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Volatile compounds of umbu (*Spondias tuberosa* Arruda) fruits during post-harvest ripening from two accessions

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Abstract

The chemical composition of volatile compounds from *Spondias tuberosa* fruits were investigated at four days of maturity and from two accessions. These days were characterized through the compounds' profiles obtained by extracting volatiles using solid-phase microextraction in headspace mode (HS-SPME) and analyzed by gas-chromatography coupled to mass spectrometry (GC-MS). A total of 27 and 22 compounds were identified from the EPAMIG-C02 and EPAMIG-C10 accessions, respectively. The main chemical class in both accessions were the esters, aldehyde, alcohols and terpenes. The study revealed a tendency to increase the ester content and decrease the aldehyde and terpene content during four days of post-harvest ripening for the two accessions. This behavior may be monitored by five key compounds such as two esters (ethyl butanoate and ethyl hexanoate) and three aldehydes (hex-2-enal, nonanal and dec-2-enal). These compounds may be used as markers for the maturity stage for the two accessions. The Principal Components Analysis (PCA) accumulated 73.85% of the total variance in principal components 1 and 2 and showed that it is possible to differentiate the fruit ripening stages through these compounds.

Keywords: headspace extraction; aromatic fruit; caatinga fruits; *Spondias*; post-harvesting.

Practical Application: Understanding physiology, quality and flavor fresh umbu and beneficiated products.

1 Introduction

The Caatinga is one of the main biomes in Brazil and has stood out for its variety of typical and exotic fruit species which present high potential for the food and agro-industries (Filizola & Sampaio, 2015; Costa, 2011). Brazil is the world's biggest fruit producer, mainly from the country's semi-arid region (Barbosa, 2006; Costa, 2011).

Within this scenario, we may highlight *Spondias tuberosa* fruits, popularly called umbu (Cavalcanti et al., 2000; Costa, 2011; Lima et al., 2018; Saturnino & Souza, 2019). This fruit is abundant in this region due to it being highly adaptable to severe conditions in the Brazilian Caatinga biome (Cavalcanti et al., 2000; Lima et al., 2018).

S. tuberosa fruits have already exerted significant economic representativeness, which is tending to increase due to the fruit domestication in progress, to the growing international interest in new exotic fruit species and consequently the increase in commercial crops (Donato et al., 2019; Neves & Carvalho, 2019; Saturnino & Souza, 2019).

Despite all of the economic and social importance that *S. tuberosa* fruits have shown, a significant part of *S. tuberosa* production has still been lost, which has been attributed to a lack of better post-harvest knowledge (Costa, 2011; Lima & Castricini, 2019). Some studies have evaluated the variation in chemical parameters during the post-harvest stage in *S. tuberosa* fruits, such as pH, titratable acidity, soluble solids, sugar contents and others (Campos et al., 2018; Galvão et al., 2010; Menezes et al., 2017). However, there are few scientific studies which have evaluated the chemical composition of the volatile fraction of *S. tuberosa* fruits (Thomazini et al., 1998 as cited in Franco & Janzantti, 2005; Galvão et al., 2011). The work carried out by Galvão et al. (2011) studied volatile compounds at two maturation stages (half-ripe and ripe), but used solvent extraction and heating. Solid phase microextraction in headspace mode (HS-SPME) is currently the main method for extracting volatile compounds from fruits because it does not use solvents and enables using mild temperatures, therefore it avoids changes in the chemical structure of the compounds of interest (Chen et al., 2020; Rahman et al., 2021; Yang et al., 2020; Zhang et al., 1994).

In this sense, the chemical composition of these volatile substances is strongly dependent on the species, accessions, environment and agricultural conditions, maturity stage, and extraction conditions (Barreiros et al., 2018; Cuevas et al., 2017; Kader, 2008; Liu et al., 2017; Silva et al., 2019). These compounds are continuously synthesized during growth and maturation of fruits; thus, volatile compounds' composition may change at different maturity stages. A detailed chemical characterization of volatile compounds from *S. tuberosa* fruits is important to

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understand their nutritional value and to estimate the quality and value of the final product.

Therefore, the aim of this study was to analyze the chemical composition and evolution of the volatile compounds from *S. tuberosa* fruits from two accessions during four days of post-harvest maturity using solid-phase microextraction in headspace mode (HS-SPME). These results were used to classify the samples by principal component analysis (PCA) according to the content and chemical composition of volatile compounds.

2 Materials and methods

2.1 Fruit

Fruits from two accessions with different geographic origins (EPAMIG-C02 and EPAMIG-C10) were harvested in the experimental accession collection from EPAMIG NORTE in Nova Porteirinha city, Minas Gerais State, Brazil (SisGen registration number: A6AA0F7). The area is delimited by 15° 48' 8.932" S, 43° 17' 49.445" W; 15° 48' 3.060" S, 43° 17' 43.811" W; 15° 48' 4.075" S, 43° 17' 42.648" W; 15° 48' 10.159" S, 43° 17' 48.188" W. This experimental accession collection is the result of selection and planting in the Institution of *S. tuberosa* distributed in the North of Minas Gerais, specifically EPAMIG-C02 and EPAMIG-C10 were obtained from matrices respectively located in *Porteirinha-MG* and *Januária-MG* (Moreira et al., 2007).

Physiologically ripe fruits with uniform characteristics of a smooth surface and a maturity stage called "swollen" by the regional population were harvested from the trees in February 2019. As expected, fruits of different origin showed different characteristics, even though they were at a similar ripeness stage (Lima & Castricini, 2019). Fruits from the EPAMIG-C10 accession showed bright green peels and oval shape, while fruits from the EPAMIG-C02 accession had a rounded shape and light green peels (Figure 1). The fruits of each accession were harvested on the same day, distributed into four groups, kept at environmental temperature, and analyzed in the: (*i*) first, (*ii*) second, (*iii*) third, and (*iv*) fourth days after harvest. The visual changes in the fruits as a function of the post-harvest period due to ripening may be seen in Figure 1(c).

The fruit pulps from each accession were separated from the peel and seeds and mixed using a domestic mixer for 30 s. Thus, 0.20 g of NaCl salt was added per gram of fruit pulp to increase the polarity of the matrix and reduce the solubility of volatile compounds in the matrix, and again mixed for 60 s. Finally, 4.8 g from the sample was added into 20 mL vials and were sealed for volatile compound extract.

2.2 Extraction

The extraction of volatile compounds was performed by solid phase microextraction in headspace mode (HS-SPME). A manual holder and SPME-fiber divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) (Supelco - São Paulo, Brazil) were used in the procedure. For each repetition, about 5 fruits (peel and pulp) of the same bunch were homogenized and immediately submitted to HS-GC-MS. Each vial with 4.8 g from samples were incubated in a thermostatic bath at 40 °C for 10 min and then the SPME-fiber was inserted in the vials for 20 min. All procedures were performed in duplicate.

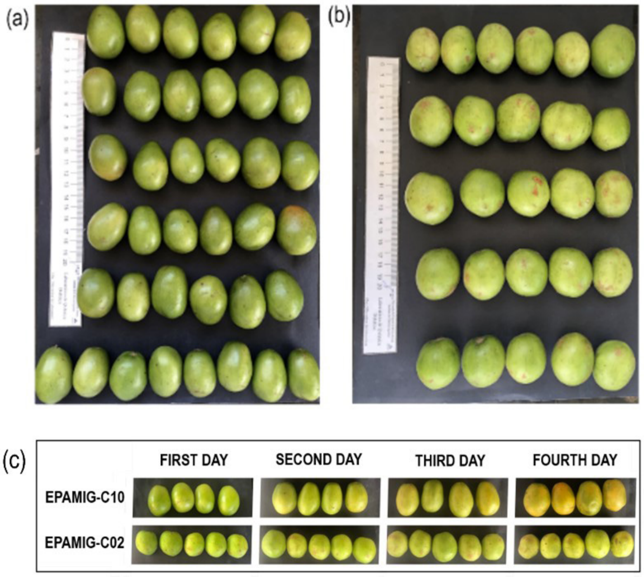

Figure 1. *S. tuberosa* fruit photographs harvested from (a) EPAMIG-C10 and (b) EPAMIG-C02 accessions and (c) EPAMIG-C10 and EPAMIG-C02 accessions during the ripening process.

2.3 Gas chromatography-mass spectrometry analysis

SPME-fiber was injected into the gas-chromatograph after the extraction for compound desorption and was maintained in the device until the end of the chromatographic analysis. Static headspace analysis was performed using a PAL Syr HS 2.5 mL for combi-PAL. GC-MS analyses were carried out using an Agilent Technologies (GC 7890A) apparatus coupled with a mass spectrometer (MS 5975C) which was equipped with MS reference libraries (NIST 2.0 library). Analyses were carried out using a DB-5 MS capillary column of 30 m x 0.32 mm x 0.25 µm. All samples were injected in splitless mode at 220 °C. The programmed temperature of the GC oven started at 60 °C, then increased by 3 °C min^{-1} to 240 °C. Helium (99.9999% purity) was used as carrier gas at a flow rate of 1 mL min^{-1}. The interface temperature was 280 °C, and the acquisition mass range was 45-600 m/z. A standard solution from a series of saturated alkanes (C7 - C40) from Sigma-Aldrich was injected under the same conditions to calculate the Van den Dool and Kratz retention index (LRI) of the sample compounds. The volatile compounds were identified by comparing the mass spectra obtained with those from the NIST library (NIST 2.0 database) and the retention index obtained (LRI) with those from literature.

2.4 Multivariate analysis

The mean values of volatile compounds in the pulp of the four ripening stages were examined by analysis of variance (5%) using the free version of the Assistant 7.6 beta statistical software program (2011). Duncan's multiple range test was used to compare various mean values for this variable when significant differences were detected.

The data in the multivariate analysis were arranged into a matrix consisting of variables (columns) as each identified compound content represented by its chromatographic peak area relative; and the objects (rows) were the sampled populations. The matrix was self-scaled and then the PCA was performed, with the latter using the algorithm of mean (Correia & Ferreira, 2007). Data were analyzed using the chemometrics MATLAB version 5.3 software program and the PLS_Toolbox package (Version 2.0) (Wise & Gallagher, 1999).

3 Results and discussion

The chemical composition of the volatile fraction of *S. tuberosa* fruits during maturation from two accessions was determined by GC-MS. The chromatograms obtained are shown in Figure 2 and the volatile compounds detected on each post-harvest maturation day for the two accessions are shown in Table 1.

It was possible to observe that total ion chromatograms of the volatile fraction of *S. tuberosa* fruits from the two accessions were significantly different, indicating that the volatile compounds released by the fruits of each accession are also different. Similarly, the chromatograms showed that the chemical composition of the volatile fraction of the fruits was also different on each post-harvest maturation day, revealing that the compounds released by the fruits of each post-harvest day are also different.

It was possible to detect 30 compounds in fruits from the EPAMIG-C02 accession on the first day post-harvest, of which the main compounds identified were hex-2-enal (13.6%) and myrcene (16.1%). Methyl salicylate was only detected on this day, which indicates it may be used as marker for the maturity stage. The same number of compounds was detected on the second day post-harvest, but the main identified compound was myrcene (18.7%) and the nonanal and dec-2-enal were only detected until this day, indicating that these compounds may be recommended as markers. A total of 29 compounds were detected on the third day post-harvest, and the major compounds detected were selina-3,7(11)-diene with 14.4%, and an unidentified compound which presents a retention time equal to 28.7 min. The mass spectrum of this compound may be seen in the supplementary material Figure S1. Finally, it was possible to extract 30 compounds on the fourth day post-harvest, of which the main compound identified was ethyl hexanoate (17.2%). In addition, it is also important to highlight that ethyl butanoate was detected on the third- and fourth-days post-harvest, indicating that these compounds may be used as markers for the maturity stage.

On the order hand, it was possible to detect 16 compounds regarding the EPAMIG-C10 accession, of which the main identified

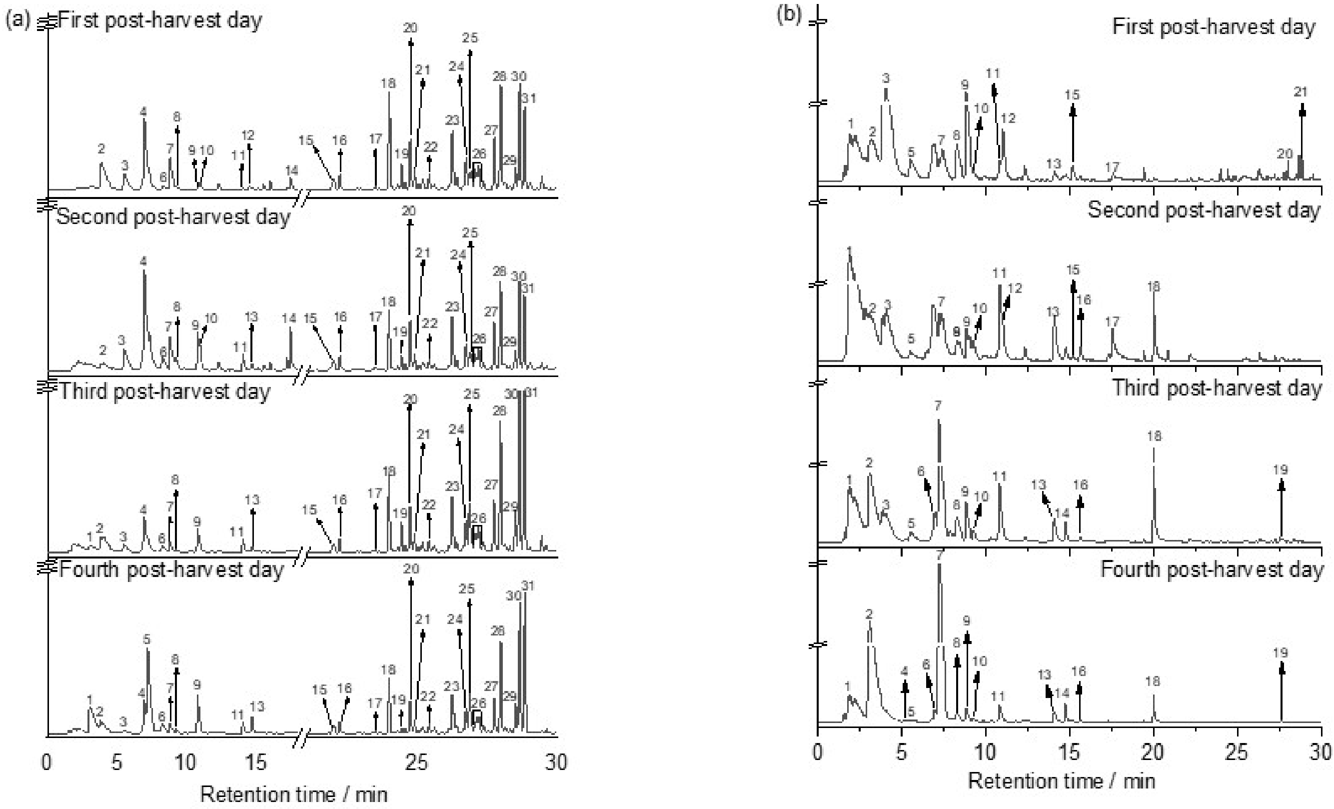

Figure 2. Total ion chromatograms of the volatile fraction of *S. tuberosa* fruits from (a) the EPAMIG-C02 accession and (b) the EPAMIG-C10 accession after harvest. The numbers referring to the compounds detected in the EPAMIG-C02 and the EPAMIG-C10 accession are shown in Table 1.

Table 1. Relative areas of volatile compounds from *S. tuberosa* fruits at four post-harvest maturity days (1st, 2nd, 3rd and 4th) for two accessions and two storage periods under controlled conditions.

Peak[a]	Identification	*Class*	RT	LRI[c]	LRI[d]	Fruit post-harvest day			
						1st	2nd	3rd	4th
						EPAMIG-C02 accession			
1	Ethyl butanoate	Ester	3.1	816	808	0.00 ± 0.00	0.00 ± 0.00	1.23 ± 0.47	9.40 ± 0.52
2	Hex-2-enal (mixture of isomers)	Aldehyde	3.8	859	856	13.59 ± 1.83	2.96 ± 0.48	5.44 ± 2.80	3.13 ± 0.06
3	α-Pinene	Terpene	5.5	937	942	5.25 ± 0.38	6.76 ± 1.04	2.40 ± 0.23	0.95 ± 0.02
4	Myrcene	Terpene	7.0	993	992	16.07 ± 2.33	18.76 ± 6.32	7.91 ± 1.21	3.54 ± 0.11
5	Ethyl hexanoate	Ester	7.2	1001	999	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	17.17 ± 0.56
6	Limonene	Terpene	8.3	1032	1035	0.92 ± 0.06	2.75 ± 0.33	1.35 ± 0.19	2.41 ± 0.06
7	Ocimene	Terpene	8.8	1046	1046	6.23 ± 0.70	5.14 ± 1.88	1.98 ± 0.21	2.20 ± 0.07
8	γ-Terpinene	Terpene	9.3	1058	1064	0.13 ± 0.01	0.78 ± 0.20	0.44 ± 0.09	0.84 ± 0.04
9	Linalool	Alcohol	10.8	1102	1101	0.13 ± 0.01	3.44 ± 0.36	3.83 ± 0.87	7.54 ± 0.57
10	Nonanal	Aldehyde	11.0	1106	1104	0.77 ± 0.04	0.50 ± 0.01	0.00 ± 0.00	0.00 ± 0.00
11	Terpin-4-en-1-ol	Alcohol	14.1	1180	1175	0.42 ± 0.02	3.37 ± 0.57	1.91 ± 0.61	2.01 ± 0.21
12	Methyl salicylate	Ester	14.5	1191	1192	0.52 ± 0.18	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
13	unidentified compound		14.7	1196		0.00 ± 0.00	1.29 ± 0.35	0.68 ± 0.23	2.63 ± 0.25
14	Dec-2-enal	Aldehyde	17.5	1261	1263	1.87 ± 0.13	5.77 ± 1.11	0.00 ± 0.00	0.00 ± 0.00
15	Isoledene	Terpene	22.0	1367	1373	1.09 ± 0.05	1.06 ± 0.10	1.07 ± 0.03	0.90 ± 0.05
16	α-Copaene	Terpene	22.2	1372	1377	0.93 ± 0.05	1.07 ± 0.16	1.04 ± 0.03	0.85 ± 0.03
17	α-Gurjunene	Terpene	23.5	1402	1409	0.18 ± 0.01	0.23 ± 0.04	0.19 ± 0.00	0.15 ± 0.02
18	Caryophyllene	Terpene	24.0	1415	1420	6.97 ± 0.03	4.86 ± 0.76	5.60 ± 0.33	3.88 ± 0.01
19	γ-Elemene	Terpene	24.4	1425	1433	1.74 ± 0.14	0.86 ± 0.05	2.11 ± 0.25	0.29 ± 0.01
20	Aromadendrene	Terpene	24.7	1433	1442	3.37 ± 0.07	3.95 ± 0.74	3.20 ± 0.21	2.09 ± 0.24
21	unidentified compound		24.9	1437		1.13 ± 0.00	0.90 ± 0.05	1.11 ± 0.17	0.66 ± 0.03
22	unidentified compound		25.4	1450		1.00 ± 0.02	0.69 ± 0.08	0.87 ± 0.07	0.61 ± 0.02
23	γ-Muurolene	Terpene	26.2	1470	1478	4.39 ± 0.07	4.64 ± 0.94	4.34 ± 0.59	2.84 ± 0.48
24	β-Selinene	Terpene	26.7	1482	1487	2.28 ± 0.05	1.98 ± 0.40	1.95 ± 0.15	1.42 ± 0.07
25	unidentified compound		26.9	1487		1.71 ± 0.09	1.66 ± 0.22	3.63 ± 0.13	2.62 ± 0.07
26	α-Selinene/ Epizonarene/ α-Muurolene	Terpenes	27.2	1493	1496 1497 1499	3.34 ± 0.09	3.35 ± 0.72	3.40 ± 0.21	2.53 ± 0.10
27	γ-Cadinene	Terpene	27.8	1508	1515	3.66 ± 0.01	4.04 ± 1.10	3.92 ± 0.32	2.43 ± 0.04
28	Cadinene	Terpene	28.0	1513	1524	7.39 ± 0.35	6.66 ± 1.19	9.50 ± 0.84	6.22 ± 0.00
29	unidentified compound		28.5	1527		1.37 ± 0.09	1.23 ± 0.17	2.72 ± 0.32	1.81 ± 0.12
30	unidentified compound		28.7	1531		7.61 ± 0.48	6.34 ± 0.30	13.78 ± 1.52	9.08 ± 0.15
31	Selina-3,7(11)-diene	Terpene	28.9	1536	1542	5.93 ± 0.38	4.96 ± 0.05	14.41 ± 1.73	9.77 ± 0.15
						EPAMIG-C10 accession			
1	1,1-Dimethylprop-2-enol	Alcohol	1.9	<800	620	12.40 ± 2.04	44.23 ± 0.09	18.95 ± 0.17	8.36 ± 1.06
2	Ethyl butanoate	Ester	3.3	822	808	5.39 ± 1.30	2.89 ± 0.38	17.60 ± 2.99	33.73 ± 2.01

RT: retention time in minutes; ^{TI} tentatively identified compound. [a]The numbers of the peaks refer to the compounds in Figure 2. [C]Linear retention index calculated from experimental results. [D]Linear retention index on DB-5 (or equivalent) column from literature (Avsar et al., 2004; Baccouri et al., 2007; Balbontín et al., 2007; Dehghan et al., 2007; Flamini et al., 2003, 2007; Högnadóttir & Rouseff, 2003; Karioti et al., 2003; Pino et al., 2004; Masoudi et al., 2006; Macchioni et al., 2003).

Table 1. Continued...

Peak[a]	Identification	*Class*	RT	LRI[c]	LRI[d]	Fruit post-harvest day			
						1st	2nd	3rd	4th
3	Hex-2-enal (mixture of isomers)	Aldheyde	4.1	861	856	33.03 ± 7.96	14.30 ± 1.02	7.23 ± 2.27	0.00 ± 0.00
4	Methyl caproate	Ester	5.2	925	925	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.12 ± 0.00
5	α-Pinene	Terpene	5.5	938	942	5.04 ± 1.01	1.67 ± 0.12	1.78 ± 0.41	0.39 ± 0.07
6	Myrcene	Terpene	7.0	993	992	0.00 ± 0.00	0.00 ± 0.00	1.28 ± 0.37	0.76 ± 0.12
7	Ethyl hexanoate/ Octanal	Aldheyde	7.4	1007	999/1007	5.03 ± 1.11	6.35 ± 0.47	23.33 ± 0.07	44.02 ± 0.62
8	Limonene	Terpene	8.3	1031	1035	7.90 ± 2.31	3.34 ± 0.08	3.40 ± 0.72	1.33 ± 0.24
9	Ocimene	Terpene	8.8	1046	1046	19.67 ± 5.95	4.06 ± 0.04	4.91 ± 1.02	2.27 ± 0.42
10	γ-Terpinene	Terpene	9.3	1059	1064	0.28 ± 0.00	1.09 ± 0.09	1.16 ± 0.23	0.48 ± 0.08
11	Linalool	Alcohol	10.8	1102	1101	0.67 ± 0.06	4.40 ± 0.54	7.26 ± 0.73	2.70 ± 0.50
12	Nonanal	Aldheyde	11.0	1106	1104	4.35 ± 0.15	0.33 ± 0.08	0.00 ± 0.00	0.00 ± 0.00
13	Terpin-4-en-1-ol	Alcohol	14.1	1181	1175	1.21 ± 0.01	6.28 ± 0.06	2.84 ± 0.08	1.38 ± 0.10
14	Ethyl caprylate	Ester	14.8	1198	1197	0.00 ± 0.00	0.00 ± 0.00	1.72 ± 0.11	1.82 ± 0.32
15	Decanal	Aldheyde	15.2	1207	1205	1.42 ± 0.14	0.41 ± 0.11	0.00 ± 0.00	0.00 ± 0.00
16	p-Menth-1-en-9-al	Aldheyde	15.6	1218	1232	0.00 ± 0.00	1.34 ± 0.23	0.48 ± 0.04	0.23 ± 0.09
17	Dec-2-enal	Aldheyde	17.6	1264	1263	1.94 ± 1.10	3.76 ± 0.55	0.00 ± 0.00	0.00 ± 0.00
18	Methyl geranate	Ester	20.0	1321	1323	0.00 ± 0.00	5.55 ± 0.44	7.54 ± 1.20	2.15 ± 0.38
19	Farnesene	Terpene	27.5		1506	0.00 ± 0.00	0.00 ± 0.00	0.51 ± 0.12	0.27 ± 0.13
20	Cadinene	Terpene	28.0	1513	1524	0.80 ± 0.13	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
21	Selina-3,7(11)-diene	Terpene	28.8	1535	1542	0.87 ± 0.08	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00

RT: retention time in minutes; [TI] tentatively identified compound. [a]The numbers of the peaks refer to the compounds in Figure 2. [C]Linear retention index calculated from experimental results. [D]Linear retention index on DB-5 (or equivalent) column from literature (Avsar et al., 2004; Baccouri et al., 2007; Balbontín et al., 2007; Dehghan et al., 2007; Flamini et al., 2003, 2007; Högnadóttir & Rouseff, 2003; Karioti et al., 2003; Pino et al., 2004; Masoudi et al., 2006; Macchioni et al., 2003).

compounds were hex-2-enal (33.0%), ocimene (19.7%) and 1,1-dimethylprop-2-enol (12.4%) on the first day after harvest; these compounds together represent 65.1% from the total relative area. As cadinene and seline-3,7(11)-diene are only identified on this day, they may be used as markers of the initial ripeness stage. It was possible to extract 16 compounds on the second day post-harvest, of which the main identified compounds were 1,1-dimethylprop-2-enol (44.2%) and hex-2-enal (14.3%), representing 56.5% of the total relative area. Next, 16 compounds were detected on the third- and fourth-days post-harvest, and the compounds identified in major amounts were ethyl hexanoate and octanal mixture (23.3% e 44.0%), 1,1-dimethylprop-2-enol (18.9% e 8.4%) and ethyl butanoate (17.6% e 33.7%), representing 59.9% and 86.1% of the total relative area from the 3rd and 4th days, respectively. Myrcene, ethyl caprylate and farnesene were only identified on these days, indicating that they may be used as markers. In addition, methyl caproate was only detected on the fourth day post-harvest, revealing that it may be an indicator of complete maturity.

A comparison between the two accessions showed that 14 compounds were identified in both fruits, namely ethyl butanoate, hex-2-enal, α-pinene, β-myrcene, ethyl hexanoate, limonene, ocimene, γ-terpinene, linalool, nonanal, terpin-4-en-1-ol, dec-2-enal, cadinene, and selina-3,7(11)-diene. The evolution of each compound content during the post-harvest ripening period may be observed in Figure 3.

These results revealed that the same compounds in both accessions showed similar behavior during the post-harvest period. Note that the increase of ethyl butanoate and ethyl hexanoate contents occur in both accessions, which corroborates their indication as markers for the final ripening stages. These

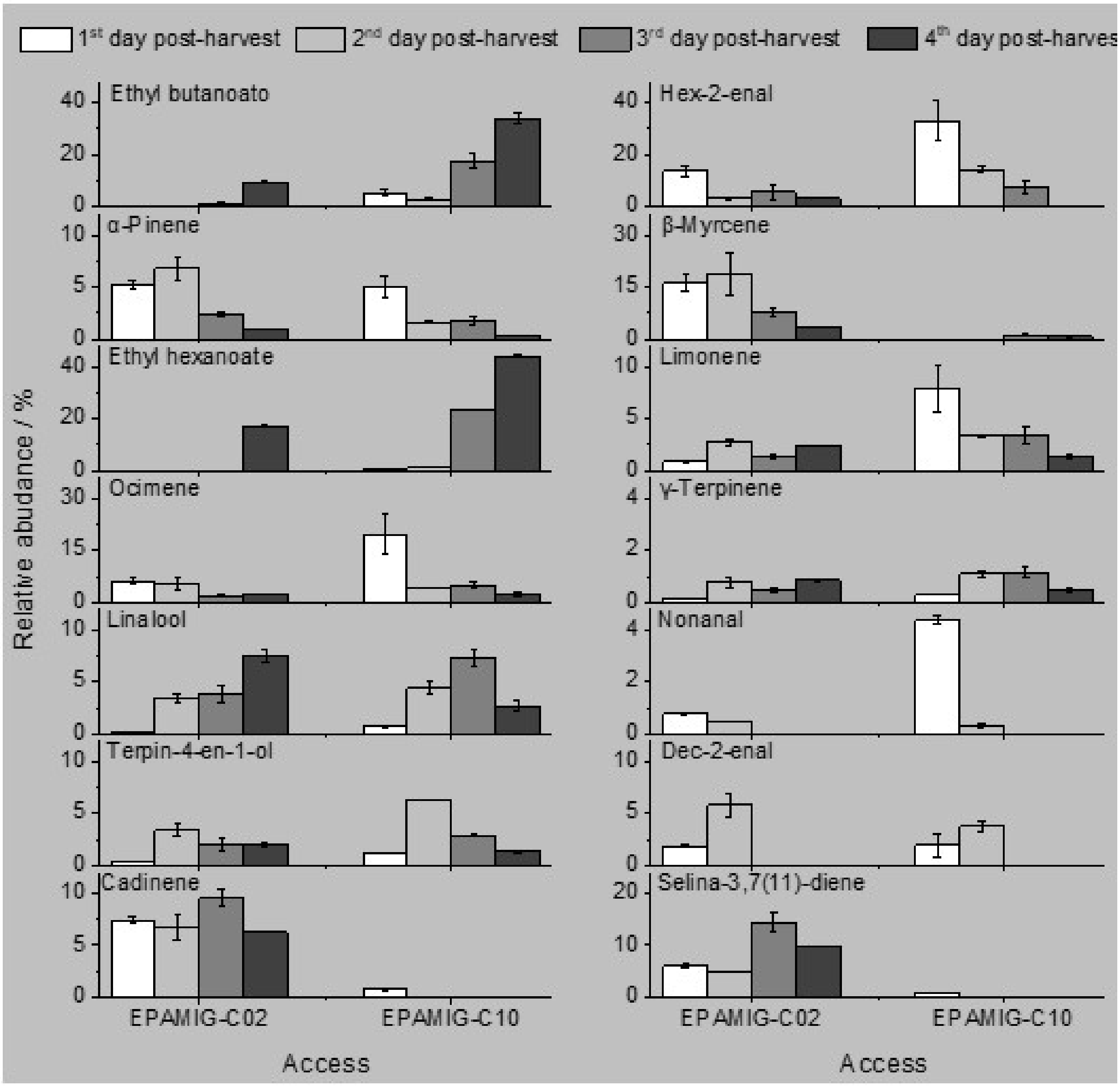

Figure 3. Evolution of volatile compound contents identified in *S. tuberosa* fruits from EPAMIG-C02 and EPAMIG-C10 during the post-harvest period.

compounds have also been found in the mature *Butia Capitata* fruits (Aguiar et al., 2014). In contrast, hex-2-enal and nonanal contents decreased, and constituted a general trend for both accessions, while dec-2-enal was only detected in the first days post-harvest. Likewise, the similar trend in two different accessions increases the possibility that these compounds may be markers of early ripening stages for *S. tuberosa*. It should be noted that (*E*)-Hex-2-enal content decreased during *Annona muricata* L. cv. Elita ripening (Marquéz et al., 2011). The nonanal and (*Z*)-dec-2-enal contents also showed a decreasing trend during maturation in grapes (Yang et al., 2011). Some of these five important compounds were also detected in *Spondias tuberosa* in a previous work such as hex-2-enal, (E)-dec-2-enal and ethyl butanoate (Galvão et al., 2011). It is especially important that ethyl butanoate has previously been detected in ripe umbu fruits and not detected in half-ripe ones (Galvão et al., 2011). This supports the use of this compound as a progress marker in the ripening process once again.

A comparison between the main chemical classes detected in the volatile fraction of the two accessions is shown in Figure 4.

Terpenes were the predominant chemical class in fruits from EPAMIG-02 during four post-harvest ripening days. Terpenes and aldehydes were the predominant compounds in the EPAMIG-10 accession on the first day, alcohols predominated on the second day, while esters were the major chemical classes on the third and fourth post-harvest ripening days, as may be seen in Figure 4. These results agree with the literature, because terpenes were found in high amounts in other species of the *Spondias* genus using the same extraction method (Barreiros et al., 2018; Ceva-Antunes et al., 2003). Different results were found for *Spondias Tuberosa* in a previous work, probably due to the difference in extraction techniques (Galvão et al., 2011).

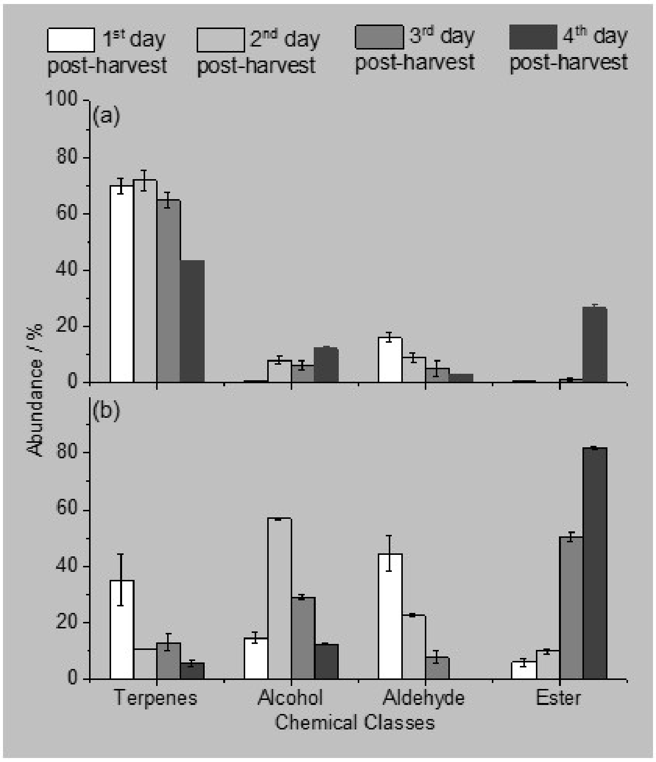

Figure 4. Relative chromatographic areas of the main chemical classes identified in the volatile compounds of *S. tuberosa* fruits from (a) the EPAMIG-C02 and (b) EPAMIG-C10 accessions at four maturity stages.

The evolution of each chemical class during the post-harvest ripening period was very similar, because the fruits of both accessions mainly showed a reduction in the terpene and aldehyde content, while the ester content increased in this period. It may be seen that *S. tuberosa* fruits showed much lower ester content in the first two post-harvest days (1st and 2nd) than the other last two days (3rd and 4th), indicating that the ester content may be used in characterizing the maturity stage. This behavior regarding chemical classes is similar to that observed in *Butia capitata* and in *Musa sp.* as a function of ripening progress (Aguiar et al., 2014; Zhu et al., 2018).

The results of the present study show that great modifications occur during *S. tuberosa* fruit maturation and detailed chemical characterization is important to control and to understand the maturation process in this important fruit from the Brazilian Caatinga. This information was used to classify the samples by principal component analysis (PCA) and according to the content and chemical composition of volatile compounds.

3.1 PCA analysis

Considering the EPAMIG-C02 accession and its ripening days, a description of the influences of the compounds in PC1 and PC2 are shown in Figure 5, which explain 81.83% of the total variance. These compounds are shown in Table 1 with their respective chemical classes and contents.

The aldehydes, esters and terpenes detected on the first and third day of ripening are arranged in PC1 negative and PC2 positive, and the compounds arranged in this quadrant were hex-2-enal, methyl salicylate, isoledene, caryophyllene, γ-elemene, unidentified compounds (peaks 21 and 22), β-selinene, α-selinene/epizonarene/α-muurolene and cadinene. The second ripening day showed PC1 negative and PC2 negative. The main chemical classes detected in this stage were aldehydes and terpenes, and the compounds responsible for this location were α-pinene, β-myrcene, ocimene, nonanal, dec-2-enal, α-copaene, α-gurjunene, aromadendrene, γ-muurolene and γ-cadinene. The fourth day of ripening showed PC1 positive and PC2 negative and positive, in which esters, alcohols and terpenes were the main chemical classes detected, and ethyl butanoate, ethyl hexanoate, limonene, γ-terpinene, linalool, terpin-4-en-1-ol, unidentified compounds (peaks 13, 25, 29 and 30) and Selina-3.7(11)–diene were the compounds responsible for this location.

Considering the EPAMIG-C10 accession and its ripening days, a description of the influences of the compounds in PC1 and PC2, which accumulated 88.80% of the explored variance, is shown in Figure 6. The compounds detected are shown in Table 1 with their respective chemical classes and chromatography area.

The first ripening day is arranged in PC1 negative and PC2 negative, in which the detected compounds were two aldehydes (hex-2-enal and dec-2-enal). However, the detected compounds for PC1 negative and PC2 positive were classified as aldehydes and

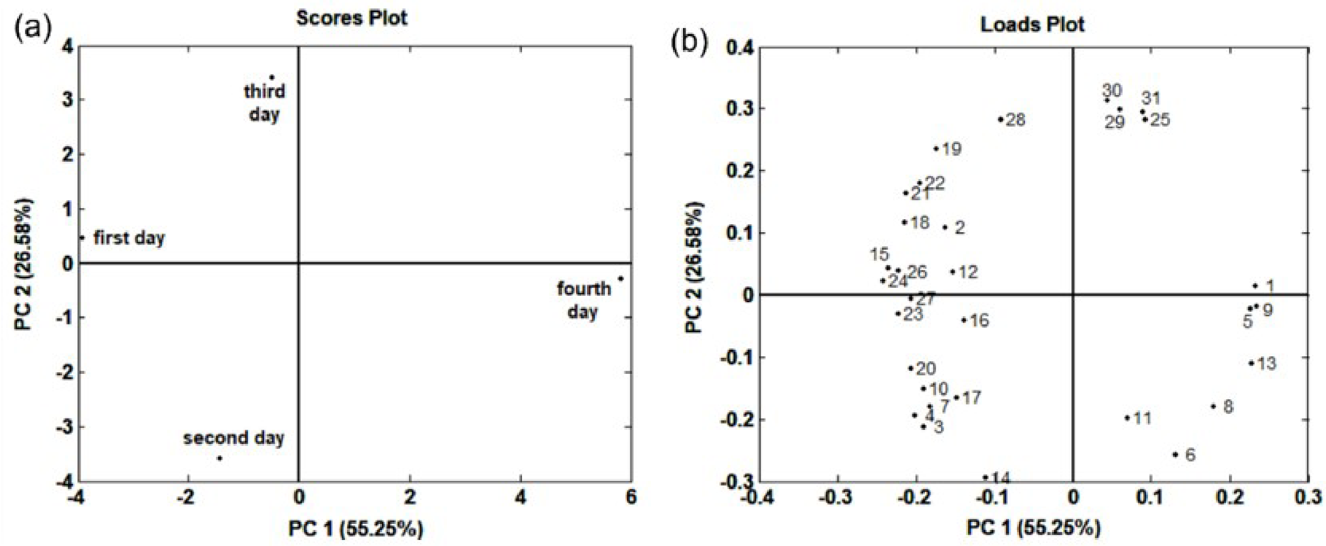

Figure 5. (a) Score graph for the ripening days of EPAMIG-C02 samples, in which the last day is separated from the first, second and third days by PC1 with 55.25% of the explained variance, and the first and third days are separated from the second and fourth days by PC2 with 26.58% of the explained variance; and (b) Load graph for the ripening days of compounds in EPAMIG-C02 fruit, in which 64.52% of the compounds are identified on the first, second and third days, while 35.48% of the compounds are identified on the fourth day. The numbers refer to the compounds in Table 1.

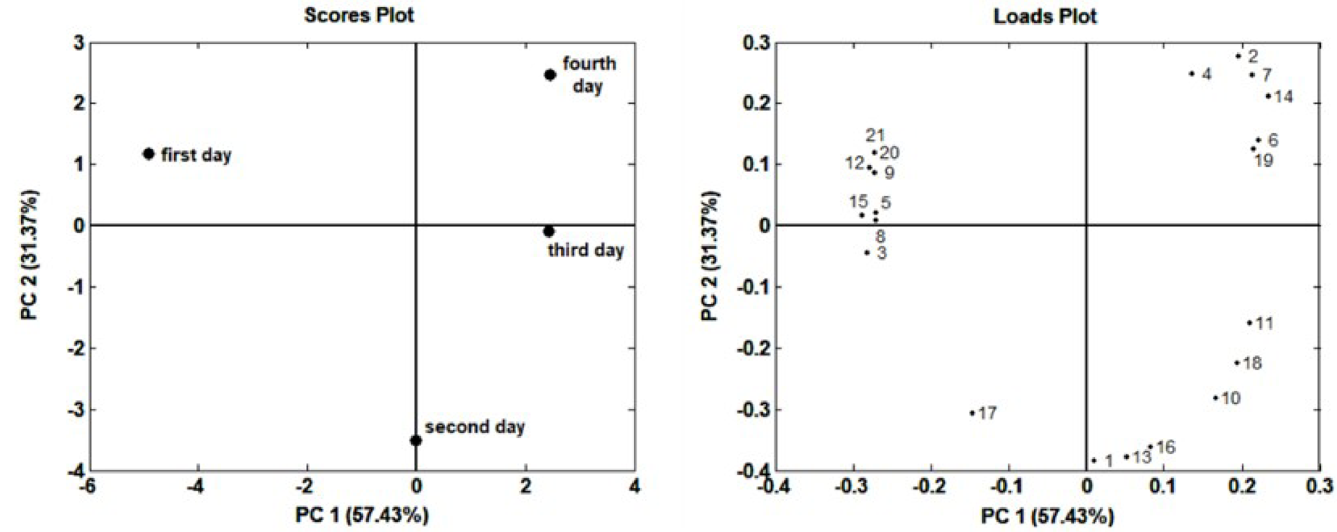

Figure 6. (a) Score graph for the ripening days of ten *S. tuberosa* fruit accession samples, in which the last three days are separated from the first day by PC1 with 57.43% of the explained variance, and the first and fourth days are separated from the second and third days by PC2 with 31.37% of the explained variance; and (b) Loadings graph for the ripening days of compounds found in EPAMIG-C10 samples, in which 42.86% of the compounds are identified on the first day, 28.57% of the compounds are identified on the third and fourth days, and 28.57% of the compounds are identified on the second and third days of ripening. The numbers refer to the compounds in Table 1.

terpenes (α-pinene, limonene, ocimene, nonanal, decanal, cadinene and selina-3,7(11)–diene). The compounds of these two PC1 negative quadrants are responsible for separating the first day from the others, corresponding to 42.86% of the detected compounds in this stage, totaling four aldehydes and five terpenes. The compounds detected in the PC1 positive and PC2 negative quadrant, which shows the second and third day, were 1,1-dimethylprop-2-enol, γ-terpinene, linalool, 1-terpin-4-en-1-ol, p-menth-1-in-9-al and methyl geranate. The compounds located in PC1 and PC2 positive on the fourth day were ethyl butanoate, methyl caproate, β-myrcene, ethyl hexanoate/octanal, ethyl caprylate and farnesene.

In addition, 57.14% of the total identified compounds on the second, third and fourth days were responsible for separating those days from the first, and the same amount of compounds from that percentage were produced to group the second and third days compared to the fourth day.

4 Conclusions

This study reports a detailed volatile compound profile of *Spondias* fruits for four days of post-harvest ripening using HS-SPME/GC-MS for the first time. The results showed that volatile compounds were significantly influenced by post-harvest maturation stage. The study revealed a tendency to increase the ester content and decrease the aldehyde and terpene content during four days of post-harvest ripening for two accessions. There were notable quantitative differences in five key compounds such as two esters (ethyl butanoate and ethyl hexanoate) and three aldehydes (hex-2-enal, nonanal and dec-2-enal). These compounds may be used as markers for the maturity stages for the two accessions. The principal components analysis showed that the different compounds identified over the ripening period may classify the fruits, in addition to indicating the compounds which must be monitored on each ripening day showing the compounds over time.

Acknowledgments

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Supplementary Material

Supplementary material accompanies this paper.

Figure S1: Mass spectra from compound detected in 28.7 minutes, assigned as 30 in Table 1.

This material is available as part of the online article from https://www.scielo.br/j/cta.