

Article

The Active Aroma of “Cerrado” Cashew and Cagaita Fruits: Comparison between Two Extraction Methods

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Abstract: The objective of the present work is to characterize the aroma of “Cerrado” cashew (*Anacardium othonianum* Rizz.) and cagaita (*Eugenia dysenterica*) pulps. For this, we used headspace (HS) and two extraction methods (solid-phase extraction, SPE and solid-phase microextraction, SPME), as well as gas chromatography-olfactometry (GC-O) and gas chromatography-mass spectrometry (GC-MS) for identification of aroma compounds. While SPME was more efficient and extracted 17 and 21 compounds for “Cerrado” cashew and cagaita pulps, respectively, the SPE method extracted 13 compounds for both pulps. SPME showed higher modified frequency (MF), that is, compounds perceived with higher intensity and by number of judges during olfactometry. On the other hand, the results obtained in this work showed that the extraction techniques seem complementary, since some compounds were not identified by SPE, but were identified by SPME, and vice versa.

Keywords: *Anacardium othonianum* Rizz.; *Eugenia dysenterica*; native fruits; Cerrado biome



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1. Introduction

The Cerrado is the second largest of the six biomes that Brazil presents, with an area of approximately 2,036,448 km², representing 23.92% of the Brazilian territorial area [1]. Some native savanna fruit have been described as good sources of unique sensory characteristics and bioactive compounds that present health-promoting properties [2,3]. Because of the virtually unknown information about most native species, however, they have so far been commercially devalued [4].

Studies cover the chemical composition of fruits native to Brazilian biomes, but these fruits are also widely reported for sensory characteristics, such as aroma, that provide unique experiences when consumed [5–7]. The “Cerrado” cashew tree (*Anacardium othonianum* Rizz.) has larger and obovate leaves in comparison to common cashew (*Anacardium occidentale*). The peduncles are smaller red or orange and either rounded or obovate conical [8]. The *A. othonianum* Rizz. pseudofruits have been described as a good source of vitamin C content (10 to 71 mg/100 g) [9–11]; phenolic compounds; flavonoids, such as vitexin and hesperidin [12]; anthocyanins, such as cyanidin, delphinidin, pelargonidin, and peonidin [9,10]. The cagaiteira (*Eugenia dysenterica*) is a half-height tree (4 to 10 m) with a crooked trunk and branches and axillary inflorescence. Cagaita fruits have been reported as rich in phenolic compounds, such as ellagic acid and kampeferol, as well as epicatechin [13]. The chemical composition of fruit is normally responsible for the odor-producing compounds of fruit aroma [14]. In this way, it becomes important to study

the aroma of native fruits because they are derived from a unique and species-specific chemical composition.

In aroma studies, the most used technique is gas chromatography (GC) coupled with mass spectrometry (MS) [14]. While GC is used to separate the compounds previously extracted present in the aroma, MS will identify these compounds. Thus, the olfactometry technique is used with GC-MS to determine the importance of each isolated compound (intensity and perception description), as it can be perceived by a sensory panel [15]. The preparation of the sample is the most critical step to be carried out for aroma compounds research. The extract or sample isolate that will be used for the analysis must represent the aroma composition present in the food. Therefore, a representative method for the isolation of volatile compounds must include qualitative and quantitative aspects. In this context, the extract can be (i) prepared directly from the sample and represent the composition of the food, or (ii) extracted with headspace and represent the composition of the volatile compounds released by the sample in a closed system, with the inert gas flow through the system [16,17].

Among these techniques, those that offer simplicity, automation, and cost reduction are solid-phase extraction (SPE) and solid-phase microextraction (SPME) [18]. SPE separates the aroma compounds using a solid adsorbent phase, with the function of retaining the compounds, and a mobile phase, which will elute these compounds (liquid, emulsified, or a gas) [16,19]. Meanwhile, SPME extraction uses a silica-coated fiber, solid phase, which adsorbs the compounds released by the sample, which is directly injected into the GC [18].

The objective of the present work is to characterize the aroma compounds of “Cerrado” cashew (*Anacardium othonianum* Rizz.) and cagaita (*Eugenia dysenterica*) pulps. For this we used headspace (HS) and two methods (solid-phase extraction, SPE, and solid-phase microextraction, SPME) for aroma compounds extraction, as well gas chromatography-olfactometry (GC-O) and gas chromatography-mass spectrometry (GC-MS) for their identification of aroma compounds.

2. Materials and Methods

2.1. Plant Material

The fruits of cagaita and “Cerrado” cashew were collected in Montes Claros de Goiás city (latitude 16°06'20, longitude 51°17'11, 459 m), washed, sanitized (NaClO, 15 mL/L for 15 min), and rinsed in water. The cashew pseudofruits were homogenized in an industrial blender and filtered (nylon screens) to remove the residue. The cagaita fruits were separated manually from the seed, homogenized, and filtered (nylon screens). Each pulp was combined with 5 g of ascorbic acid and 0.4 g of sodium fluoride [20], stored in 300 mL sterile bottles, and frozen (−6 °C) for transport.

The “Cerrado” cashew pulp showed moisture, protein, lipid, carbohydrate, and ash contents of 87.99, 1.02, 0.11, 10.23, and 0.64 g/100 g, respectively (Table 1). The cagaita pulp showed moisture, protein, lipid, carbohydrate, and ash contents of 93.65, 2.93, 0.01, 3.06, and 0.32 g/100 g, respectively. While the pH of the pulps was close (3.26 and 3.23 for “Cerrado” cashew and cagaita pulps, respectively), the soluble solids in the “Cerrado” cashew pulp (13.43 °Brix) were almost twice that compared to the cagaita pulp (7.40 °Brix).

Table 1. Chemical composition of “Cerrado” cashew and cagaita pulps.

	Cashew	Cagaita
Moisture (g·100 g ^{−1})	87.99 ± 0.74	93.65 ± 0.14
Protein (g·100 g ^{−1})	1.02 ± 0.18	2.93 ± 0.11
Lipids (g·100 g ^{−1})	0.11 ± 0.01	0.01 ± 0.00
Carbohydrates (g·100 g ^{−1})	10.23 ± 0.85	3.06 ± 0.04
Ash (g·100 g ^{−1})	0.64 ± 0.00	0.32 ± 0.02
Energy (kcal)	45.68 ± 2.97	24.11 ± 0.55
pH	3.26 ± 0.08	3.23 ± 0.08
Total solids soluble (°Brix)	13.43 ± 0.29	7.40 ± 0.00

2.2. Gas Chromatography-Olfactometry Study

2.2.1. Preparation of the Extract

Two methods were used for the extraction of the compounds present in the aroma of the pulps studied: (i) solid-phase extraction (SPE) and (ii) solid-phase microextraction (SPME).

For SPE, the volatile compounds from 30 g of pulp were collected using a previously described trapping system [17]. Briefly, the trapping system consisted of a standard polypropylene solid-phase extraction tube containing 400 mg of LiChrolut EN resin (Merck, Darmstadt, Germany). The cartridge was placed on top of a gas extraction vessel which contained the pulp. The gas extraction vessel (as Figure 1 described in another review by our group [14]) was kept in a water bath at 37 °C, and a nitrogen stream (60 mL/min) was flushed through the vessel for 210 min. Volatile compounds released in the vessel headspace were trapped in the cartridge and later eluted with 2 mL of dichloromethane in methanol (95:5, *v/v*). The extract was then concentrated under a nitrogen stream to a final volume of 500 µL.

For SPME, 2 g of pulp was collected into the vial (20 mL) and conditioned for 10 min at 37 °C while SPME fiber (divinylbenzene/carboxen/polydimethylsiloxane (PDMS/DVB) fiber of 2 cm–50/30 µm (Bellefonte, PA, USA)) was conditioned in the chromatograph for the same time. For SPME, the fiber was stored at room temperature and subjected to the heating process (250 °C for 5 min) for cleaning before analysis. From there, it was then conditioned in the chromatograph at 37 °C for 10 min, to be exposed to the headspace for 60 min, at 37 °C. The SPME fiber was then exposed to the headspace of the sample for 60 min at 37 °C.

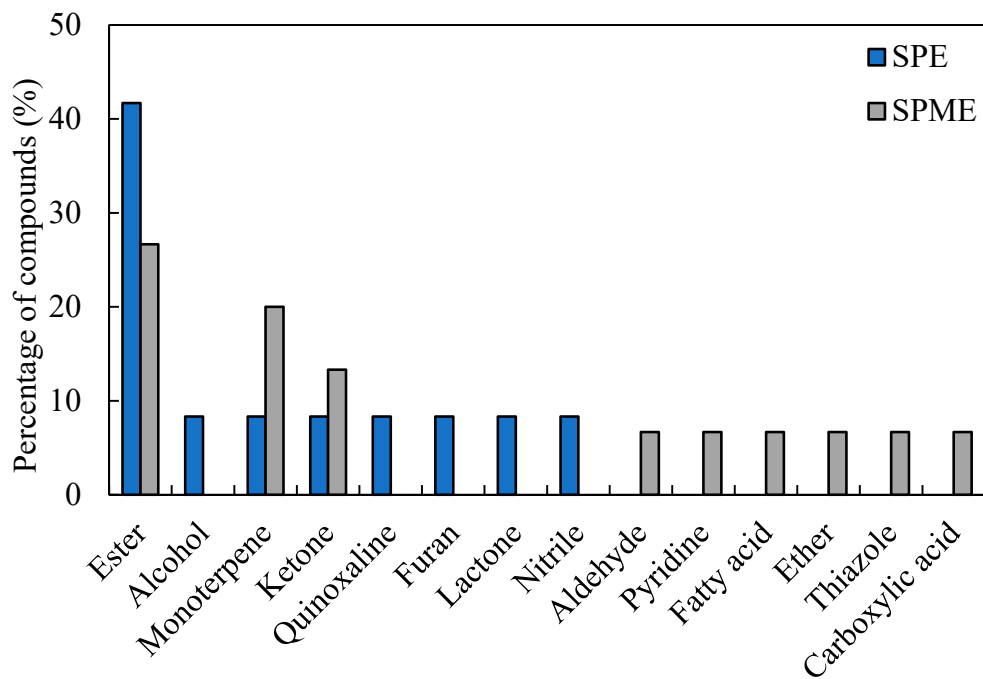
2.2.2. GC-O and GC-MS Analysis

The concentrated extract (1 µL) obtained for SPE was used for GC-O analysis. The analyses were carried out using an Agilent HP 5890 Series II Plus gas chromatograph (Santa Clara, CA, USA) equipped with a flame ionization detector (FID) and a sniffing port. The column used was a DB-WAX (30 m × 0.25 mm I.D., 0.5 µm film thickness; J&W Scientific, Folsom, CA, USA). The chromatograph had a standard split/spitless injector, and an SPME liner with a 0.75 mm internal diameter was used. The injection mode used was pulsed-spitless at a temperature of 250 °C with a pressure pulse of 62 kPa for 3 min. The carrier gas was H₂ at a rate of 1 mL/min and a pressure of 45 kPa. At the output of the chromatographic column, the flow was divided into equal parts between the olfactometry detector and the FID. Injector and detector were both kept at 250 °C. The oven temperature was held initially at 40 °C for 3 min, then increased by 5 °C/min to 220 °C, and finally kept for 59 min.

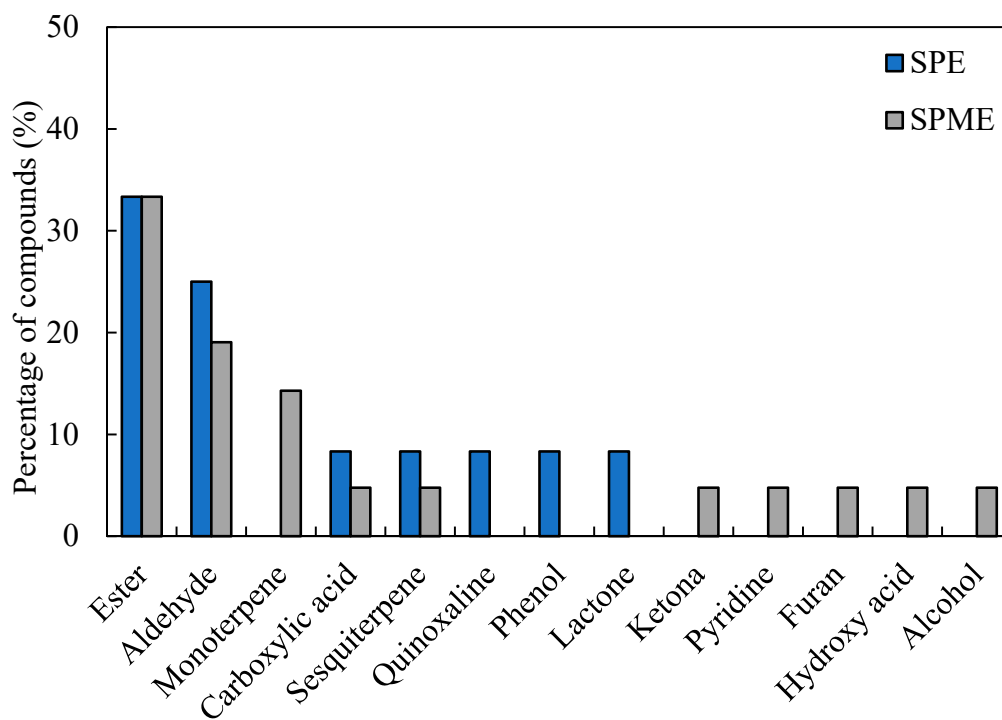
A panel of five expert judges (two women and three men, with ages ranging from 20 to 37) from the laboratory staff with extensive experience in GC-O analysis was used in this study. Snorting time was approximately 15 min per judge, randomly distributed during the section, per replicate. Panelists were asked to score the intensity of each odor stimulus using a 4-point scale (0 = not detected, 1 = weak, 2 = light but not intense note, 3 = intense note) [21]. Afterward, the modified frequency (MF) was calculated [22] with Equation (1).

$$MF(\%) = [F \cdot I]^{\frac{1}{2}} \quad (1)$$

where *F* is the detection frequency of an aromatic attribute, expressed as a percentage of the total number of judges, and *I* is the average intensity, expressed as a percentage of the maximum intensity. Only those odorants that reached an *MF* higher than 15% in at least one of the samples are included in the present work.



(A)



(B)

Figure 1. Percentage of compounds by chemical classification identified in “Cerrado” cashew (A) and cagaita (B) pulps obtained using headspace solid-phase extraction (HS-SPE) and headspace solid-phase microextraction (HS-SPME) with gas chromatography-olfactometry (GC-O).

The gas chromatograph mass spectrometry analyses were carried out in an Agilent 6890 gas chromatograph (Santa Clara, CA, USA) simultaneously coupled to an odoriferous door (Gerstel ODP, Linthicum, MD, USA) 2 and a 5973 Network mass spectrometry detector with a quadrupole analyzer. The chromatograph had a standard split/spitless injector

(270 °C) with a pressure pulse of 62 kPa for 3 min. Helium was used (analytical grade 5.0) as the carrier gas at a constant flow of 1 mL/min during the entire analysis.

The chromatograph was equipped with the HP INNOWax column (50 m × 0.25 I.D., 0.25 µm film thickness) (Agilent, Santa Clara, CA, USA). The oven temperature was held initially at 50 °C for 3 min and then increased to 160 °C by 4 °C/min. It was later increased to 250 °C by 25 °C/min and finally kept for 22 min at 250 °C.

An alkane solution (C₈–C₂₈) (Sigma-Aldrich Corp., St. Louis, MO, USA), 10 mg/L in dichloromethane, was used to calculate the linear retention indices (LRI) for each analyte. The odorants were identified by a comparison of their odor and chromatographic retention index (LRI) on the DB-WAX column and MS spectra with those of pure chemical standards. The Spectral Works AnalyzerPro software, equipped with NIST 2.0 MS library (NIST, Gaithersburg, MD, USA), was utilized in the identification.

2.3. Statistical Analysis

The experiment was replicated three times and the results correspond to the mean of the experiments.

3. Results

The present work identified a total of 22 and 30 odor zones for “Cerrado” cashew and cagaita pulps, respectively. The “Cerrado” cashew and cagaita pulps showed 17 and 21 compounds in aroma by SPME, respectively, while 13 compounds for both pulps were found using SPE. The compounds extracted by SPME showed higher modified frequency (MF); that is, the calculation based on the intensity of the compounds perceived with and/or number of judges that perceived during olfactometry.

The advantages of the SPME method are (i) higher velocity of the technique due to its practicality of operation, (ii) lower cost of analysis due to the possibility of reusing the fiber and no use of solvents, and (iii) less contamination with other analytes [18,19]. In contrast, SPE promotes the maximization of the concentration and consequently increases the identification of the aroma compounds in the sample [15,16,19]. In the present work, more compounds with higher MF were found by SPE compared with SPME, regardless of the fruit pulp used.

Table 2 shows the compounds obtained by SPE and SPME for the aroma of “Cerrado” cashew pulp and its comparison with the compounds reported in the literature for *Anacardium occidentale* [23–28]. The table provides the chromatographic retention data, the odor description, the chemical identity of the odorant responsible for the odor, the olfactometric scores (expressed as MF (%)), and the identification method for each of the different aromatic compounds detected in the olfactometric experiments. Between the two methods (SPE and SPME) used for the “Cerrado” cashew pulp, similarity in the identification of compounds occurred with methyl propanoate (62.36 and 59.63%), isobutyl acetate (47.14 and 70.71%), δ-3-carene (47.14 and 57.74%), 1,5-octadien-3-ol (47.14 and 66.67%), methyl butanoate (52.70 and 94.28%), ethyl isobutyrate (62.36 and 88.19%), and 1-octen-3-one (47.14 and 66.67%). Among these, the compounds that showed the highest MF for both methods were isobutyl acetate, methyl butanoate, and ethyl isobutyrate.

Table 2. Gas chromatography retention data, olfactometry description, chemical identification, and modified frequency (MF) (%) for odorants identified in “Cerrado” cashew obtained using headspace solid-phase extraction (HS-SPE) and headspace solid-phase microextraction (HS-SPME) with gas chromatography-olfactometry (GC-O).

LRIDB WAX	Literature LRI	Compounds	Description	MF (%) SPE	SPME	Reference That Reported the Compound
823	821	Isobutyraldehyde	Green, fruity, cashew ^a	-	63.25	
923	927	Methyl propanoate	Cashew, sweet ^a	62.36	59.63	
928	968	2-methyl-3-buten-2-ol	Green ^b	43.46	-	[25]
957	955	Ethyl isobutyrate	Cashew, sweet, fruity ^b	62.36	88.19	[25]
984	990	Methyl butanoate	Cashew, sweet, fruity ^b	52.70	94.28	[29]
1049	1015	Isobutyl acetate	Vanilla, cashew, sweet ^b	47.14	70.71	[24]
1071	1060	Ethyl 3-methylbutanoate	Fruity, sweet ^b	48.30	-	[24,25,27,28]
1129	1148	δ-3-carene	Acid, lemon ^b	47.14	57.74	[23]
1208	1201	D-limonene	Orange, fresh ^b	-	57.74	[26,27]
1304	1336	1-Octen-3-one	Sweet, mushroom ^a	47.14	66.67	
1336	1336	6-methyl-5-hepten-2-one	Unpleasant ^b	-	66.67	[29]
1360	1354	Ethyl pyridine	Coffee, peanut ^a	-	81.65	
1459	1458	Sabinene trans hydrate	Sweet, guava ^a	-	52.70	
1634	1637	2-methyl quinoxaline	Toasted, peanut ^a	56.76	-	
1659	1665	Isovaleric acid	Pungent, insect ^b	-	74.54	[24,25,28,29]
1699	1655	Estragole	Citrus, guava ^a	-	60.55	
1734	1750	(cis) linalool oxide	Acid ^b	40.82	-	[29]
1764	1767	Acetyl thiazole	Earth, lavender ^a	-	52.70	
1965	1962	(E)-2-hexenoic acid	Nasty, peanut ^b	-	54.77	[24,25]
2509	2465	Coumarin	Apple, sweet ^a	52.70	-	
2560	2650	Hydrocyanic acid	Fungus, toasted ^a	40.82	-	

LRI, linear retention index. -, not identified. ^a Identification based on the similarity of observed chromatographic retention on DB-WAX column, odor, and mass spectrometric data. ^b Identification based on the similarity of observed chromatographic retention on DB-WAX column and odor description data were similar to those reported in the literature.

According to the MF (Table 2), the most potent odorants in the “Cerrado” cashew were methyl propanoate (~63%) and methyl butanoate (~94%), by SPE and SPME, respectively. The presence of these compounds in the pulp aroma correlates with a sweet aroma described for *A. othonianum* juice, by descriptive sensory analysis in another study by our team [11].

This is the first report in the literature of the aroma composition of *A. othonianum*, and, therefore, the compounds found for this variety were compared with another species of the same genus (*A. occidentale*) that was previously reported in the literature. Eleven of the compounds found in the present work were previously reported for *A. occidentale* in the literature (Table 2). Mamede, et al. [30] reported that the presence of ethyl butanoate is known to be an important ester for the aroma of other tropical fruits, such as cashew fruit (or cashew apple); however, this compound was not found in this present work (Table 2). The current work is the first report of isobutyraldehyde, methyl propanoate, 1-octen-3-one, ethyl pyridine, sabinene trans hydrate, 2-methyl quinoxaline, estragole, acetyl thiazole, coumarin, and hydrocyanic acid for the *Anacardium* genus.

Oct-1-en-3-one, ketone analog of the alkene 1-octene, was reported in the present work. Lipid peroxides of the skin are formed by oxidation, either enzymatically by lipoxygenases or by air oxygen. This compound has already been identified as important for lychee (*Litchi chinensis* Sonn.) [31].

Coumarins are intermediate compounds for the biosynthesis of flavonoids in vegetables. They are derived from the metabolism of phenylalanine with p-hydroxy-cinnamic acid, known as p-coumarinic acid, as precursors, which are hydroxylated at the C-2 position. These compounds were found for the “Cerrado” cashew pulp when the SPE was used in the extraction (Table 2). The identification of coumarins corroborates what was reported by Oliveira, Silva, Resende, Pereira, Silva and Egea [12], who reported the presence of flavonoids for *A. othonianum* pseudofruits.

Thus, it was possible to observe that although the two species (*A. othonianum* and *A. occidentale*) are often confused in the literature and reported as the same species, they

have different and unique sensory characteristics, as well as nutritional aspects, as already highlighted in other works of our team [11,12,32].

Table 3 shows the compounds obtained by the SPE and SPME methods in the aroma of cagaita pulp and the comparison with the compounds reported in the literature [33]. Between the two methods used for aroma extraction of the cagaita pulp, the similarity in the identification of compounds occurred with ethyl acetate (57.74 and 59.63%), methyl butanoate (57.74 and 81.65%), and 2-octenal (47.14 and 57.74%). Only four of the compounds found in the present work were previously reported for cagaita pulp in the literature.

Table 3. Gas chromatography retention data, olfactometry description, chemical identification, and modified frequency (MF) (%) for odorants identified in cagaita pulp obtained using headspace solid-phase microextraction (HS-SPME) and headspace solid-phase extraction (HS-SPE) and gas chromatography-olfactometry (GC-O).

LRI DB WAX	Literature IR	Compounds	Description	MF SPE	SPME	References That Reported the Compound
923	907	Ethyl acetate	Sweet, green ^b	57.74	59.63	[33]
954	951	N-ethyl propanoate	Green, cagaita ^a	-	81.65	
981	983	2-pentanone	Green ^a	-	57.74	
994	990	Methyl butanoate	Coffee, sweet ^a	57.74	81.65	
1146	1178	α -terpinene	Orange ^b	-	66.67	[33]
1207	1220	Ethyl hexanoate	Balsamic, green ^b	-	74.54	[33]
1305	1358	Ethyl lactate	Citric ^a	-	62.36	
1316	1320	2-octenal	Green ^a	47.14	57.74	
1349	1354	Ethyl pyridine	Coffee, peanut ^a	-	62.36	
1356	1360	Hexanol	Green, flower ^a	-	62.36	
1360	1401	2,4-heptadienal	Nut, earth ^a	-	62.36	
1399	1445	Propyl hexanoate	Green, coffee, cherry ^a	-	59.63	
1442	1464	2-(3-methyl-2-butenyl)-3-methylfuran	Spice ^a	-	66.67	
1463	1467	limonene oxide	Green, sweet, fruity ^a	-	57.74	
1552	1546	β -cubebene	Green, lemon ^a	-	53.75	
1572	1523	Propanoic acid	Citric ^b	-	53.75	[33]
1634	1637	2-methyl quinoxaline	Sweet, fruity, green ^a	66.67	-	
1717	1753	4-ethyl benzaldehyde	Sweet, balsamic ^a	-	59.63	
1757	1779	(E)- α -bergamotene	Fresh, soil ^a	-	59.63	
1779	1795	Methyl laurate	Sugar ^a	-	52.70	
1806	1807	2-dodecenal	Citric ^a	47.14	-	
1829	1829	Hexanoic acid	Soap, sweet ^a	47.14	-	
2146	2139	Ethyl cinnamate	Sweet, fruity ^a	47.14	-	
2176	2170	4-Ethylphenol	Bitter, sour ^a	47.14	-	
2223	2246	β -eudesmol	Green, apple ^a	47.14	-	
2283	2284	δ -undecalactone	Green, melon ^a	47.14	-	
2318	2358	Diethyl tartrate	Coffee, almond ^a	-	56.76	
2330	2358	Isopropyl palmitate	Sweet ^a	47.14	-	
2562	2517	Vanillin	Vanilla, soil, coffee ^a	-	64.98	
2610	2612	Ethyl vanillin	Green, floral ^a	47.14	-	

LRI, linear retention index. -, not identified. ^a Identification based on the similarity of observed chromatographic retention on DB-WAX column, odor, and mass spectrometric data. ^b Identification based on the similarity of observed chromatographic retention on DB-WAX column and odor description data were similar to those reported in the literature.

According to the MF list in Table 3, the most potent odorants in the cagaita by SPE and SPME, respectively, were 2-methyl quinoxaline (~67%) and n-ethyl propanoate and methyl butanoate (~82%). Methyl butanoate is the most important odorant in strawberry fruit (*Fragaria* \times *ananassa*) [34].

Ester compounds were the most prevalent class in “Cerrado” cashew and cagaita pulps (Figure 1). Indeed, esters (described as fruity, floral, and sweet aromas) are the predominant volatile compounds in many fruits, including apples, bananas, and pineapples [35]. These compounds have already been reported to be responsible for the aroma of other tropical fruits, such as sweet passion fruit, yellow and purple passion fruits [30], and banana [36], among others.

In the present work, alcohol was the second most perceived group in “Cerrado” cashew (Figure 1A). In addition to being important for the active aroma of fruits, these compounds can be precursors in the formation of esters, the most perceived class of compounds in this work for both fruits. Alcohols form esters by catalysis of different alcohol acyl-transferases (AATs) [34]. Meanwhile, for cagaita pulp, the second most found class was aldehydes (Figure 1B). Volatile aldehydes are formed by oxidative degradation of fatty acids by lipoxygenase or hydroperoxide lyase, which then convert to alcohols by alcohol dehydrogenases (ADHs). Aldehydes also are converted into esters by the actions of ADH and AAT [34]. Thus, the presence of alcohols or aldehydes perceived in “Cerrado” cashew and cagaita pulps, respectively, corroborate the fact that ester was considered the most important group for the active aroma of both fruits.

Terpenes were identified as a second and third class, with more compounds for “Cerrado” cashew and cagaita pulps, respectively. Among the terpenes found in the present work, only sabinene trans hydrate has not been reported for *A. occidentale*, until the present moment. Terpenes are a class of compounds considered important for the aroma of grape [37] and mango fruits [38].

Silva, Bueno et al. [33] had reported that monoterpene (34.64%) and esters (36.28%) were the predominant classes in cagaita pulp. Indeed, in the present work, the aldehyde class was found to be the second most important class (Figure 1B). Although the predominant composition of C₆ aldehydes in volatile fruit profiles has previously been associated with immaturity, these compounds have already been reported for Atlantic Forest native fruits, such as strawberry and lemon guava [20].

4. Conclusions

In the present work, the SPE and SPME techniques were evaluated for two fruits native to the Cerrado. SPE was able to better capture the more significant number and intensity of perceived aroma compounds. On the other hand, the results obtained in this work showed that the extraction techniques seem complementary, since some compounds were not identified by SPE but were identified by SPME, and vice versa.

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