



Use of pulp, peel, and seed of *Annona crassiflora* Mart. in elaborating extracts for fingerprint analysis using paper spray mass spectrometry

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ABSTRACT

The Brazilian cerrado is considered one of the most critical biomes in the world. Araticum (*Annona crassiflora* Mart.) is a native plant from the Brazilian cerrado, abundant in nutrients and highly energetic. This study aimed to obtain chemical fingerprints of different parts of the araticum fruit, i.e. pulp, peel, and seed. Extracts from these three parts were prepared using different solvents (ethanol, water, and mixtures of ethanol and water) and later analyzed by paper spray ionization mass spectrometry. In general, ethanol extracted more metabolites than the other solvents. The chemical profiles varied according to the fruit part, geographic location, and extractor solvent. Among the metabolites, acetogenins (62.3%) and alkaloids (20.7%) predominated. Principal component analyses revealed that the samples were grouped according to the fruit part, regardless of the extractor solvent used. Araticum shows remarkable potential due to the beneficial properties of the metabolites for human health. The insertion of araticum in the human diet is still underexplored but is a promising alternative.

1. Introduction

The Cerrado is the second largest biome in Brazil, distributed mainly in the central region of the country (Prado et al., 2020; Ribeiro Neto et al., 2020; Vasconcelos et al., 2016). This biome is considered one of the world's biodiversity hotspots (Brasil, 2019; Prado et al., 2020) and occupies approximately 57 % of the state of Minas Gerais (Ribeiro Neto et al., 2020). It constitutes a great diversity of renewable natural resources, emphasizing exotic and unconventional fruit species with peculiar sensory characteristics (Cândido et al., 2015).

These attributes make these fruits a potential source for developing innovative and healthy products in the food industry (Schiasi et al., 2018). In addition, its characterization has aroused scientific interest due to the presence of compounds with health-promoting characteristics (da Silva et al., 2019). Furthermore, as they possess a considerable consumption potential, they can promote income generation for small

producers and habitat preservation.

Araticum (*Annona crassiflora* Mart.) stands out among the fruits of the Cerrado biome. It belongs to the Annonaceae family (Arruda et al., 2018; Ramos et al., 2021). The fruit is oval or rounded, with green skin before ripening and brown when ripe, weighing from 0.5 to 4.5 kg. Its seeds are dark brown, flat, and oval (Arruda et al., 2018). The harvest occurs between September and April (Arruda et al., 2015; Morais et al., 2017).

The fruit stands out for its pulp with high energy value, as it is rich in fiber, vitamins (A, C, and E), and bioactive compounds (Barros et al., 2019). It has excellent sensory characteristics (da Silva et al., 2013), such as the sweetness of the pulp, the yellowish color, and the very intense aroma (Arruda et al., 2015), favoring a good acceptance by consumers (Barros et al., 2019).

The pulp is popularly consumed fresh or processed in ice cream, popsicles, jellies, and juices (H. S. Arruda & Pastore, 2019). The peel and

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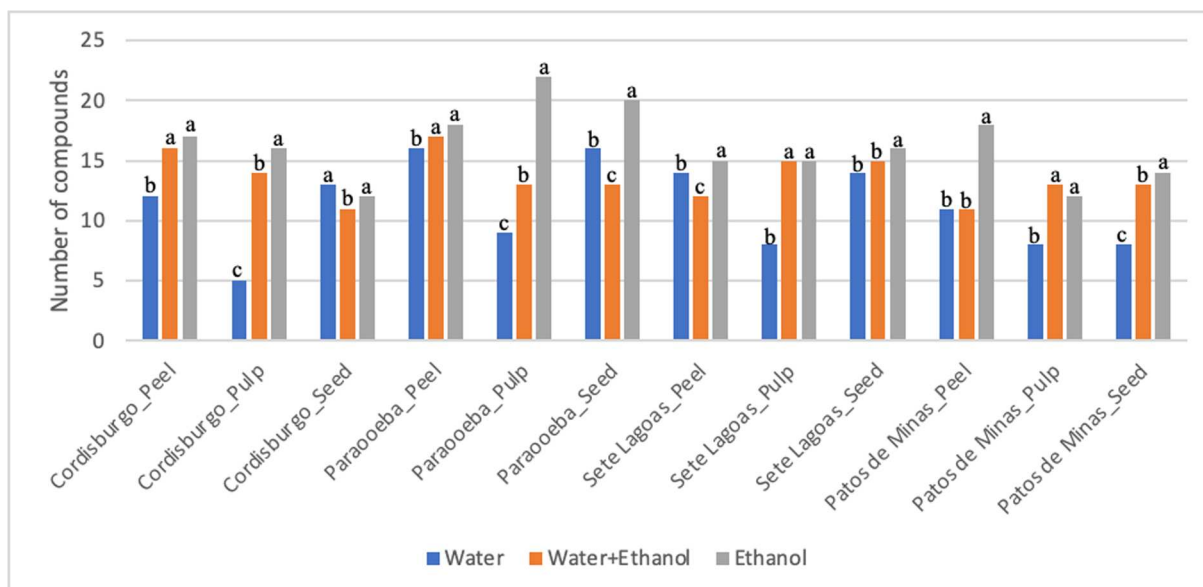


Fig. 1. The number of compounds listed in the evaluation of araticum parts using different solvents. Mean values of three replicates. The means followed by the same letter for the same part of the fruit and region do not differ statistically by the Bonferroni test, at 5% probability.

seeds of the fruit are treated as waste despite studies showing that the peel has a high antioxidant (Roesler, 2011), antibacterial (da Silva et al., 2014), and hepatoprotective capacity (Justino et al., 2017). The seeds have anticholinesterase, antiproliferative (Formagio et al., 2015), insecticidal (Krinski & Massaroli, 2014), and antioxidant properties (Roesler, 2011; da Silva et al., 2013).

Araticum has gained prominence due to the benefits of its fruits for human health. These benefits are related to its unique phytochemical diversity and outstanding nutritional characteristics (Arruda et al., 2018). However, its chemical composition must be thoroughly and effectively investigated. The paper spray ionization mass spectrometry technique has become popular due to the simplicity and fast implementation, and the possibility of performing *in situ* analyses (Bartella et al., 2019).

As araticum is part of the Brazilian biodiversity and produces fruits with relevant nutritional and bioactive characteristics, whole fruit consumption is potentially advantageous and can become a dietary alternative for the population. Thus, this study aims to apply paper spray mass spectrometry to attain the chemical fingerprinting of the pulp, peel, and seeds of araticum (*Annona crassiflora* Mart.) fruits, also evaluating various solvents (ethanol, water, and mixtures of ethanol and water) to prepare the extracts.

2. Material and methods

2.1. Plant material

The fresh fruits were collected in Cordisburgo (19°07'32.7" S and 44°19'12.8" W), Paraopeba (19°16'26.4" S and 44°24'00.3" W), Patos de Minas (18°35'14.2" S and 46°30'24.4" W) and Sete Lagoas (19°27'29.9" S and 44°14'49.7" W), in the state of Minas Gerais, Brazil, in 2020. Fruits were from the same harvest and with the same degree of maturity. The parts of the fruit (peel, pulp, and seed) were manually separated, maintained at a freezing temperature of -18°C , and protected from light in metal packaging until use.

2.2. Obtaining the extracts

The extracts (pulp, peel, and seed) were obtained in three different ways. The fruit parts were crushed and homogenized with a blender (L-99-FR, Mondial). 1.0 g of each sample, previously homogenized, were

weighed, then the solvents for each extraction were added: 8 mL of ethanol (ethanolic extract); 8 mL of water (aqueous extract); 4 mL of ethanol, and 4 mL of water (hydroethanolic extract).

The samples were vortexed for 30 s and kept at rest for 1 h at room temperature (25°C). Subsequently, the centrifugation was performed for 20 min at 4°C with a rotation of $25407 \times g$. The supernatant was transferred to microtubes (2 mL), and the extracts were stored at freezing temperature until the PS-MS analysis.

2.3. PS-MS analysis

PS-MS analysis of the araticum fruit extracts were conducted on a Thermo LCQ-Fleet mass spectrometer (ThermoScientific, San Jose, USA) in positive-ion mode. The instrumental conditions were as follows: voltage applied to the paper, 4.5 kV; capillary temperature, 275°C ; capillary voltage, 40 V; tube lens voltage, 120 V. Full scan mass spectra were acquired over a 100–1000 m/z range. Chromatographic paper was cut with scissors to manufacture triangular papers with the dimension of $1.0 \times 1.5 \times 1.5$ cm. The PS source was built according to the methodology described by Ramos et al. (2020) and García et al. (2021). The fruit extracts (2 μL) were applied to the triangular base. After drying, methanol (40 μL) was dropped onto the paper base, and the voltage was applied through the metal clip. Ion fragmentation was performed using collision energy from 15 to 45 units. The mass spectra data were processed using the Xcalibur software version 2.1 (Thermo Scientific, San Jose, CA, USA) (Thermo, 2011). Spreadsheet software (Excel, 2020, Microsoft, Redmond, WA, USA) (Microsoft: Redmond, 2020) was used to list and organize the average mass spectra for further analysis. The metabolites were putatively identified by comparing their masses and fragmentation patterns to those described in literature.

2.4. Statistical analysis

SPSS software version 15.0 (SPSS Inc., Chicago, Ill., USA) was used for data evaluation and statistical treatment subjected to the one-way analysis of variance (ANOVA) and Bonferroni's test ($p < 0.05$) to evaluate the averages. Principal component analysis (PCA) was performed using the central average of the data using the MatLab software version R2021a (9.10.0.1602886) (Mathworks, Natick, MA, USA) and the PLS Toolbox extension version 8.9 (Eigenvectors Research, Manson, WA, USA).

Table 1
The fingerprint of araticum samples by PS-MS.

n ^o	m/z	Ion Type	MS/MS	Identification Attempt	Cordisburgo			Paraopeba			Sete Lagoas			Patos de Minas			Reference
					Peel	Pulp	Seed	Peel	Pulp	Seed	Peel	Pulp	Seed	Peel	Pulp	Seed	
Acetogenins																	
1	595	[M + H] ⁺	505, 451, 277	Annonacinone	X	X	-	X	X	-	-	X	-	-	X	-	(Avula et al., 2018)
2	598	[M + H] ⁺	580, 561, 543, 507	Annonacin	-	-	-	-	-	X	-	-	-	-	-	-	(Avula et al., 2018)
3	617	[M + Na] ⁺	559, 523, 505, 495	Squamocin B	-	-	X	-	-	X	-	-	-	-	-	X	(Avula et al., 2018)
4	630	[M + Na] ⁺	572, 554	Desacetylurarin	-	-	-	-	-	X	-	-	X	-	-	X	(Avula et al., 2018)
5	646	[M + Na] ⁺	606, 588, 569, 551,533	Squamocin	-	-	X	-	-	X	-	-	X	-	-	X	(Avula et al., 2018)
6	648	[M + Na] ⁺	608, 690, 572, 535	Annomontacin	-	X	-	-	-	X	-	-	X	-	-	X	(Avula et al., 2018)
7	380	[M + H] ⁺	-	Squamostolide	-	-	-	-	-	-	-	X	-	-	-	-	(Bermejo et al., 2005)
8	550	[M + H] ⁺	451, 395, 367	Artemoin-A + B + C + D	-	-	-	-	-	-	-	-	-	-	X	-	(Bermejo et al., 2005; Chang et al., 1999)
9	552	[M + H] ⁺	-	Montalycin-A	-	X	-	-	-	-	-	-	-	-	X	-	(Bermejo et al., 2005)
10	560	[M + H] ⁺	397	Corepoxylone	-	-	-	-	X	-	-	X	-	-	X	-	(Bermejo et al., 2005; Gromek et al., 1993)
11	562	[M + H] ⁺	351, 281, 247	Robustocin	-	-	-	-	X	-	-	-	-	-	-	-	(Bermejo et al., 2005; Gleye et al., 2000)
12	574	[M + H] ⁺	323	Dieporeticanin-2	X	-	-	X	-	-	X	-	-	-	-	-	(Bermejo et al., 2005; Tam et al., 1994)
13	578	[M + H] ⁺	451, 351, 333, 297, 281, 279, 263	Annocatacin-B	X	-	-	-	-	-	-	-	-	-	-	-	(Bermejo et al., 2005; Chang et al., 2003)
14	588	[M + H] ⁺	-	Annodienin (CO,10)	X	-	-	X	X	-	X	-	-	X	-	-	(Bermejo et al., 2005)
15	590	[M + H] ⁺	377,347,295	Bullatencin (D23)	X	-	-	X	-	-	X	-	-	-	-	-	(Bermejo et al., 2005; Hui et al., 1992)
16	592	[M + H] ⁺	574,556,323,305,269	Montanacin-E (CO,10)	X	-	-	X	X	-	X	-	-	-	-	-	(Bermejo et al., 2005; Wang et al., 2000)
17	594	[M + H] ⁺	363,345,311,283	Squamolinone	X	X	-	X	X	-	-	X	-	-	X	-	(Bermejo et al., 2005; Hopp, 1998)
18	596	[M + H] ⁺	439,353,283	Itrabin	-	X	-	-	-	X	-	X	-	-	X	-	(Bermejo et al., 2005;

(continued on next page)

Table 1 (continued)

n°	m/z	Ion Type	MS/MS	Identification Attempt	Cordisburgo			Paraopeba			Sete Lagoas			Patos de Minas			Reference
					Peel	Pulp	Seed	Peel	Pulp	Seed	Peel	Pulp	Seed	Peel	Pulp	Seed	
19	612	[M + H] ⁺	570,540,522,504,486,430,412,397,341,285,269,252,215	Montanacin-J + 34- <i>epi</i>	-	-	X	-	X	X	-	-	X	-	X	-	Cortes et al., 1991 (Bermejo et al., 2005; Wang et al., 2001)
20	614	[M + H] ⁺	-	Muricatatin-C (CO,10)	-	-	-	-	-	X	-	-	-	-	-	-	(Bermejo et al., 2005)
21	620	[M + H] ⁺	449,361,311,309,293,291,241	Guanacone (CO,10)	-	-	-	-	-	X	-	-	-	-	-	X	(Bermejo et al., 2005; Gallardo et al., 1998)
22	622	[M + H] ⁺	640,623,621	Bullatacinone	-	-	X	-	X	X	-	-	X	-	X	-	(Bermejo et al., 2005; Hui et al., 1989)
23	624	[M + H] ⁺	453,435,417,407,383,365,319,313,311,,267,241,223,	Tucumaninf	-	-	X	-	-	X	-	-	X	-	-	X	(Barrachina et al., 2004; Bermejo et al., 2005)
24	626	[M + H] ⁺	381,363,269,267,229	Montanacin-H + 34- <i>epi</i> (CO,10)	-	-	-	-	-	X	-	-	-	-	-	-	(Bermejo et al., 2005; Wang et al., 2001)
25	628	[M + H] ⁺	429,411,393,375,357,341,339,323,305,299,251,245,211,193,181	Murihexocin-C	-	-	-	-	-	-	-	-	X	-	-	X	(Bermejo et al., 2005; Kim et al., 1998)
26	636	[M + H] ⁺	-	9-oxo-asimicinone (CO,9)	-	-	X	-	-	-	-	-	X	-	-	-	(Bermejo et al., 2005)
27	638	[M + H] ⁺	397,379,361,327,309,291,209	9-OH-asimicinone	-	-	X	-	X	X	-	-	X	-	X	X	(Bermejo et al., 2005; Hopp et al., 1999)
28	640	[M + H] ⁺	595,525,451,381,363,311,293,283,269,241,	Otivarinf	-	-	X	-	X	X	-	-	X	-	X	X	(Bermejo et al., 2005; Cortes et al., 1993)
29	644	[M + H] ⁺	539,495,337	Coriheptocin-B	-	-	X	-	-	X	-	-	X	-	-	X	(Bermejo et al., 2005; Da Silva et al., 1997)
30	654	[M + H] ⁺	563,521,507,493,479,465,451,437,423,409,395,365,307,237	Salzmanolind	-	-	-	-	-	X	-	-	X	-	-	-	(Bermejo et al., 2005; Queiroz et al., 2003)
31	656	[M + H] ⁺	647,619,605,591,577,563,549,535,521,561,549,493,491,477,463,449,433,435,421,407,403,379,365	Parisin	-	-	X	-	X	X	-	-	X	-	-	X	(Bermejo et al., 2005; Queiroz et al., 2003)
32	662	[M + H] ⁺	-	24-acetylguanacone (CO,10)	-	X	X	-	X	X	-	-	X	-	X	X	(Bermejo et al., 2005)
33	664	[M + H] ⁺	-	Guanaconetin-4	-	X	X	-	X	X	-	-	X	-	-	X	(Bermejo et al., 2005)

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Table 1 (continued)

n°	m/z	Ion Type	MS/MS	Identification Attempt	Cordisburgo			Paraopeba			Sete Lagoas			Patos de Minas			Reference	
					Peel	Pulp	Seed	Peel	Pulp	Seed	Peel	Pulp	Seed	Peel	Pulp	Seed		
Fatty acid																		
34	284	[M] ⁺	253, 241, 143	Heptadecanoic acid, methyl ester	-	X	-	-	-	-	-	-	-	-	X	-	-	(Hagr et al., 2019)
35	296	[M] ⁺	180, 97	9- octadecenoic acid, methyl ester	X	X	-	X	-	-	X	-	-	X	X	-	-	(Hagr et al., 2019)
36	324	[M] ⁺	324,294,292,263,250,221,208,180,166,123	Cis-11-Eicosenoic acid, methyl ester	-	-	-	-	-	-	-	-	-	-	X	-	-	(Hagr et al., 2019)
37	326	[M] ⁺	326,295,283,269,255,241,227,213,199,185,171,143	Eicosanoic acid, methyl ester	-	-	-	-	-	-	X	-	-	-	-	-	-	(Hagr et al., 2019)
Alkaloid																		
38	268	[M + H] ⁺	219, 191	Asimilobine	-	-	-	-	X	-	-	-	-	-	-	-	-	(de Sousa, 2016)
39	280	[M + H] ⁺	276, 249	Roemerine	X	X	-	X	X	-	X	X	-	X	X	-	-	(Santos, 2015)
40	281	[M] ⁺	280, 266, 252, 237, 211, 178, 165, 152	Nornuciferine	-	X	-	X	X	-	X	X	-	-	X	-	-	(Rinaldi et al., 2017)
41	298	[M + H] ⁺	281, 269, 254, 238, 192, 161, 146	Stepharine	-	-	-	-	-	-	-	-	-	-	-	-	-	(Avula et al., 2018)
42	282	[M + H] ⁺	281,280,266,250,252,237,221,178,165,152	Nornuciferine	X	X	-	X	X	-	X	X	-	X	X	-	-	(Pinto et al., 2017; Rinaldi et al., 2017)
43	300	[M + H] ⁺	300,269,237,192,175,143,107	N-methylcoclaurine	X	X	-	X	X	-	X	X	-	X	X	-	-	(Coria-Téllez et al., 2019; Lima et al., 2021)
44	310	[M + H] ⁺	310,301,274,168	Guattescidine	X	X	-	X	X	-	X	X	-	X	X	-	-	(Rabelo et al., 2014)
45	311	[M] ⁺	310, 282, 266, 251, 181	Actinodaphnine	X	X	-	X	X	-	X	X	-	X	-	-	-	(Rinaldi et al., 2017)
46	328	[M + H] ⁺	297, 265, 250, 237	Isoboldine	X	X	-	X	X	-	X	X	-	X	X	-	-	(Bruginski, 2016)
47	330	[M + H] ⁺	330,299,267,192,175	Reticuline	X	-	-	X	-	-	X	-	-	-	-	-	-	(Coria-Téllez et al., 2019)
48	342	[M + H] ⁺	311, 280	N-methylaurotetanine	X	-	-	X	X	-	X	-	-	X	X	-	-	(Dantas et al., 2020)
Ester																		
49	301	[M + H] ⁺	-	1,13-tridecanediol-diacetate	X	-	-	X	-	-	-	-	-	-	-	-	-	(Coria-Téllez et al., 2019)
Flavonoid																		
50	291	[M + H] ⁺	291	(-)-epicatechin	-	-	-	-	-	-	-	X	-	-	-	-	-	(de Galvão et al., 2016)
51	597	[M + H] ⁺	456,303	Quercetin-O-pentosyl-hexoside	-	-	-	-	-	X	-	-	X	-	-	-	-	(Silva et al., 2019)
Phenilpropanoid																		
52	371	[M + H] ⁺	230,231	Sinapaldehyde glucoside	-	-	-	-	-	-	-	X	-	-	-	-	-	(Hung, 2016)
53	395	[M + Na] ⁺	-	Eleutheroside B	-	-	-	-	-	-	-	X	-	-	-	-	-	(Hung, 2016)

Ions detected in positive ionization mode of ethanolic extracts. * - = not detected.

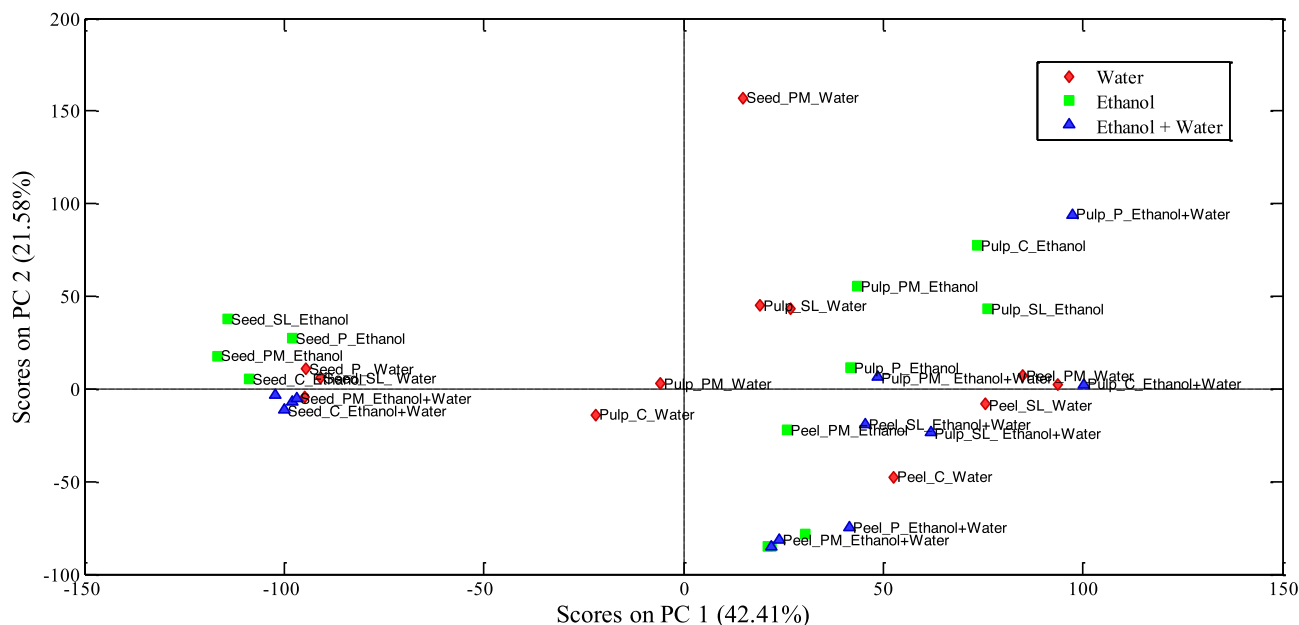


Fig. 2. Representation of araticum extracts in the first and second dimensions through Principal Component Analysis (PCA).

3. Results and discussion

Fig. 1 shows the extraction efficiency of each solvent (ethanol, water, and water/ethanol) by estimating the number of compounds extracted. Fig. 1 also displays the number of compounds extracted according to the fruit part (peel, seed, and pulp) and the region where the fruit was collected.

Solid-liquid extraction is the most common method for extracting metabolites from plant matrices. However, efficiency is affected by several factors, mainly the type of extractor solvent (Dorta et al., 2012). Ethanol presented a superior performance for 75 % of the samples, followed by water/ethanol (16.7 %), and water (8.3 %). Water/ethanol also showed acceptable efficiency, close to that observed for ethanol in some cases (for instance, for the pulp sample from the Sete Lagoas region). Conversely, the water/ethanol mixture extracted more compounds than ethanol for the Patos de Minas sample, whereas water was the most efficient solvent in extracting compounds from seeds collected in Cordisburgo. Finally, the sample with the highest number of compounds extracted by ethanol (22) was the pulp from Paraopeba. Therefore, the results displayed in Fig. 1 defined ethanol as the solvent selected for the subsequent extractions. These results also indicated that the chemical profiles varied according to the fruit part (peel, pulp, and seed) and maturation. Other factors influencing the chemical profile are geographic location, soil, and climate (Santos et al., 2022).

Table 1 shows the putative identification of the compounds extracted by ethanol. These compounds were identified by comparing their mass-to-charge ratio and fragmentation pattern with those available in literature. Such compounds were grouped into six different classes: acetogenins, alkaloids, fatty acids, esters, flavonoids, and phenylpropanoids. Acetogenins and alkaloids were the predominant classes, representing 62.3 % and 20.7 % of all compounds listed, respectively. Acetogenins and alkaloids are secondary metabolites in plants and possess well-known therapeutic potential (Prado et al., 2020).

Acetogenins with long aliphatic chains (32 to 34 carbon atoms) and with an unsaturated or saturated terminal γ -lactonic ring (Paes et al., 2016) are derived from long-chain fatty acids (Bermejo et al., 2005). They constitute a class of natural products isolated from species of the Annonaceae family, being present in practically all parts of the plant. They have antitumor and antibacterial activities (Paes et al., 2016; Bermejo et al., 2005; Justino et al., 2021; da Silva et al., 2014), in

addition to cytotoxic (Liaw et al., 2016), antineoplastic, antiparasitic, immunosuppressant, neurotoxic and pesticide effects (Neske et al., 2020).

Alkaloids are pharmacologically active substances (de Souza et al., 2021) and appear regularly in different plants of the *Annona* species (Avula et al., 2018). They are the main compounds responsible for the remarkable antimicrobial properties of these plants (Zhao et al., 2016).

The presence of alkaloids and acetogenins varied according to the fruit part. However, acetogenins were detected in most of the ethanol extracts. Based on the proposed identification, some acetogenins, such as anonacinone and squamolinone, were detected as their protonated forms (m/z 595 and 594, respectively). According to Avula and coworkers (Avula et al., 2018), these compounds were observed in the fruit pulps of all *Annona* species. Moreover, they were also detected in the seeds of *Annona squamosa* and *Annona X atemoya*, and leaves of *Annona squamosa*, *Annona muricata*, *Annona X atemoya*, and *Annona montana*. Bermejo and coworkers (2005) also identified squamolinone in *Annona squamosa* as the ion of m/z 594.

The compounds squamocin (m/z 646) and otivarinf (m/z 640) were identified in the seeds. Squamocin is present in seeds of different species of Annonaceae, namely *Annona squamosa*, *Annona muricata*, and *Annona X atemoya* (Avula et al., 2018), whereas otivarinf is related to *A. cherimolia* (Bermejo et al., 2005). Finally, the ion of m/z 588, referring to the protonated form of anodienine (CO,10), was the only acetogenin found in all the peel samples. This acetogenin was previously reported in branches of *Annona jahnii* (Bermejo et al., 2005; Colman-saizarbitoria et al., 1999).

Other compounds were also listed in the present work, such as fatty acids, esters, flavonoids, and phenylpropanoids, as well as in other works with species of the Annonaceae family. According to Hagr and coworkers (2019), the antioxidant activity of these plants is due to the unsaturated fatty acids. Flavonoids and phenylpropanoids are also related to the antioxidant activity of the fruits of different *Annona* species (de Moura et al., 2022). In addition to the pulp, the commonly consumed part of *Annona crassiflora*, the antioxidant activity of seeds has also been reported (Roesler et al., 2007). The presence of alkaloids and acetogenins has already been described for several genera of the Annonaceae family, the *Annonas* being the most notable of them (Peña-Hidalgo et al., 2021). Different parts of araticum have been widely used in popular medicine to treat inflammation, microbial infections,

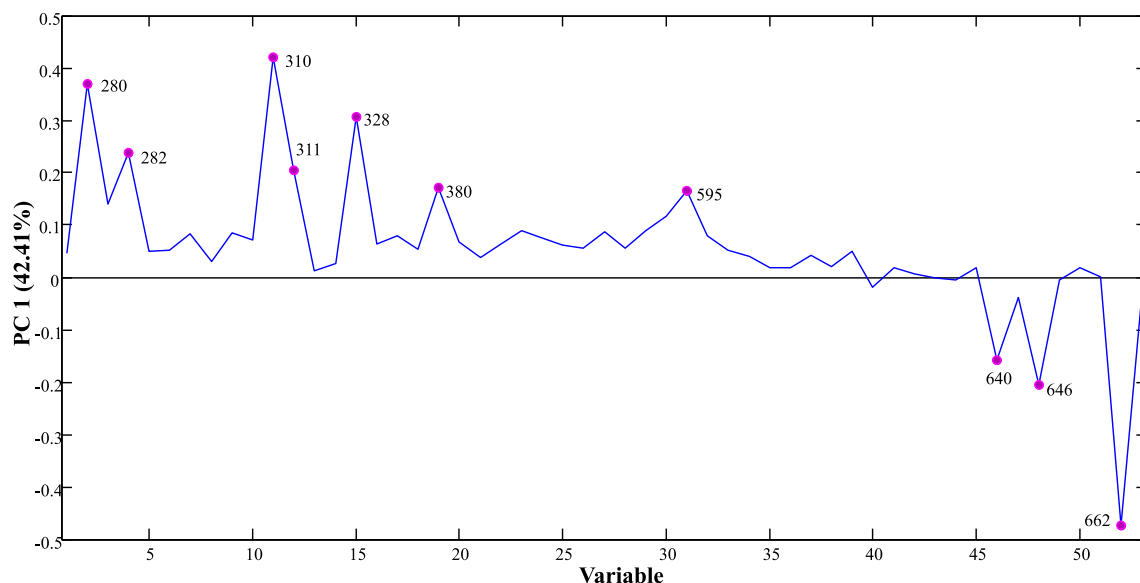


Fig. 3. Representation of the main ions responsible for sample separation.

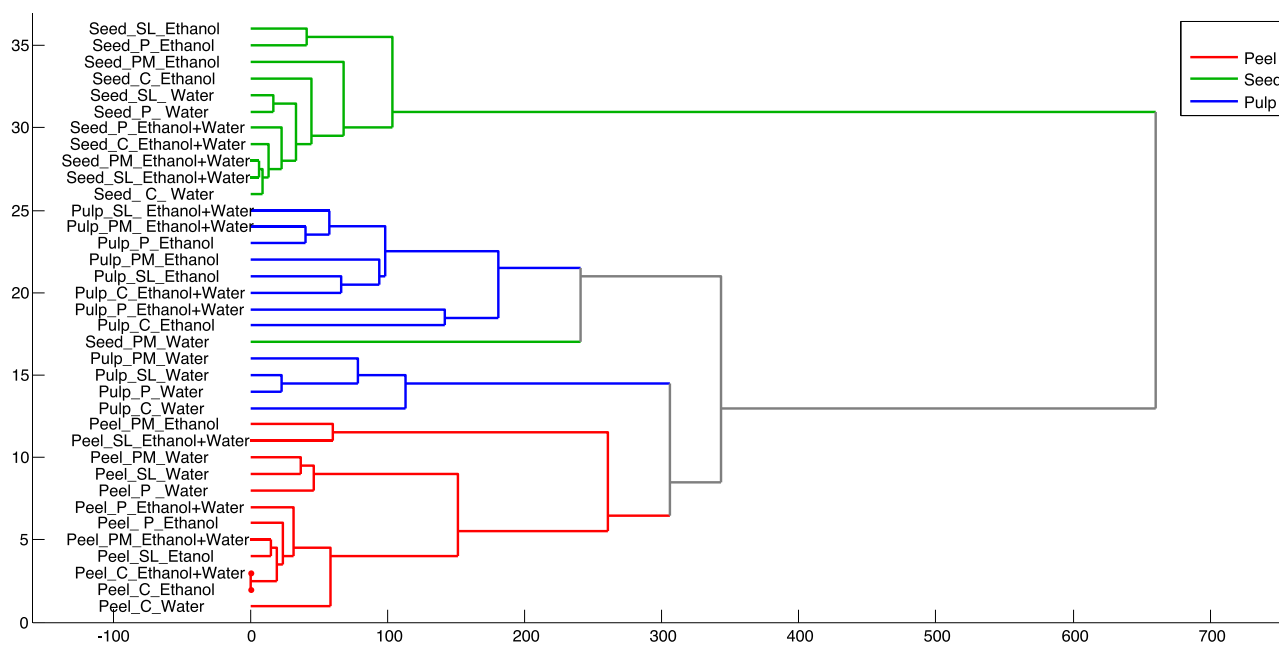


Fig. 4. Dendrogram obtained from the Analysis of Hierarchical Clusters (HCA) in the representation of different solvents. SL: Sete Lagoas; P: Paraopeba; PM: Patos de Minas; C: Cordisburgo.

malaria, venereal diseases, snakebites, diarrhea, and as cancer chemopreventive agents (Allisson B. Justino et al., 2021).

Ion intensities in the mass spectra were subjected to exploratory analysis using principal components (PCA). PCA was performed with the data from a matrix built with 36 lines (samples) and 53 variables (ions with their respective relative intensities). The model was built by selecting two principal components, as shown in Fig. 2.

The model explained 63.79 % of the total variance. PC1 (41.78 % of the total variance) allowed the separation of pulp and peel samples (positive scores) from the seed samples (negative scores). The samples were grouped according to the part of the fruit used regardless of the extractor solvent used. The ions responsible for separating each group are shown in Fig. 3. The compounds accountable for splitting the peel and pulp samples were highlighted as roemerin (m/z 280), norruciferin (m/z 282), guattescidin (m/z 310), actinodaphnin (m/z 311), isoboldine

(m/z 328), squamostolide (m/z 380), and anonacinone (m/z 595) (Avula et al., 2018; Bermejo et al., 2005; Bruginiski, 2016; Coria-Téllez et al., 2019; Rabelo et al., 2014; Rinaldi et al., 2017; Santos, 2015), mostly belonging to the class of alkaloids. The ions of m/z 640 (otivarin), 646 (squamocin), and 662 (24-acetylguacone) (Avula et al., 2018; Bermejo et al., 2005) were highlighted as responsible for separating the seed samples. Many of these compounds have relevant biological activity, thus indicating that all fruit parts may be helpful and should not be ruled out.

PCA is a handy chemometric tool for discriminating sample variations and revealing relationships between variables and samples. Besides PCA, hierarchical clustering analysis (HCA) is also used to validate PCA results (Cruz et al., 2022). Thus, HCA was performed to corroborate the PCA results and provide a better rationale for the sample grouping (Fig. 4).

As equally noticed for PCA (Fig. 2), the HCA methodology (Fig. 4) grouped the samples according to the parts of the fruit, i.e. seeds, pulp, and peel. Therefore, these findings suggest that the extractor solvent has no significant effects on the samples' chemical fingerprinting.

4. Conclusion

The results of this study emphasized the vast application possibilities of araticum (*Annona crassiflora* Mart.), a typical fruit of the Brazilian Cerrado's biome. The PS-MS analysis revealed that not only the pulp but also the peel and seed, treated as food waste, contain compounds with noticeable biological activities, such as alkaloids and acetogenins, among other secondary metabolites. The chemical profiles of this fruit's peel, seed, and pulp are somewhat distinct and depend on the collection region. Moreover, the extractor solvent did not distinguish among these different sample types. The results emphasized the richness of this Brazilian native fruit, including parts that are treated as food waste, such as peel and seed. In conclusion, the results reported herein open new possibilities for using a still underexploited product.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodres.2022.111687>.

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