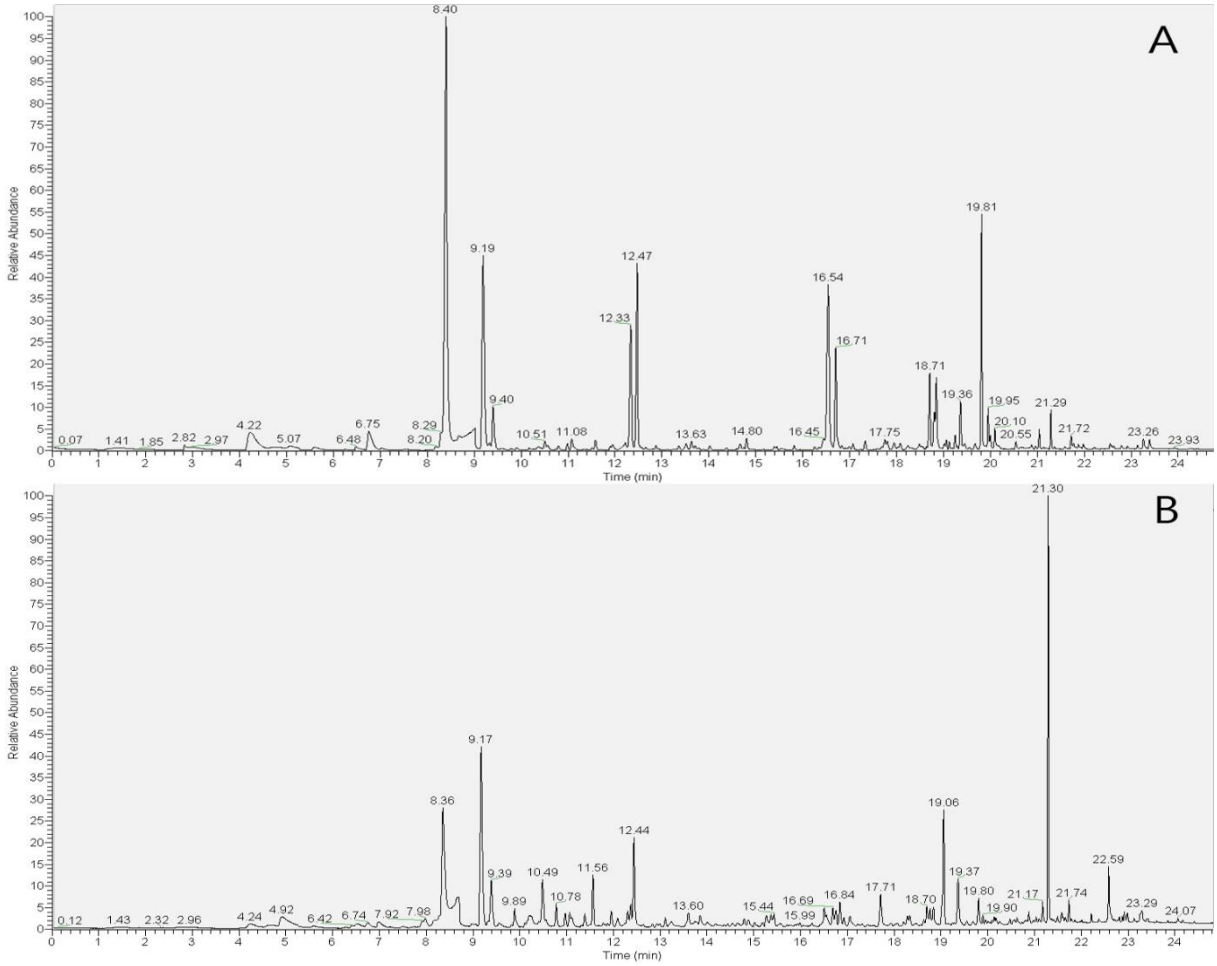
8	Siringic acid hexoside	–	359	153, 197	+	+	Abu-Reidah *et al*. (2015); Barros *et al*. (2012)
18	Dimethyl ellagic acid hexoside	57499-59-9	491	454	+	+	Gordon *et al*. (2011)
19	Glicosídeo ácido elágico	476-66-4	721	–	+	+	-
20	Galagil-hex	–	781	–	+	+	–
21	Pentoside of ellagic acid	476-66-4	895	–	+	+	–
			Flavonoids				
9	Kaempferol-3-O-malonilglucosíde	–	533	–	+	+	–
10	Quercetin acetyl hexoside	–	505	–	+	+	–
11	Quercetin-3-O-glucuronide	22688-79-5	477	–	+	+	–
12	Quercetin acetyl hexoside	–	667	–	+	+	–
13	Vitexin	3681-93-4	431	341	+	+	Wang *et al*. (2017); Koolen *et al*. (2013)
14	Cianidin-3-O-rutinoside	–	593	–	+	+	–
			Other compounds				
15	Hexose	42752-07-8	215	71, 89, 179	+	+	Guo *et al*. (2017); Wang *et al*. (2017)
16	Hexose	42752-07-8	179	71, 89	+	+	Roesler *et al*. (2007); Wang *et al*.(2017)
17	Hexose or sucrose	42752-07-8	377	341	+	+	Chen *et al*. (2011)

Source: Authors (2020)

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, has it can be observed in Figure 5.

Figure 5. (A) Chromatogram of the cagaita pulp sample; (B) chromatogram of the cagaita jelly sample.



Source: Authors (2020)

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
			Ester			
1	Ethyl butyrate	$C_6H_{12}O_2$	105-54-4	43, 14, 55, 07, 71, 04, 87,99	X	X
2	Methyl hexanoate	$C_7H_{14}O_2$	106-70-7	43, 01, 74, 05, 39, 14, 87,1	X	ND
3	Butyl hexanoate	$C_{10}H_{20}O_2$	626-82-4	173, 41, 11, 43,1	X	ND
4	Pentyl decanoate	$C_{15}H_{30}O_2$	5933-87-9	173, 12, 55, 4,	X	ND

				73,26		
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	$C_{15}H_{30}O_2$	3681-78-5	201, 1, 157, 17, 55, 41, 73, 22	X	ND
7	Ethyl trans-2-decenoate	$C_{12}H_{22}O_2$	7367-88-6	55, 26, 41, 19, 73, 23, 69,63	X	ND
8	Hexyl octanoate	$C_{14}H_{28}O_2$	1117-55-1	145, 14, 41, 21, 57, 38, 89,41	X	ND
9	Ethyl dodecanoate	$C_{14}H_{28}O_2$	106-33-2	157, 2, 73, 41, 55, 25, 185,12	X	ND
10	Tetrahydroionyl acetate	$C_{15}H_{28}O_2$	68555-59-9	97, 33, 57, 29, 123,29	X	X
11	Methyl-2-furoate	$C_6H_6O_3$	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	$C_{12}H_{24}O_2$	6378-65-0	41, 44, 117, 11, 43, 37, 56, 27	ND	X
14	Ethyl dodecanoate	$C_{12}H_{24}O_2$	110-38-3	157, 1, 73, 45, 55, 21, 41, 2	ND	X
	Monoterpenes					
15	3-carene	$C_{10}H_{16}$	13466-78-9	93, 16, 79,25	X	X
16	Nerol	$C_{10}H_{18}O$	106-25-2	41, 15, 43, 37, 67, 17, 69,14	X	X
17	2,6-Dimethyl-2,4,6-octatriene	$C_{10}H_{16}$	3016-19-1	121, 13, 105, 25, 136,06	X	ND
18	Linalyl acetate	$C_{12}H_{20}O_2$	115-95-7	93, 18, 43, 37, 55, 43, 91, 26	ND	X
19	1,5,5-Trimethyl-6-methylene-cyclohexene	$C_{10}H_{16}$	514-95-4	121, 15, 105, 24, 136, 13, 43, 37	ND	X
	Sesquiterpenes					
20	Valencene	$C_{15}H_{24}$	4630-07-3	105, 29,147, 27, 133, 24, 161,19	X	X
21	1,4-metanoazulene-7 (H) -one, octa-hydro-4,8,8,9-tetramethyl,(+)	$C_{15}H_{24}O$	–	41, 28, 43, 38, 165, 19, 107, 24	ND	X
22	Geranyl isovalerate	$C_{15}H_{26}O_2$	109-20-6	41, 26, 71, 49, 57, 48, 43, 4	ND	X
23	Patchouli alcohol	$C_{15}H_{26}O$	5986-55-0	57, 51, 41, 42, 71, 35, 43, 41	ND	X
	Others					

24	3-Furaldehyde	$C_5H_4O_2$	498-60-2	95, 12, 96, 01, 39, 16, 97	ND	X
25	2-Acetylfuran	$C_6H_6O_2$	1192-62-7	95, 21, 151, 06, 110, 17, 39, 14	ND	X
26	3-Hydroxy-4-(2-hydroxyethyl) furan-2(5H)-one	$C_6H_8O_4$	114533-59-4	101, 12, 143, 98, 43, 27, 55, 34	ND	X
27	Ethyl hexanoate	$C_8H_{16}O_2$	123-66-0	43, 27, 73, 19, 145, 06, 55,21	ND	X
28	Octanoic acid	$C_8H_{16}O_2$	124-07-2	39, 38, 73, 21, 55, 24, 60, 18	ND	X
29	5-Hydroxymethylfurfural	$C_6H_6O_3$	67-47-0	97, 12, 39, 29, 69, 34, 125, 98	ND	X
30	2'-Hydroxy-5'-methylacetophenone	$C_9H_{10}O_2$	1450-72-2	150, 16,135, 32, 107, 38, 77,25	ND	X
31	3-(2,6,6-Trimethyl-1-cyclohexen-1-yl)acrylaldehyde	$C_{12}H_{18}O$	4951-40-0	163, 14, 73, 46, 145, 32, 121, 25	ND	X
32	3-(1-Hydroxy-5-methyl-2-propan-2-ylcyclohexyl)prop-2-ynoic acid	$C_{13}H_{20}O_3$	–	41, 46, 191, 23, 57, 56, 43, 46	ND	X
33	Hexanoic acid	$C_6H_{12}O_2$	142-62-1	60, 09, 39, 16, 73, 05, 41,15	X	X

Source: Authors (2020)

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-decenoic acid; ethylic ester; 3,8a-dimethyloctahydro-1(2H)-naftalenone; octanoic acid; hexilic ester; lauric acid. And sesquiterpenes: decanoic acid; pentilic 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: β-caryophyllene; myrcene; α-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

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 monoterpene 3-carene which was present too in the jelly. However, in the later, furaldehyde was obtained as a product of the heating process.

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