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Perfil químico de polpa de *Eugenia brasiliensis* (Grumixama) por *paper spray* PS/MS e microextração em fase sólida SPME-GC/MS

Chemical profile of *Eugenia brasiliensis* (Grumixama) pulp by PS/MS paper spray and SPME-GC / MS solid-phase microextraction

Perfil químico de la pulpa de *Eugenia brasiliensis* (Grumixama) por paper spray PS/MS e microextracción em fase sólida SPME-GC/MS

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Resumo

A *Eugenia brasiliensis* conhecida como grumixama é um fruto nativo da biodiversidade brasileira e, ela possui sabor e aroma característicos, compostos bioativos com propriedades antioxidantes e características benéficas para a saúde. Considerando que o mercado consumidor visa à procura de produtos com apelo natural e funcional, este estudo teve como objetivo caracterizar a polpa de grumixama, avaliar o potencial antioxidante e traçar o perfil químico e de compostos orgânicos voláteis deste fruto. Para isto foram realizadas análises de acidez titulável, pH, umidade, proteínas, cinzas, fibras, açucares totais e lipídeos. A determinação dos compostos fenólicos totais foi realizada pelo método do *Folin-Ciocalteu* e a atividade antioxidante utilizou teste com o radical ABTS. A caracterização do perfil químico consistiu na obtenção de *fingerprints* empregando-se o *Paper spray* PS/MS e a extração dos compostos orgânicos voláteis por meio de microextração em fase sólida (SPME) utilizando fibra PDMS/DVB e posterior separação e identificação por CG-MS. A polpa de grumixama destacou-se pela acidez e elevado teor de fibras (20,34 g/100 g de polpa), além de apresentar teores médios de compostos fenólicos totais (173,85 ± 3,21 mg/100 g de polpa) e atividade antioxidante (844,86 ± 2,03 μM/100 g de polpa). Em relação ao perfil químico da polpa foram listados por PS/MS 45 compostos, destacando-se os flavonoides, compostos fenólicos, carotenoides, açúcares, catequina e derivados da quercetina. Foram identificados 19 compostos voláteis orgânicos todos eles pertencentes à classe dos terpenos, sendo 94,7% sesquiterpenos e 5,3% monoterpenos, compostos estes que são responsáveis por diversas características sensoriais dos frutos. Os resultados demonstraram que a associação entre a atividade antioxidante promovida pelos bioativos e os COVs da polpa da grumixama tornam este fruto promissor para aceitação no mercado podendo ser adicionada em diversos produtos aumentando seu valor nutricional e funcional.

Palavras-chave: *Myrtaceae;* Compostos orgânicos voláteis; Atividade antioxidante; Cereja brasileira.

Abstract

The *Eugenia brasiliensis*, known as grumixama, is a fruit native to the Brazilian biodiversity and has characteristic flavor and aroma, bioactive compounds with antioxidant properties and benefical health characteristic. Since the consumer market is focused on the demand for products with natural and functional appeal, this study aimed to characterize the grumixama pulp, evaluate the antioxidant potential and trace chemical and volatile organic compounds of this fruit profile. For this purpose, analyzes of titratable acidity, pH, moisture, proteins, ash, fibers, total sugars, and lipids were performed. The determination of total phenolic compounds used the Folin-Ciocalteu method, and the antioxidant activity used the radical ABTS test. The characterization of the chemical profile consisted of obtaining fingerprints using Paper spray PS/MS and the extraction of volatile organic compounds employing solid-phase microextraction (SPME) using PDMS/DVB fiber and subsequent separation and identification by CG-MS. The grumixama pulp stood out for its acidity and high fiber content (20.34g/100g of pulp), in addition to presenting average levels of total phenolic compounds (173.85 ± 3.21 mg 100 g of pulp) and antioxidant activity (844.86 ± 2.03 mM/100g of pulp). Regarding the chemical profile of the pulp, 45 compounds were listed by PS/MS, with emphasis on flavonoids, phenolic compounds, carotenoids, sugars, catechins and quercetin derivatives. Nineteen volatile organic compounds can be identified, all of them belonging to the terpene class, 94.7% sesquiterpenes, and 5.3% monoterpenes, compounds that are responsible for several sensory characteristics of the fruits. The results showed that the association between the antioxidant activity promoted by the bioactive and the VOCs of the grumixama pulp make this fruit promising for acceptance in the market and can be added to various product elaborations, increasing its nutritional and functional value.

Keywords: *Myrtaceae*; Volatile organic compounds; Antioxidant activity; Brazilian cherry.

Resumen

Eugenia brasiliensis conocida como grumixama es una fruta nativa de la biodiversidad brasileña con sabor y aroma característicos, compuestos bioactivos con propiedades antioxidantes y características saludables. Teniendo en cuenta que el mercado consumidor busca productos con atractivo natural y funcional, este estudio tuvo como objetivo caracterizar la pulpa de grumixama, evaluar el potencial antioxidante y rastrear el perfil

químico y los compuestos orgánicos volátiles de esta fruta. Por tal motivo, se realizaron análisis de acidez titulable, pH, humedad, proteínas, cenizas, fibras, azucares totales y lípidos. La determinación de los compuestos fenólicos totales fue realizada utilizando el método Folin-Ciocalteu y para la actividad antioxidante fue utilizada una prueba con radical ABTS. La caracterización del perfil químico consistió en la obtención de *fingerprints* usando Paper Spray PS/MS y la extracción de los compuestos orgánicos volátiles empleando microextración en fase sólida (SPME) usando la fibra PDMS/DVB y posterior separación e identificación por CG-MS. La pulpa de grumixama se destacó por su acidez y elevado contenido de fibras (20,34 g/100 g de pulpa), además de presentar niveles medios de compuestos fenólicos totales (173,85 ± 3,21 mg/100 g de pulpa) y actividad antioxidante (844,86 ± 2,03 mM/100 g de pulpa). En relación al perfil químico de la pulpa fueron listados 45 compuestos por PS/MS, destacándose los flavonoides, compuestos fenólicos, carotenoides, azucares, catequina y derivados de la quercetina. Fueron identificados 19 compuestos orgánicos volátiles, todos ellos pertenecientes a las clases de los terpenos, de los cuales 94,7% pertenecientes a los sesquiterpenos y 5,3% monoterpenos, compuestos responsables por diversas características sensoriales severas de esta fruta. Los resultados demostraron que la asociación entre la actividad antioxidante promovida por los bioactivos y los COVs de la pulpa de grumixama hacen que este fruto tenga adecuada aceptación en el mercado pudiendo ser adicionado en diversos productos, incrementando así su valor nutricional y funcional.

Palabras clave: *Myrtaceae;* Compuestos orgánicos volátiles; Actividad antioxidante; Cereza brasileña.

1. Introduction

The *Myrtaceae* family is one of the most important in the Brazilian flora, presenting potential and significant economic interest for Brazil. The grumixama (*Eugenia brasiliensis Lamarck*), commonly known as Brazilian cherry, belongs to this family and is a fruit from the trees of the Brazilian forests distributed in the south and southeast regions of the country (Flores et al., 2012; Luciane de Lira Teixeira et al., 2015), having a significant presence in the Atlantic Forest biome (Pellis, 2019). In Brazil, commercial production can be found mainly in the "Vale do Paraíba" region, in the state of São Paulo (Luciane de L. Teixeira et al., 2018).

The fruit has chemical compounds such as anthocyanins, phenylpropanoids, flavonoids, ellagitannins, polyphenols, carotenols, sugars, vitamins (Machado et al., 2017; N. A. da Silva et al., 2014) among others. Due to these characteristics, to reveal the

nutritional and functional importance, they need to be appropriately identified. Studies show the characterization and potential of these compounds present in the leaves, bark, seed, pulp and crude grumixama extract (de Araújo et al., 2019; Flores et al., 2012; Infante et al., 2016; M. A. Magina et al., 2010; Siebert et al., 2017).

A striking feature in some varieties of grumixama is the purple color, which is an important attribute that indicates the presence of anthocyanin pigments. In other fruits of the same family, such as jamelão (*Syzygium cumini (L.) Skeels*), (Banerjee et al., 2005), pitanga *(Eugenia Uniflora),* jaboticaba (*Myrciaria jaboticaba (Vell)* O. Berg) and jambo (*Syzygium malaccense*) these pigments are found and have already been well characterized. Anthocyanins have an antioxidant action capable of reducing free radicals, causing positive effects on the manifestation of several pathologies, such as cancer and atherosclerosis (Cardoso et al., 2011) Therefore, there is a growing search for untapped sources of these compounds in order to reduce the imbalance in the antioxidant defense system of the human organism (Pimentel et al., 2005).

For a more detailed characterization of the fruit, identification is carried out using high-performance liquid chromatography, desorption/ionization laser-assisted electrospray (ELDI) mass spectrometry ionization electrospray by desorption (DESI-MS) and paper spray (Flores et al., 2012; Reynertson et al., 2008; Siebert et al., 2017; N. A. da Silva et al., 2014; M. Silva, Freitas, et al., 2019; Luciane de Lira Teixeira et al., 2015). The paper spray (PS/MS) has been highlighted, for allowing a detailed analysis with the identification of several substances present in complex matrices, making it possible to obtain the fingerprint of the sample in wide mass ranges (M. Silva, Freitas, et al., 2019).

The grumixama also has characteristics such as astringency, being traditionally used for the production of jellies, pies, and liqueurs (Flores et al., 2012). The fruit aroma is one of the characteristics most appreciated by consumers, and this is due to the presence of carboxylic acids, alcohols, aldehydes, ketones, esters and terpenes, which are the leading representatives of volatile organic compounds (VOCs) (Bicas et al., 2011; M. Silva, Bueno, et al., 2019). Knowing that the set of VOCs is specific to each fruit species and variety, and is responsible for the formation of the peculiar aroma (El Hadi et al., 2013), it is necessary to expand the studies on the characterization of these fruits. Various VOC extraction methods can be used, such as vacuum distillation, simultaneous distillation and concentration of volatiles, static and dynamic headspace analysis (Queiroga et al., 2005), and among these, solid-phase microextraction in the headspace mode (HP-SPME) (García et al., 2019). The latter is an advantageous extraction method because it is fast, simple, without the use of

solvent, but sensitive, thus providing satisfactory results for a wide range of concentrations and analytes (Merkle et al., 2015).

The microextraction is carried out by using a fiber stripper that may be of different polarities, and the efficiency of extraction is related to the polarity of the compounds present in the sample. Studies show that semipolar fiber Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) is one of the best at performing the extraction of compounds as the terpenoids (Francisco et al., 2020; García et al., 2019), a significant classes responsible by the flavor. The detection of extracted volatiles is carried out utilizing gas chromatography coupled with mass spectrometry (GC-MS).

Given the above, the objective of this work was to perform the physical-chemical characterization of the pulp of the grumixama fruit, as well as the evaluation of the antioxidant potential, tracing its chemical profile, using the technique of mass spectrometry by ambient ionization in paper spray (PS-MS) and the extraction of VOCs by HP-SPME with the separation and identification by gas chromatography coupled to mass spectrometry (GC-MS).

2. Material and Methods

2.1 Plant material

The frozen grumixama pulp of the "Sítio do Bello" brand was purchased in stores located in the city of São Paulo - Brazil (23° 27`53.94 "south and 45º 42`31.88" west), on December 2018. Approximately 3 kg of pulp were used from the same batch and with the same degree of ripeness, according to information from the manufacturer the fruit remained under a temperature of -18 º C and protected from light until time of use.

2.2 Methods

2.2.1 Physico-chemical characterization of grumixama pulp

Analyzes of titratable acidity, ash, fiber, pH, protein, and moisture were carried out in triplicate, according to the methods described by the Association of Official Analytical Chemists (AOAC, 2012); lipids according to the Bligh & Dyer (1959) extraction method.

The survey of sugars (total, reducing and non-reducing) was done according to methodologies described by the Ministério da Agricultura Pecuária e Abastecimento (2005) and *Association of Official Analytical Chemists* (AOAC, 2012).

2.2.2 Obtaining pulp extracts

The pulp extracts (0.5 grams of the sample, previously homogenized) obtained according to the methodology described by Rufino et al. (2010) with adaptations, were weighed. 1 ml of a 50% methanol solution was then added and the sample was shaken in a vortex shaker for 20 seconds and incubation continued for 1 hour at room temperature (25ºC) protected from light. After the incubation time, the sample was centrifuged for 15 minutes at 4°C with a rotation of 15000 x g in a centrifuge. Afterwards, the supernatant was collected in a 5 ml volumetric flask.

Extraction was repeated in the same Eppendorf, this time using 70% acetone. Again, agitation and resuspension was performed, proceeding with incubation and centrifugation, as mentioned above.

The supernatant transferred to the same volumetric flask (5 mL) and its volume made up with deionized water. The extracts were stored at freezing temperature until the moment of use for the analysis of total phenolic composition, antioxidant activity, and chemical profile PS/MS.

2.2.3 Analysis of total phenolic compounds and antioxidant activity

The phenolic compounds were determined using Follin-Ciocalteau reagent and reading on the spectrophotometer at 750 nm, as described by Rufino et al. (2010). The data expressed as mg of gallic acid (AGE) / 100 g of pulp.

The antioxidant activity evaluated by capturing the radical ABTS (2,2 - azinobis (3-ethylbenzothiazoline-6-sulfonic acid)) followed by a spectrophotometric reading at 734 nm and the results expressed in µM Trolox/100 g pulp (M. S. M. Rufino et al. 2007). Both analyzes were performed in triplicate and protected from light.

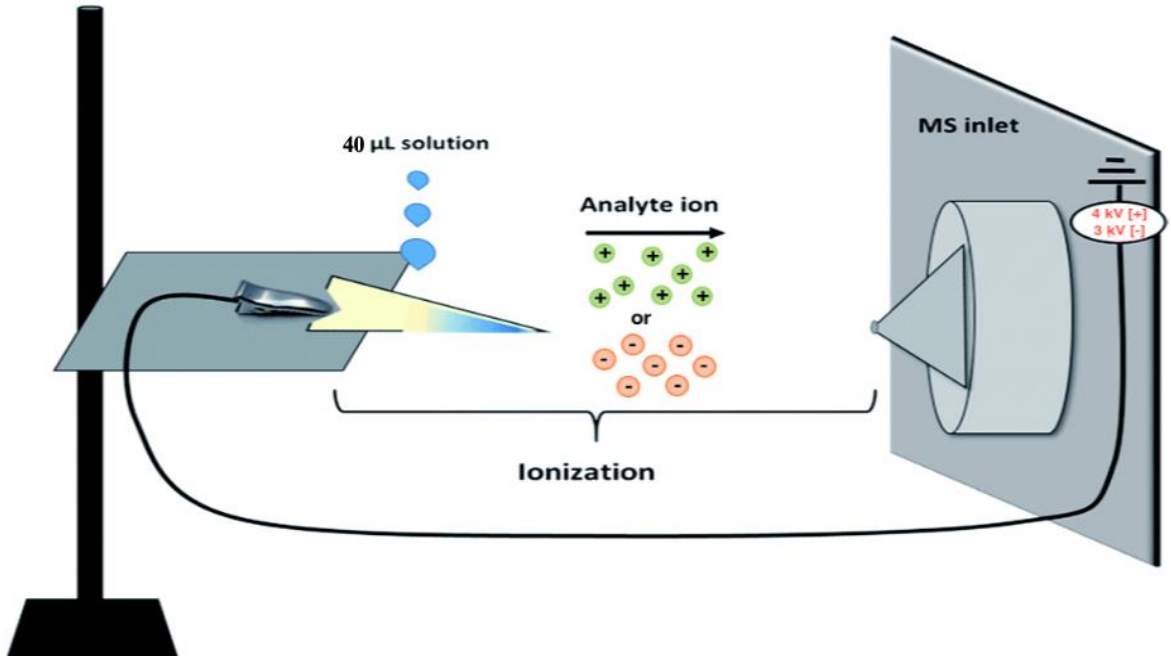
2.2.4 Chemical profile of grumixama pulp by Paper spray – MS

The analysis of the chemical profile of the samples was conducted using a LCQ Fleet mass spectrometer (Thermo Scientific, San Jose, CA, USA) equipped with an ambient ionization source by paper spray. It was performed in triplicate in positive and negative ionization modes, according to Silva et al. (2019). For the analysis, 2 µL of the samples and 40 µL of methanol was applied to the chromatographic paper triangle attached to the equipment and the voltage source connected for data acquisition (Figure 1).

The instrumental conditions of the analyzes were: voltage of the PS-MS source + 4 kV (positive mode) and - 3 kV (negative mode); capillary voltage of 40 V; transfer tube temperature 275°C; tube lens voltage of the 120 V; mass load range from 100 to 1000 m/z in positive and negative modes. The ions were fragmented using a collision energy of 15 to 45 eV.

The results for the mass spectra obtained were processed using the Xcalibur software version 2.1 (Thermo Scientific, San Jose, CA, USA). The average PS-MS spectra of positive and negative modes were determined using Excel, 2016 (Microsoft, Redmond, WA, USA). For the attempt to identify the compounds, a comparison was made of the mass load data ratios in the literature with the instrumental signals obtained and the subsequent fragmentation carried out using sequential mass spectrometry.

Figure 1. Diagram of the process of ionization by paper spray. Adapted from (Almeida de Paula et al., 2015).



Source: Authors.

2.2.5 Profile of volatile compounds

The extraction of volatile organic compounds was conducted using the solid-phase microextraction method in the headspace mode (HS-SPME) as described by García et al. (2019) using the Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) semipolar fiber. The extracted VOCs were separated and identified in the gas chromatograph (Trace GC Ultra) coupled to a mass spectrometer (Polaris Q) (GC-MS), with an "ion-trap" analyzer.

The fresh pulp was weighed (2.0 g) in headspace flasks with a capacity of 20 mL and closed with an aluminum seal. The flasks were then preheated on a hot plate without stirring for 5 minutes. After that time, the PDMS/DVB fiber was inserted into the flask, and exposed to the sample for 10 minutes. In sequence, the fiber was removed from the flask and manually inserted into the CG-MS at a temperature in the injector of 250°C, for a desorption time of 5 minutes. The temperature of the ion source was 200°C and ian nterface of 275°C. The carrier gas was helium with a flow rate of 1 $mL.min^{-1}$, and the VOCs were separated using a capillary column (HP-5ms) 5% phenyl and 95% methylpolysiloxane (30 mx 0.25 mm x 0.25

µm; Agilent Technologies Inc., Germany). Initially, the column was maintained at 40°C for 5 min, and then the temperature was increased at a rate of 2.5°C min^{-1} to 125°C, followed by an increase of 10°C.min^{-1} to 245°C and maintained for 3 min. Data acquisition occurred in the full scan mode by electronic impact ionization (EI) and a power of 70 eV with an interval of 50 to 300 m/z.

The identification of volatile compounds was based on the mass-charge ratio (m/z) of the ion fragments of the sample, using each mass spectrum in the range of 50 to 300 m/z. Using Xcalibur software version 2.1 (Thermo Scientific, San Jose, CA, USA), a comparison was made of the mass spectra corresponding to each peak observed in the chromatogram with the data obtained by the NIST library (National Institute of Standards and Technology) considering similarity level (reverse search index, RSI) greater than 600.

3. Results and Discussion

3.1 Determination of physical-chemical characterization

The results of the physical-chemical composition of the grumixama pulp are shown in Table 1.

Table 1. Physicochemical composition of the Grumixama pulp, on a wet basis.

Parameter	Grumixama pulp
pH	3.23 ±0.06
Titratable Acid (g citric acid/100 g pulp)	11.34 ±0.13
Soluble solids content (ºBrix)	6.03 ±0.06
Moisture (%)	91.66 ±0.13
Proteins (g/100 g of pulp)	0.41 ±0.02
Ash (%)	0.34 ±0.01
Lipids (g/100 g of pulp)	0.14 ±0.02
Insoluble fiber (g/100 g of pulp)	14.75 ±0.09
Soluble fiber (g/100 g of pulp)	5.59 ±0.19
Total sugar (g / 100 g of pulp)	3.93 ±0.30
Reducing sugar (g / 100 g of pulp)	2.78 ±0.18
Non-reducing sugar (g / 100 g of pulp)	1.15 ±0.42

Mean values of triplicates ± standard deviation expressed on a wet basis. Source: Author (2020).

The average pH of grumixama was 3.23, which classified it an acidic fruit. This may be supported by the titratable acidity values of 11.34 g citric acid / 100 g pulp. This

characteristic of low pH and high acidity is related to the characteristic acidic flavor of a fruit (Camlofski, 2008).

The moisture content found in the grumixama pulp samples was 91.66%, corroborating those found by Nascimento et al. (2017), Silva et al. (2014) and Zola et al. (2019). Those authors found, respectively, 90.70; 90.80 and 90.15% moisture in 100g of fruit pulp, which is a common characteristic of fruits of the *Myrtaceae* family (Medeiros de Aguiar et al., 2016; Luciane de Lira Teixeira et al., 2015; Zola et al., 2019). In relation to the protein content and minerals, °Brix and lipids, similar values to those of the present study were found in the literature. A variation was observed from 0.27 to 0.66 g/100 g pulp for protein content; 0.23 to 0.56 g/100 g of pulp for mineral content; 2.69 to 14° Brix, depending on the maturation stage of the fruit, and close to 0.14 g/100 g of pulp for lipid content (Helt et al., 2018; Medeiros et al., 2015; Medeiros de Aguiar et al., 2016; Luciane de L. Teixeira et al., 2018; Luciane de Lira Teixeira et al., 2015; Zola et al., 2019).

In the pulp analyzed, the total fiber content was 20.34%, 5.59% corresponding to soluble fiber and 14.75% corresponding to insoluble fiber. In the species of the *Mytarceae* family, fiber is characterized as mostly insoluble (Schimidt, 2018). The total sugar content was 3.93, with 2.78% reducing and 1.15% non-reducing sugars. Normative instruction n°01, of January 7, 2000 (MAPA, 2000) describes the Identity and Quality standards for Fruit Pulp and requires minimum and maximum values of sugar required for pulp of some fruits. However, in this case the grumixama does not have specific legislation for this parameter. The presence of sugars in fruit pulp is important for being responsible for, together with other compounds, desirable characteristics such as flavor.

3.2 Total phenolic compounds and antioxidant activity

The content of total phenolic compounds found in the grumixama pulp was 173.85 mg AGE/100g of pulp. Vasco; Ruales; Kamal-Eldin, (2008) classify the fruit as having low levels <100 mg AGE/100 g, medium 100 to 500 mg AGE/100 g) and high> 500 mg AGE/100 g. Therefore, according to the results found in this study, the fruit pulp has average levels of total phenolic compounds. The organic solvent used for the preparation of the plant extract can influence the extracted content due to the polarity of the solvent and the compounds present, thus resulting in higher or lesser extraction. Other interferences, such as the presence of lipids, terpenes, and the type of phenolic standard used, can also affect the results of these compounds (Vu et al., 2018).

The antioxidant activity, by the ABTS radical capture method, of the grumixama pulp was 844.86 mM Trolox/100 g of pulp. Zola et al. (2019) observed 1159.00 mM Trolox/100 g of grumixama pulp, using the same methodology, and 883.00 mM Trolox/100g cherry pulp, which is also a Eugenia, which is a very close result to that found in the present study. In the literature, there is a scarcity of studies on antioxidant activity using the ABTS method as use in the present study. The variations from one study to the next can be explained by the difference in climate, soil composition, degree of fruit maturation, geographic location (Haminiuk et al., 2012), as well as the solvent and its quantity used for the preparation of extracts exerting significant influence (Flores et al., 2012).

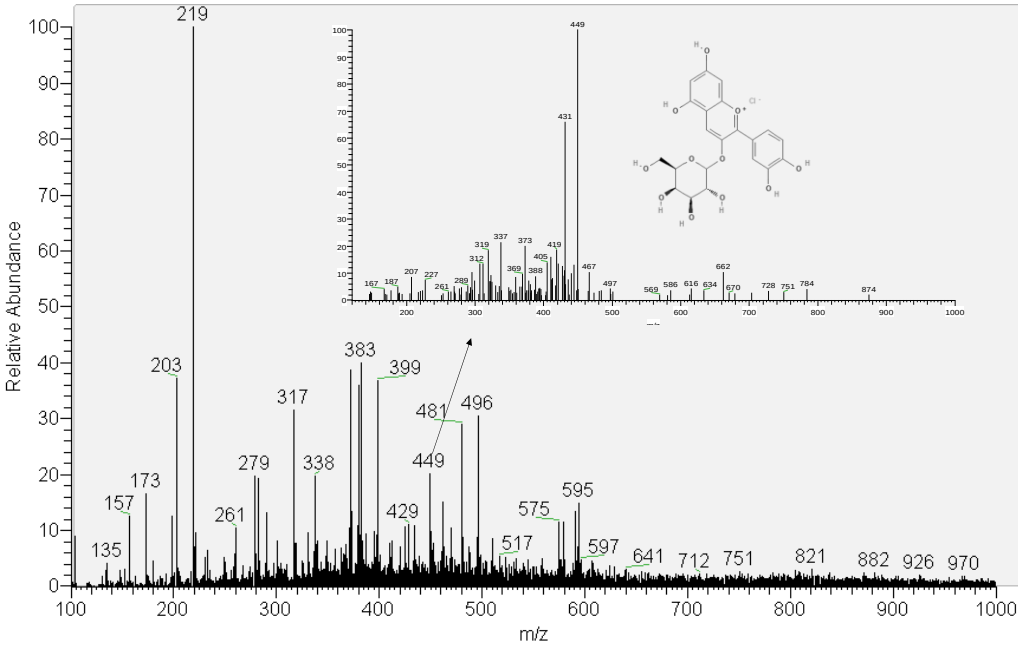
3.3 Chemical profile

The spectra of the chemical profile of the grumixama pulp sample in the positive and negative modes are shown in Figures 2 and 3, respectively. Through the identification attempt, it was possible to list 45 compounds in the grumixama pulp through PS-MS.

In the positive ionization mode, there were 18 compounds and 27 compounds in the negative mode. Flavonoids (46.66%) were found, followed by phenolic compounds (26.67%) and other compounds (26.67%) that include sugars and carotenoids. These possible compounds identified are shown in Table 2 for the positive ionization mode and in Table 3 for the negative ionization mode.

Figure 2. Representation of PS positive mode - MS from the Grumixama pulp sample.

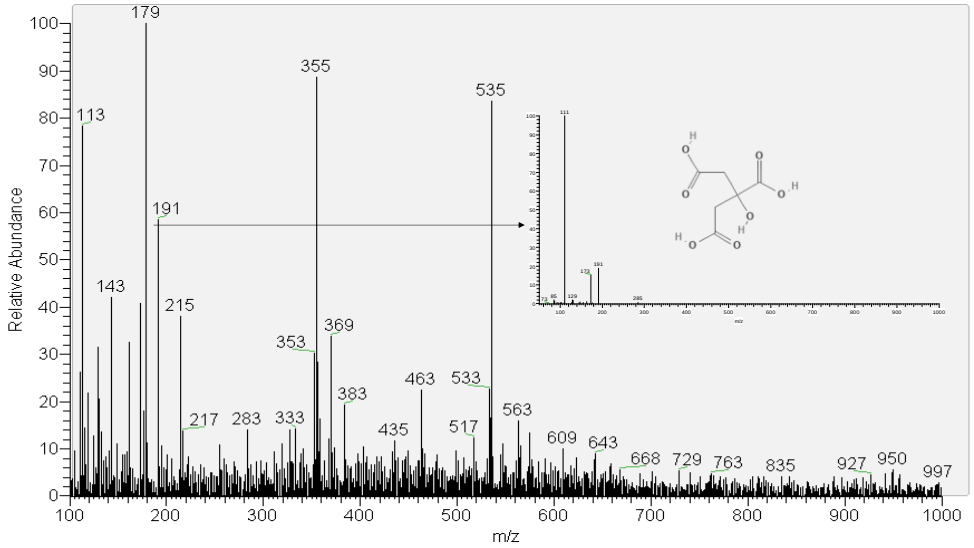
Source: Author (2020).



Source: Authors.

Figure 3. Representation of (a) PS negative mode - MS of the grumixama pulp sample.

Source: Author (2020).



Source: Authors.

Table 2. Chemical profile of the grumixama pulp sample by PS-MS in positive mode.

n°	Attempted identification	CAS	ID	Formula	m / z [] +	MS / MS	Reference
Phenolic compounds							
1	Galloyl- glucose ester	-	[M + Na] +	-	355	263 233	(Faria et al., 2011)
2	Dihydrosynapic acid	14897-78-0	[2M + Na] +	$C_{11}H_{14}O_5$	475	457	(Paudel et al., 2013)
Flavonoid							
3	Cyanidin 3-galactoside	27661-36-5	[M - 162] +	$C_{21}H_{21}ClO_{11}$	449	287	(Luciane de Lira Teixeira et al., 2015)
4	Catechin	18829-70-4	[M + H] +	$C_{15}H_{14}O_6$	291	273	(Stefova & Ivanova, 2011)
5	Diosmetin	520-34-3	[M + H - CO 3] +	$C_{16}H_{12}O_6$	301	286	(Wang et al., 2017)
6	Kaempferol rhamnoside	20196-89-8	[M + H] +	$C_{21}H_{20}O_{10}$	433	415	(Lee et al., 2005)
7	Myricetin rhamnoside	17912-87-7	[M + H] +	$C_{21}H_{20}O_{12}$	465	447	(Lee et al., 2005)
8	Quercetin-monoglucuronide	-	-	$C_{21}H_{18}O_{13}$ $C_{21}H_{20}O_{13}$	479	435 303	(Mascherpa et al., 2012)
9	Myricetin- glucoside	19833-12-6	[M + H] +		481	335	(Mascherpa et al., 2012)

10	Micricetin-3- glcA	15648-86-9	$[M + H]^+$	$C_{21}H_{20}O_{13}$	495	319	(Stefova & Ivanova, 2011)
11	5- pyranopellargonidin-3-O-glucoside	-	$[M]^+$	-	501	295	(Kajdžanoska et al., 2010)
12	Syringetin-3-glc	40039-49-4	$[M + H]^+$	$C_{23}H_{24}O_{13}$	509	481	(Stefova & Ivanova, 2011)
Other compounds							
13	Tryptophan	73-22-3	$[M + H]^+$	$C_{11}H_{12}N_2O_2$	205	188	(Kosinska et al., 2013)
14	Lycanic acid	623-99-4	$[M + H - 2H_2O]^+$	$C_{18}H_{28}O_3$	293	257	(Wang et al., 2017)
15	Sucrose	57-50-1	-	$C_{12}H_{22}O_{11}$	365	203	(Guo et al., 2017)
16	Gomphrenin	17008-59-2	$[M + H]^+$	$C_{30}H_{37}N_2O_{18}^+$	551	389	(García-Cruz et al., 2017)
17	All-trans- zeaxanthin All-trans- lutein	144-68-3 127-40-2	$[M + H-18]^+$	$C_{40}H_{56}O_2$	569	551	(Faria et al., 2011; N. A. da Silva et al., 2014)
18	6 ' -O-malonyl-2-descarboxy-isobetanin	-	$[M + H]^+$	-	593	345 507	(García-Cruz et al., 2017)

Source: Author (2020).

Table 3. Chemical profile of the grumixama pulp sample by PS-MS in negative mode.

nº	Attempted identification	CAS	ID	Formula	m/z [ ]⁻	MS/MS	Reference
Phenolic compounds							
19	Ferulol malic acid	-	$[MH]^-$	$C_{14}H_{14}O_8$	309	291	(Spínola et al., 2015)
20	Hexoside of p- coumaric acid	-	$[M-H]^-$	-	325	145, 163	(Kajdžanoska et al., 2010)
21	Caffeoyl-2-hydroxethane-1,1,2-tricarboxylic acid	-	$[M-H-44]^-$ $[M-H-2\times44]^-$	-	339	295 251	(Ben Said et al., 2017)
22	Caffeic acid-3-glucoside	24959-81-7	$[M-H-2H_2O]^-$	$C_{15}H_{18}O_9$	341	305	(Wang et al., 2017)
23	Dihydro- caffeyl -O- glucoside	-	([MH]⁻ - glc .)	-	343	181	(El-Sayed et al., 2017)
24	4-O-caffeyl quinic acid (cryptochlorogenic acid)	905-99-7	-	$C_{16}H_{18}O_9$	353	353	(Huang et al., 2017)
25	Caffeoyl-gluconic acid	-	([MH] - -Caf.)	$C_{15}H_{16}O_{11}$	371	209	(El-Sayed et al., 2017)
26	Derivatives of caffeic acid	-	$[MH]^-$	$C_{21}H_{16}O_{11}$	443	245 443	(Huang et al., 2017)
27	Hydroxy-methoxyphenyl-O - (O-galloyl) -hexose	-	$[MH]^-$	$C_{20}H_{22}O_{12}$	453	169, 313	(Abu-Reidah et al., 2015)
28	Tinosposid A	-	$[M-H]^-$	$C_{27}H_{35}O_{11}$	535	517	(Jiao et al., 2018)

Flavonoid

29	Kaempferol	520-18-3	$[M - H]^-$	$C_{15}H_{10}O_6$	285	241, 217, 213, 197	(Ben Said et al., 2017)
30	Luteolin	491-70-3	$[MH]^{\cdot}$	$C_{15}H_{10}O_6$	285	285, 267, 241, 217, 213,197	(El-Sayed et al., 2017)
31	Taxifoline	480-18-2	$[M - H - HO]^-$ $[M - H - HO - 44]^-$ $[M - H - CO - 58{-}18]^-$	$C_{15}H_{12}O_7$	303	285 241 199 125	(Chen et al., 2016)
32	Galocatechin	970-73-0	$[M - H - CO]^-$ $[CHO]^{-}$ 753	$C_{15}H_{14}O$	305	137, 261	(Wang et al., 2017)
33	Ether Dimethyl of quercetin	4382-17-6	$[M - H]^-$	$C_{17}H_{14}O_7$	329	314	(Ben Said et al., 2017)
34	quercetin 3-glucoside	482-35-9	$[M - H]^-$	$C_{21}H_{20}O_{12}$	463	301/151	(Luciane de Lira Teixeira et al., 2015).
35	Hexosídeo of quercetin	482-35-9	$[M - H - 162]^-$	-	463	301	(N. A. da Silva et al., 2014)
36	3 ', 4-Dihydroxy-5,6-dimethoxy-7-O-glucoside	-	$[M - H]^{\cdot}$	-	491	473	(Gouveia & Castilho, 2010)

37	Quercetin acetylhexoside	-	$[M - H]^-$	-	505	301	(Ben Said et al., 2017)
38	Di-glucoside of di - hydro-myricetin	-	$[MH-162]^-$	-	643	481	(Faria et al., 2011)
39	Methyl- di - hydro-miricetin glucoside	-	[MH]	-	657	477	(Faria et al., 2011)
Other compounds							
40	Citric acid	77-92-9	$[M - H - HO - COOH - OH]^-$	$C_6H_8O_7$	191	173, 111	(M. Silva, Freitas, et al., 2019; Wang et al., 2017)
41	Palmitic acid	57-10-3	$[M - H - HO]^-$	$C_{16}H_{32}O_2$	255	237	(Wang et al., 2017)
42	Sucrose	57-50-1	[M + HCOO] -	$C_{12}H_{22}O_{11}$	387	341	(Gabbanini et al., 2010)
43	Sweroside lactone	-	-	-	403	167	(Guo et al., 2017)
44	Derived from glucaric acid	-	-	$C_{16}H_{26}O_{12}$	409	209	(Díaz-de-Cerio et al., 2018)
45	Iso - Pentyl - di-hexose	-	$[M - H]^-$	-	411	249	(El Sayed et al., 2016)

Source: Author (2020).

Among the flavonoids, in this identification attempt, catechin stands out (m/z = 291); derivatives of quercetin as monoglucuronide of quercetin (m/z = 479), ether, dimethyl ether of quercetin (m/z = 329), 3-glucoside of quercetin (m/z = 463) hexosídeo of quercetin (m/z = 463), quercetin acetylhexoside (m/z = 505); and also gallocatechin (m/z = 305). These substances are naturally present in grumixama (M. D. A. Magina et al., 2012; N. A. da Silva et al., 2014; Luciane de Lira Teixeira et al., 2015), substances which provide beneficial effects such as antioxidant activity (M. D. A. Magina et al., 2012).

The detection of the cyanidin 3-galactoside compound (m/z = 449) confirms the presence of anthocyanins in the grumixama pulp, as found in other studies of the same fruit (Nascimento et al., 2017; Luciane de Lira Teixeira et al., 2015). These compounds have potential effects on human health, such as aid in reducing obesity and in insulin resistance (Lenquiste et al., 2012), in addition to exercising therapeutic activities such as the ability to sequester free radicals (Almeida et al., 2019). Besides that they are also flavonoids, generally responsible for red pigments, widely distributed in the plant kingdom (Aguilera-Otíz et al., 2011). The fruit can thus be considered a new source of these compounds, adding value to grumixama that is a still little explored fruit (Nascimento et al., 2017). In general, *E. brasiliensis* varieties are considered good sources of bioactive compounds, especially anthocyanins, ellagitannins, and carotenoids (de Araújo et al., 2019).

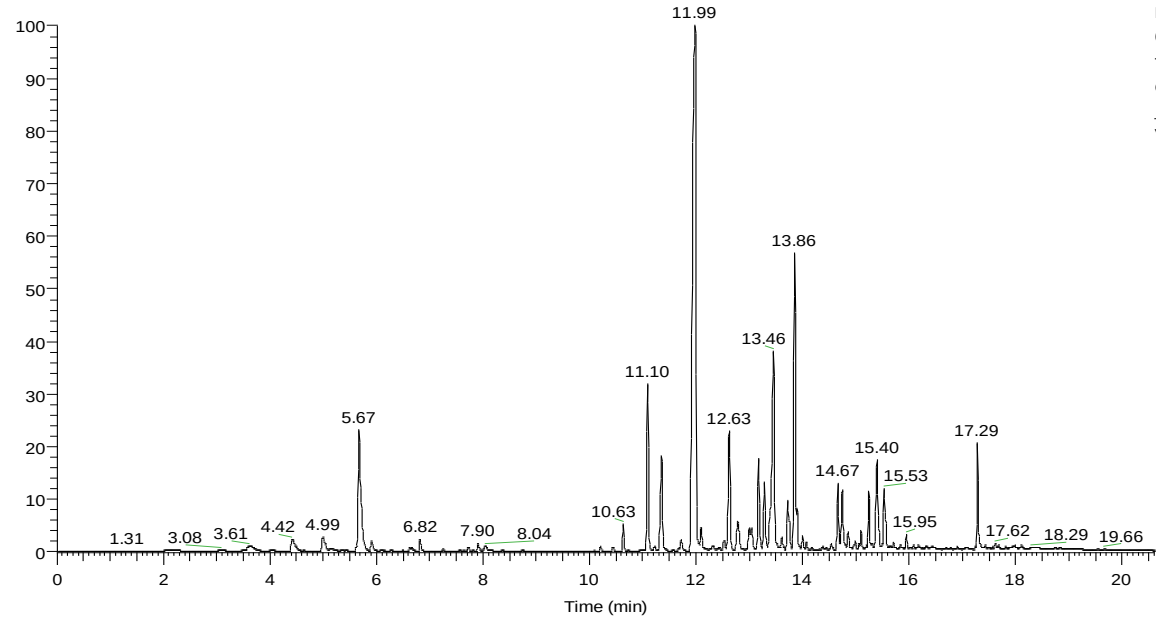
Carotenoids such as all-trans-zeaxanthin (m/z = 569) and all-trans-lutein (m/z = 569) were listed in an attempt to identify the study sample and are among the most common fat-soluble pigments found in nature with antioxidant action (Moeller et al., 2000). These compounds have also been identified in fruits such as araça (*Psidium cattleianum*) and uvaia (*Eugenia pyriformis*) both from the same family as the grumixama fruit; however, there is still little research showing the presence of these compounds in dark-skinned fruits, which can be justified by the intensity of this coloration that may mask the characteristic color of carotenoids (Nascimento et al., 2017).

In the grumixama samples, sucrose sugar was listed, both in positive (m/z = 365) and negative (m/z = 387) ionization modes. As expected, another compound identified in the grumixama pulp was citric acid (m/z = 191), since this is a natural source of organic acid, found in all citrus fruits (Aghera & Bhatt, 2019), which was also confirmed by the titratable acidity and pH analyzes.

3.4 Volatile compounds

The chromatogram for the analysis of volatiles in the grumixama pulp is shown in Figure 4.

Figure 4. Chromatogram of the volatile compounds of the grumixama pulp by CG-MS.



Source: Author (2020).

It was possible to identify 19 VOCs by comparing the mass spectra corresponding to each peak with the data obtained by the NIST library, which are shown in Table 4

Table 4. Volatile organic compounds identified in the grumixama pulp.

Number	MS / MS	CAS	Formula	Compound	Class
1	67, 79, 93 107, 121	499-97-8	$C_{10}H_{16}$	D- limonene	monoterpene
2	91,119,148,159,205	217 47-46-6	$C_{15}H_{24}$	(+) - Ledene	Sesquiterpene
3	79,91,121,161,204	22469-52-9	$C_{15}H_{24}$	(+) - Cyclosativene	Sesquiterpene
4	79,93,119,161,191	-	$C_{15}H_{24}$	1,1 4a-Trimethyl-5-6-dimethylene-decahydronaphthalene	Sesquiterpene
5	67,79,91,105,121	-	$C_{15}H_{24}O$	Allo-aromadendrene	Sesquiterpene
6	105, 119, 161,189,204	483-76-1	$C_{15}H_{24}$	Cadina - (10) 4-diene	Sesquiterpene
7	90,105,119,161,204	523-47-7	$C_{15}H_{24}$	Cadina-3,9-diene	Sesquiterpene
8	79,91,105,161,189	-	$C_{15}H_{24}$	Karyophylene	Sesquiterpene
9	91, 105, 119, 161, 204	3856-25-5	$C_{15}H_{24}$	Copaene	Sesquiterpene
10	95,105,121,161,204	473-04-1	$C_{15}H_{26}O$	Eudesm-7 (11) -en-4-ol	Sesquiterpene
11	79.91.93, 105.147	3691-11-0	$C_{15}H_{24}$	Guayana-1 (10), 11-diene	Sesquiterpene
12	79,91,103,119,161	-	$C_{15}H_{24}$	Isoleodene	Sesquiterpene
13	79, 91, 119, 133, 161	475-10-7	$C_{15}H_{24}$	Longifolene	Sesquiterpene
14	92,105,119,133,161	61262-67-7	$C_{15}H_{24}$	Longifolene-(V4)	Sesquiterpene
15	94,105,119,162,204	1405-16-9	$C_{15}H_{24}$	Patchoulane	Sesquiterpene

16	79,105,119,161,204	470-40-6	$C_{15}H_{24}$	Thujopsene	Sesquiterpene
17	91, 105, 119, 161, 204	17699-1 4-8	$C_{15}H_{24}$	α-Cubebene	Sesquiterpene
18	105,119,133,161,204	5951-67-7	$C_{15}H_{24}$	α-Elemene	Sesquiterpene
19	92, 105, 133, 147, 161	88-8 4-6	$C_{15}H_{24}$	β-Guaiene	Sesquiterpene

Source: Author (2020).

It can be observed that all compounds identified belong to the class of terpenes, being sesquiterpenes (94.7%) and a monoterpene (5.3%). C 10 (monoterpenes) and C 15 (sesquiterpenes) are among the most important volatile compounds present in fruits (Schwab et al., 2008) considered the most abundant and foremost factor responsible for determining the characteristic aroma (El Hadi et al., 2013). The pulp presented a very complex sesquiterpenes profile with 18 compounds identified with this classification.

The identified monoterpene was D- limonene. This compound is the major component found in orange peel oil, correlated with preventing dehydration and inhibiting microbial growth in vegetables (Muller, 2011). This compound is widely used in the food industry as an aromatic component and to provide flavor, and is even used in obtaining artificial flavors such as mint and mint, in the manufacture of sweets, candies and chewing gums (Santos et al., 2003). The presence of this compound in grumixama is advantageous since it has a positive relationship with flavor, desirable characteristics and is naturally present in the fruit. As in the present study, compounds such as α-cubebene, allo-aromadendrene and β-guaiene were identified in samples of araça-boi (*Eugenia stipitada*) (Franco & Shibamoto, 2000) and pitangas (*Eugenia uniflora* L) with different color biotypes (orange, red and yellow) (Mesquita et al., 2017). Sesquiterpenes are the most abundant compounds and commonly found in the *Eugenia* genus (Franco & Shibamoto, 2000; Mesquita et al., 2017). The presence of this class of compounds makes grumixama a fruit of biological value as such compounds also have activity related to antibacterial action (Becker et al., 2017).

4. Conclusion

The pulp of grumixama was characterized as acidic. The technique of paper spray allowed identification of various phenolic compounds responsible for the antioxidant action, thus confirming the values obtained in this study for pulp antioxidant capacity and phenolics and showed or efficient for a rapid identification attempt of the chemical sample profile. These results are essential to start a study of the effects on human health and bioavailability.

The HS-SPME using a semipolar PDMS/DVB fiber coupled to GC-MS is an efficient technique for extraction and identification of VOCs present in grumixama pulp, allowing the identification of compounds, 19 being mostly sesquiterpenes (94%). This result shows the importance of this study concerning the identification of volatile compounds fundamental in terms of characteristics, such as flavor of the fruit and consumer acceptance. Thus, the results of this work demonstrate that the grumixama pulp is promising in order to be explored and

has the potential to be introduced into food products.

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