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Studies on the volatile fraction composition of three native Amazonian-Brazilian fruits: Murici (*Byrsonima crassifolia* L., Malpighiaceae), bacuri (*Platonia insignis* M., Clusiaceae), and sapodilla (*Manilkara sapota* L., Sapotaceae)

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ABSTRACT

The volatile fraction of murici, bacuri and sapodilla are here studied because of their increasing interest for consumers, abundance of production in Brazil, and the general demand for new flavors and aromas. Their volatile profiles were studied by two High Concentration Capacity Headspace techniques (HCC-HS), Headspace Solid Phase Microextraction (HS-SPME) and Headspace Sorptive Extraction (HSSE), in combination with GC–MS. Murici volatile fraction mainly contains esters (38%), carboxylic acids (19%), aldehydes (11%), alcohols (14%), others (13%) and sulfur compounds; bacuri is characterized by terpenes (41%), non-terpenic alcohols (24%), esters (15%), aldehydes (6%), and others (12%); sapodilla consists of esters (33%), alcohols (27%), terpenes (18%) and others (21%). The GC–MS component co-elution was overcome by GC × GC-qMS. The adoption of modern analysis technologies afforded to achieve a better knowledge of the volatile fraction composition of these fruit pulps by increasing substantially the number of compounds identified.

1. Introduction

Brazil produces tropical, subtropical and temperate fruits because of its territorial extension, geographic position, climate and soil. It is the world's third-largest fruit producer, with 42 million tons over 2.2 million hectares throughout the country, after China and India. Thirty-one percent of fresh and processed fruits produced in Brazil are exported to different parts of the world (Clerici & Carvalho-Silva, 2011; Fachinello & Nachtigal, 2009).

A wide variety of exotic and/or native fruits is consumed in Brazil, and they represent a potential source of both antioxidants in the diet and flavours and aromas. Several Amazonian native plants are commercialized for medicinal and nutritive purposes, and they are famous for their exotic aroma, taste, and succulent pulp (Bicas et al., 2011; Clerici & Carvalho-Silva, 2011; Rezende & Fraga, 2003).

The Amazonian plant known as murici (*Byrsonima crassifolia* L., Malpighiaceae) has fragile branches supporting leaves, flowers and fruits, and grows up to five meters; fruits are harvested from December to May in Amazonian and northeastern regions of Brazil. When mature, the fruit is yellow, round shape, 1.5–2 cm wide, and the odor of its pulp resembles a fruity rancid cheese. Chemical composition shows high water content (76%), 20% of carbohydrate, 3% of lipids, less than 1% of proteins and ash, with a 11° Brix total soluble content (Guimarães & Silva, 2008; Monteiro, Sousa, Pires,

Abbreviations: HCC-HS, High Concentration Capacity Headspace; HS-SPME, Headspace Solid-phase microextraction; HSSE, Headspace sorptive extraction; GC–MS, Gas Chromatography coupled to Mass Spectrometry; GC × GC-qMS, Comprehensive two-dimensional Gas Chromatography coupled to Mass Spectrometry; LLE, Liquid-Liquid Extraction; SDE, Simultaneous Distillation Extraction; SPDE, Solid Phase Dynamic Extraction; LPME, Liquid-Phase Microextraction; SHS, Static Headspace; DHS, Dynamic Headspace; PDMS, Polydimethylsiloxane; GC-FID, Gas Chromatography with Flame Ionization detector; CARB, Carboxen; DVB, Divinylbenzene; TDU, Thermo Desorption Unit; MSD, Mass Spectrometry Detector; LRI, Linear retention indexes; AEDA, Aroma extract dilution analysis.

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Azevedo, & Borges, 2015). Pharmacological studies have shown its bactericide, antifungal, spasmogenic and anti-protozoal activities. This fruit is mainly consumed as a juice, or with ice creams and liquor (Rezende & Fraga, 2003).

Bacuri (*Platonia insignis* M., Clusiaceae) is a fruit tree15–20 m high growing in the southern Amazonian forest. It produces approximately 500 fruits per season from December to May; some plants bear fruits every two years. The fruits are ovoid to subglobose, 7–15 cm long and 5–15 cm in diameter, weighing 200–1000 g, and are very popular in the Belém market (Pará State). They chemically consist of high water content (76%), 2% of lipids, 1.5% of proteins and 0.5% ash, with a 14° Brix total soluble content (Santos, Oriá, Guedes, Barroso, & Holanda, 1988). The flavor is essentially floral with fruity notes. It contains a creamy white, mucilaginous, fibrous, juicy pulp with a strongly attractive exotic flavor. This pulp is used for the local production of canned pulp, puree, jams and ice creams (Bicas et al., 2011; Borges & Rezende, 2000).

Sapodilla (*Achras sapota* L., Sapotaceae) is a medium-sized tree native to Central America. It likely originated in southern Mexico or Central America; in Brazil, it is cultivated in the northeastern Amazonian region, and its fruits may be found from July to May. The fruit is a large ellipsoid berry, in general from 4 to 8 cm up to 15 cm wide, containing two to five seeds and is edible, when fully ripened it is very sweet in taste, slightly astringent and with a relatively low aromatic note; when unripe, it has a rather unappealing alcoholic aftertaste. It contains a high water percentage (75%), 0.5% of ash, and a 16° Brix total soluble content (Oliveira, Afonso, & Da Costa, 2011). This fruit is consumed fresh or used to produce jams, compotes, and juice (Boulanger, Chassagne, & Crouzet, 1999; MacLeod & Troconis, 1983; Pino, Marbot, & Aguero, 2003).

Food and fruit aroma in general are the result of a specific combination and mixture of different components with concentrations ranging from the low parts-per-million to parts-per-trillion (Fruits of Brazil. URL (http://flavorsofbrazil.blogspot.it/2012/03/fruits-of-brazil-sapodilla-sapoti.html) (most recent access date, 2015, Laohakunjit, Kerdchoechuen, Matta, Silva, & Holmes, 2007, McGorrin, 2011).

Several extraction and enrichment techniques have been used to study the volatile fraction of food matrices, including Liquid-Liquid Extraction (LLE), Simultaneous Distillation Extraction (SDE), Solid Phase Dynamic Extraction (SPDE), Solid Phase Microextraction (SPME), Stir Bar Sorptive Extraction (SBSE), Liquid-Phase Microextraction (LPME), Static and Dynamic Headspace (SHS and DHS), and other High Concentration Capacity Headspace Techniques (HCC-HS) Kawaguchi, Ito, Nakazawa, & Takatsu, 2013; Sides, Robards, & Helliwel, 2000; Bicchi, Cordero, Liberto, Sgorbini, & Rubiolo, 2012; Sgorbini et al., 2014. Conventional sample preparation techniques are in general time- and labor-intensive, prone to volatile loss, sometimes implying the use of toxic solvents and can induce volatile thermal decomposition and artifact formation (Bicchi et al., 2012; Fruits of Brazil, 2015; Jelen, Majcher, & Dziadas, 2012; Kataoka, Lord, & Pawliszyn, 2000; Sgorbini et al., 2014; Sides et al., 2000).

Modern microextraction methods can successfully be applied for aroma characterization because of their high sensitivity and concentration factors as well as possibility of automation and reduction of organic solvent consumption to a minimum (Jelen et al., 2012; Kawaguchi et al., 2013).

SPME is a simple, rapid and solvent-free technique that combines extraction, concentration, analyte recovery and analysis into a single step. First introduced by Pawliszyn and co-workers in 1990 for liquids and then extended to HS sampling in 1992, SPME uses a fused silica fiber coated with a polymeric or multimaterial film, which is exposed to the sample to extract and concentrate volatile compounds without interference from matrix components. It was thus successfully applied in several fields including the analysis of the flavor composition of vegetables and fruits (Belliardo et al., 2006; Cai, Liu, & Su, 2001; Kataoka et al., 2000; Pereira, Pereira, & Câmara, 2011; Sides et al., 2000; Wang, O'Reilly, Chen, & Pawliszyn, 2005).

SBSE is a sorption technique introduced in 1999 by Sandra and co-workers (Kawaguchi et al., 2013; Sgorbini, Rubiolo, Bicchi, Liberto, & Cordero, 2009) to extract organic analytes from aqueous samples by sorption onto polydimethylsiloxane (PDMS)-coated stir bars (commonly known as twister); they consist of a magnet that is incorporated into a glass jacket coated with a thick (PDMS) layer. The sorbed analytes are recovered by thermal desorption from the twister either directly into a gas chromatographic (GC) injector liner or in a thermal desorber, and then analyzed by Gas Chromatography with Flame Ionization detector (GC-FID) or coupled to Mass Spectrometry (GC–MS) Kawaguchi et al., 2013; Wang et al., 2005; Belliardo et al., 2006; Sgorbini et al., 2009; Bicchi, Cordero, Iori, Rubiolo, & Sandra, 2000; Tienpont, David, Bicchi, & Sandra, 2000; Alves & Jennings, 1979. In 2000, Bicchi et al. and Tienpoint et al. extended the use of twisters to HS sampling (Bicchi et al., 2000; Tienpont et al., 2000) and called it Headspace sorptive extraction (HSSE); since then, several applications have been described in the fields of pollution, food, plant, biological and biomedical analyses (Bicchi et al., 2000; Tienpont et al., 2000).

The literature on the composition of the volatile fraction of the above three Brazilian fruits is rather limited; a) two articles on the volatile fraction of murici pulp diluted with water, one adopting SDE and the other by DHS (Alves & Jennings, 1979; Rezende & Fraga, 2003); b) three articles on bacuri fresh pulp based on SDE results (Alves & Jennings, 1979; Borges & Rezende, 2000; Boulanger et al., 1999); and c) four articles on sapodilla, three of them using SDE on the pulp diluted with water and one applying SPME to canned and fresh fruits (Franco & Janzantti, 2005; Laohakunjit et al., 2007; MacLeod & Troconis, 1983; Pino et al., 2003).

As part of a project aiming to investigate native and commercially interesting Brazilian fruits, this work reports the results of an extensive study on the composition of the volatile fraction of murici, bacuri and sapodilla carried out by the complementary use of high concentration-capacity headspace sampling techniques (HS-SPME and HSSE) in combination with GC–MS and GCxGC-MS with polar and apolar columns.

2. Materials and methods

2.1. Plant samples

Murici (*Byrsonima crassifolia L.*, Malpighiaceae), bacuri (*Platonia insignis* M., Clusiaceae) and sapodilla (*Manilkara sapota* L., Sapotaceae) were obtained with leaves and fruits from the Ver-o-Peso local market, Belém, Pará, Brazil. The sapodilla botanical material was identified with the number RB 582173 at the Botanical Garden of Rio de Janeiro, RJ, Brazil; murici with the number 72340 and bacuri with the number 68298 at CNE Herbarium, Cenargen, Brasília, Brazil. For each species, three 200 g separated samples from three different cultivations in the Belem state (Brazil) were bought at Ver-o-Peso market (Belem). The fruits of each sample were then sanitized and pulped manually, obtaining a pulp that was used for the analysis in triplicate. The pulp from each sample was weighed and stored in a freezer (−18 °C) until analysis.

2.2. Isolation of the volatile fraction

2.2.1. Headspace-Solid phase Micro Extraction (HS-SPME)

HS-SPME conditions: a 2 cm fiber coated with PDMS/CARB/DVB (Supelco, Bellefonte, PA, USA) was used. Sampling procedure: the

SPME needle was introduced into the sample, and the fiber was exposed to the headspace of 2.0 g of each fruit in a 20-mL sealed vial for 30 min at 50 °C. After sampling, the fiber was thermally desorbed for 5 min into the GC injection port at 250 °C (with a 0.75 mm i.d. SPME liner). The sampling procedure was automatically performed with a Shimadzu AOC 5000 autosampler or an MPS-2 multipurpose sampler (Gerstel, Mülheim a/d Ruhr, Germany) that were both integrated on-line with the corresponding GC–MS system.

2.2.2. Headspace-Stir bar sorptive extraction (HSSE)

PDMS and dual-phase PDMS-Carbopack B twisters (Bicchi et al., 2005; Sgorbini et al., 2009) were used (Gerstel, Mülheim a/d Ruhr, Germany) for the HSSE sampling. The twister was suspended in the headspace of a 20-mL vial with a septum cap containing 2.0 g of each fruit sample at 50 °C for 50 min. The sampled analytes were recovered by thermal desorption and transferred on-line to the GC–MS for analysis. The analyte recovery and injection procedure was automatically performed with a MPS-2 multipurpose sampler (Gerstel, Mülheim a/d Ruhr, Germany) equipped with a Thermo Desorption Unit (TDU) and transferred to a CIS-4 PTV injector (Gerstel, Mülheim a/d Ruhr, Germany) for the following GC–MS analysis. A standard solution of cinnamyl alcohol in dibutyl phthalate at a 100 ppm concentration was used as an internal standard.

2.3. Gas chromatography

2.3.1. GC-qMS analysis

HS-SPME-GC–MS analyses were performed with a Shimadzu QP 2020 GC–MS system while HSSE-GC–MS with an Agilent 6890/5975C GC–MS both operating in EI mode at 70 eV (Agilent, Little Falls, DE, USA). A Solgel-Wax (SGE, Victoria, Australia) and Mega-SE52 (Mega, Milan, Italy)-fused silica capillary columns were used (30 m × 0.25 mm d_c, 0.25 μm d_f). The injector temperature was 250 °C, and the oven temperature program for both instrumentations and columns were as follows: from 40 °C (1 min) to 250 °C (5 min) at 3 °C/min; carrier gas: helium, flow rate: 1.0 mL/min. MSD conditions: transfer-line temperatures: 250 °C for the Solgel-Wax column and 270 °C for the Mega-SE52 column, ion source temperature: 200 °C, EI energy: 70 eV, mass range: 35–350 *m*/*z* at 1.0 s/decade. Solutions of linear *n*-alkanes (C_9-C_{25}) and ethyl esters (C_9-C_{24}) were injected under the same conditions as those reported above to determine their linear retention indexes (LRI). The components were identified by comparing their mass spectra and retention indices to those of authentic standards or they were available from commercial or homemade libraries or from the literature.

2.3.2. GC×GC-qMS analysis

An Agilent 6890 GC unit coupled to an Agilent 5975C MS detector operating in EI mode at 70 eV (Agilent, Little Falls, DE, USA) was used. The system was equipped with two jet two-stage KT 2004 loop thermal modulators (Zoex Corporation, Houston, TX, USA) cooled with liquid nitrogen, with the hot jet pulse time set at 250 ms and a modulation time of 4 s for all experiments. The fused silica capillary loop dimensions were 1.0 m length and 100 μm d_c. The following column set configuration was adopted: a ^{1}D Mega CW column (100% polyethylene glycol, 25 m × 0.15 mm i.d., 0.15 μm film thickness) coupled to a ^{2}D OV1701 column (86% polydimethylsiloxane, 7% phenyl, 7% cyanopropyl, 1 m × 0.1 mm d_c, and d_f 0.10 μm film thickness). The injector was kept at 260 °C, the carrier gas was helium at a flow rate of 0.6 mL/min, and the oven temperature program was as follows: from 50 °C (1 min), to 240 °C, 3 °C /min and then to 260 °C at 10 °C/min (5 min). Transfer line temperature: 260 °C, ion source temperature: 200 °C. Mass spectra were scanned in the 35–350 *m*/*z* range at 1.0 s/decade.

3. Results and discussion

The volatile profiles of each fruit obtained by HS-SPME-GC–MS with a polar column were taken as references. Additional experiments with HS-SPME-GC–MS using an apolar column, HSSE-GC–MS and GC × GC-qMS with polar columns were also performed for a better characterization of the volatile fraction of the investigated fruits. Tables 1–3 report the components identified in each of the investigated fruits.

Table 1
List of volatiles identified in the headspace of murici fruits sampled with HS-SPME and HSSE combined with GC–MS ordered in function of their elution sequence on polar column.

Peak #	Compound	Solgel-Wax		Mega-SE52	Other techniques	Ref.
		LRI	Peak (%)	LRI		
1m	Ethyl butyrate	1047	2.46	825		Rezende and Fraga, (2003), Alves and Jennings (1979), Alves and Franco (2003)
2m	*n*-Hexanal	1077	0.17	–		Alves and Jennings (1979), Alves and Franco (2003)
3m	Isobutanol	1079	–	–	$HSSE_{Dual}$	Rezende and Fraga (2003), Alves and Franco (2003)
4m	2-Pentanol	1102	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	Alves and Franco (2003)
5m	Isoamyl acetate	1108	0.25	882		Alves and Franco (2003)
6m	1-Butanol	1128	0.26	–		Alves and Franco (2003)
7m	Methyl hexanoate	1169	1.77	925		Rezende and Fraga (2003), Alves and Jennings (1979), Alves and Franco (2003)
8m	Limonene	1176	0.25	1026		
9m	3-Methyl-1-butanol	1183	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	Rezende and Fraga (2003), Alves and Franco (2003)
10m	Butyl butanoate	1204	1.46	998		Alves and Franco (2003)
11m	Ethyl hexanoate	1221	26.15	1002		Rezende and Fraga (2003), Alves and Jennings (1979), Alves and Franco (2003)
12m	(*Z*)-β-Ocimene	1236	0.27	1048		
13m	Isopentyl butyrate	1250	0.35	1057		
14m	3-Hydroxy-2-butanone/ *1-Hexyl acetate*	1253	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$/*HS-SPME-GCXGC-qMS*	Alves and Franco (2003)
15m	*n*-Octanal	1274	0.04	–		
16m	Propyl hexanoate	1305	0.07	1097		Alves and Franco (2003)
17m	6-Methyl-5-hepten-2-one	1320	0.05	–		
18m	2-Octanol	1333	–	–	$HSSE_{PDMS}$	

(*continued on next page*)

Table 1 (*continued*)

Peak #	Compound	Solgel-Wax		Mega-SE52	Other techniques	Ref.
		LRI	Peak (%)	LRI		
19m	1-Hexanol/ *Ethyl-2-hexenoate*	1340	1.21	876	*HS-SPME-GCXGC-qMS*	Rezende and Fraga (2003)
20m	Methyl octanoate	1375	0.15	1126		Alves and Jennings (1979), Alves and Franco (2003)
21m	*n*-Nonanal	1378	0.07	1105		
22m	Butyl hexanoate	1389	–	1193	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Alves and Jennings (1979), Alves and Franco (2003)
23m	Hexyl butanoate	1406	–	–	$HSSE_{PDMS}$	Alves and Franco (2003)
24m	Ethyl octanoate	1422	1.52	1199		Rezende and Fraga (2003), Alves and Jennings (1979), Alves and Franco (2003)
25m	Acetic acid	1435	1.32	–		Alves and Franco (2003)
26m	2-Ethylhexanol	1477	0.50	1030		
27m	*n*-Decanal	1484	0.04	1206		
28m	Benzaldehyde	1501	–	957	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Alves and Franco (2003)
29m	Pentadecane	1501	–	1500	HS-SPME- ap-GC–MS, $HSSE_{Dual}$	
30m	Linalool	1536	0.25	1100		
31m	Ethyl-3-methyl-thio-propionate	1540	0.28	1102	$HSSE_{PDMS}$,	Rezende and Fraga(2003), Alves and Franco (2003)
32m	Isobutyric acid	1544	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	Alves and Franco (2003)
33m	1-Octanol	1546	0.05	–		
34m	Hexyl hexanoate	1596	0.28	1388		Alves and Jennings (1979), Alves and Franco (2003)
35m	Butyric acid	1605	11.46	830		Rezende and Fraga (2003), Alves and Franco (2003)
36m	Acetophenone	1622	–	–	$HSSE_{PDMS}$	Alves and Franco (2003)
37m	Ethyl decanoate	1624	0.12	1397		Rezende and Fraga (2003), Alves and Jennings (1979)
38m	Ethyl benzoate	1637	0.10	1171		
39m	Isovaleric acid	1653	0.06	–		
40m	Ethyl 3-hydroxyhexanoate	1657	0.01	–		
41m	Methionol	1688	0.21	982		Alves and Franco (2003)
42m	*n*-Dodecanal	1696	–	1409	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$	
43m	*n*-Tridecanal	1806	–	–	$HSSE_{PDMS}$	
44m	Caproic acid	1821	44.54	–		Rezende and Fraga (2003), Alves and Franco (2003)
45m	2-Phenylethanol	1876	0.52	1113		Rezende and Fraga (2003)
46m	Phenylethyl butyrate	1929	0.08	–		
47m	Heptanoic acid	1936	0.02	–		
48m	1-Dodecanol	1957	–	–	$HSSE_{PDMS}$	
49m	Octanoic Acid	2038	2.66	1179		Rezende and Fraga (2003), Alves and Franco (2003)
50m	δ-Decalactone	2151	0.04	1496		
51m	1-Tetradecanol	2160	–	–	$HSSE_{PDMS}$	
52m	Decanoic acid	2252	0.13	1369		Rezende and Fraga (2003), Alves and Franco (2003)
53m	Toluene	–	–	805	HS-SPME-ap-GC–MS	
54m	2-Heptanone	–	–	893	HS-SPME-ap-GC–MS	Alves and Jennings (1979), Alves and Franco (2003)
55m	2-Heptanol	–	–	902	HS-SPME-ap-GC–MS	Alves and Franco (2003)
56m	(2*E*)-2-Heptenal	–	–	956	HS-SPME-ap-GC–MS	
57m	1-Octen-3-ol	–	–	980	HS-SPME-ap-GC–MS	Rezende and Fraga (2003)
58m	2-Phenoxyethanol	–	–	1220	HS-SPME-ap-GC–MS	
59m	Isopentyl hexanoate	–	–	1252	HS-SPME-ap-GC–MS	
60m	(*E*)-Cinnamaldehyde	–	–	1270	HS-SPME-ap-GC–MS	
61m	Butyl benzoate	–	–	1373	HS-SPME-ap-GC–MS	
62m	Tetradecane	–	–	1400	HS-SPME-ap-GC–MS	
63m	Ethyl Palmitate	–	–	1995	HS-SPME-ap-GC–MS	Rezende and Fraga (2003), Alves and Jennings (1979)
64m	1-Hexadecanol	2364	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
65m	Tridecanoic acid	2675	–	–	$HSSE_{Dual}$	

m- for murici; LRI – Linear Retention Index; Peak%:% area calculated on HS-SPME-GC-polar column-MS pattern; Ref.: literature reference of identified compounds; (–): compounds not found with the method mentioned at the head of the column; dual: PDMS-Carbopack B; ap: apolar. Components identified by HS-SPME-GCxGC-qMS are in Italics.

Table 2
List of volatiles identified in the headspace of bacuri fruits sampled with HS-SPME and HSSE combined with GC–MS ordered in function of their elution sequence on polar column.

Peak #	Compound	Solgel-Wax		Mega-SE52	Other techniques	Ref.
		LRI	Peak (%)	LRI		
1b	Ethyl butyrate	1048	0.99	825	HS-SPME-ap-GC–MS	
2b	Isobutanol	1081	1.20	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
3b	Isoamyl acetate/*3-Hexen-1-ol*	1108	1.40	882	HS-SPME-ap-GC–MS, $HSSE_{Dual}$/*HS-SPME-GCXGC-qMS*	
4b	1-Butanol	1114	–	–	$HSSE_{PDMS}$	
5b	1-Penten-3-ol	1142	0.50	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
6b	β-Myrcene	1147	0.46	990	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
7b	2-Heptanone	1166	2.50	893	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$	Boulanger et al. (1999), Alves and Jennings (1979)

Table 2 (*continued*)

Peak #	Compound	Solgel-Wax		Mega-SE52	Other techniques	Ref.
		LRI	Peak (%)	LRI		
8b	Limonene	1178	0.65	1026	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$	Borges and Rezende (2000), Boulanger et al. (1999)
9b	3-Methyl-1-butanol	1193	6.82	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
10b	(*Z*)-β-Ocimene	1213	–	1038	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
11b	(*E*)-β-Ocimene	1220	1.18	1048	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
12b	Styrene	1217	–	–	$HSSE_{PDMS}$	
13b	1-Pentanol	1223	–	–	$HSSE_{PDMS}$	Boulanger et al. (1999)
14b	γ-Terpinene	1234	–	–	$HSSE_{Dual}$	Boulanger et al. (1999), Alves and Jennings (1979)
15b	3-Hydroxy-2-butanone	1255	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	Borges and Rezende (2000)
16b	(3*E*)-4,8-Dimethyl-1,3,7-nonatriene	1295	0.18	–	–	
17b	6-Methyl-5-hepten-2-one	1321	0.27	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
18b	(*Z*)-Rose oxide	1332	0.10	1111	HS-SPME-ap-GC–MS	Borges and Rezende (2000)
19b	1-Hexanol	1340	1.36	876	HS-SPME-ap-GC–MS, $HSSE_{Dual}$	Boulanger et al. (1999)
20b	Benzyl methyl ether	1367	1.03	–	$HSSE_{PDMS}$	Boulanger et al. (1999)
21b	*n*-Nonanal	1378	0.05	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
22b	2-Butoxy-ethanol	1382	0.36	–	–	
23b	(*Z*)-Linalool oxide	1421	9.96	1072	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Borges and Rezende (2000)
24b	Furfural	1435	–	–	$HSSE_{PDMS}$	Borges and Rezende (2000), Boulanger et al. (1999), Alves and Jennings (1979)
25b	Acetic acid	1439	0.09	–	$HSSE_{PDMS}$, $HSSE_{Dual}$/ *HS-SPME-GCXGC-qMS*	
26b	(*E*)-Linalool oxide	1448	2.22	1088	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Borges and Rezende (2000), Jelen et al. (2012)
27b	2-Ethylhexanol	1477	0.72	1029	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	
28b	*n*-Decanal	1477	–	1206	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	
29b	Benzaldehyde	1493	–	957	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$	Boulanger et al. (1999)
30b	Propanoic acid	1515	–	–	$HSSE_{PDMS}$	
31b	Linalool	1537	54.52	1101	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Borges and Rezende (2000), Boulanger et al. (1999), Alves and Jennings (1979)
32b	5-Methylfurfural	1548	–	–	$HSSE_{PDMS}$	Borges and Rezende (2000)
33b	Hotrienol	1595	4.53	1105	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
34b	*n*-Hexadecane	1603	–	1599	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$	
35b	Acetophenone	1623	0.88	1065	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	
36b	Ethyl benzoate	1638	0.20	–	–	
37b	α-Terpineol	1675	1.31	1190	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Borges and Rezende (2000), Boulanger et al. (1999)
38b	*n*-Heptadecane	1701	–	–	$HSSE_{PDMS}$	
39b	2-Undecenal	1732	–	–	$HSSE_{Dual}$	
40b	Citronellol	1752	0.06	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
41b	Nerol	1780	0.09	1255	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Borges and Rezende (2000)
42b	Phenethyl acetate	1783	0.17	–	–	
43b	*n*-Octadecane	1801	–	–	$HSSE_{Dual}$	
44b	p-Cymen-8-ol	1822	0.45	1185	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
45b	Geraniol	1824	–	1256	$HSSE_{PDMS}$, $HSSE_{Dual}$	Borges and Rezende (2000), Boulanger et al. (1999)
46b	Geranylacetone	1828	–	1454	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$/ *HS-SPME-GCXGC-qMS*	
47b	Benzyl alcohol	1844	0.33	1035	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
48b	2-Phenylethanol	1876	1.37	1113	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
49b	*n*-Nonadecane	1899	–	–	$HSSE_{Dual}$	
50b	2,6-Dimethyl-3,7-octadiene-2,6-diol	1936	0.75	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
51b	1-Dodecanol	1950	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
52b	Methyl tetradecanoate	1990	–	1726	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$	Boulanger et al. (1999)
53b	*n*-Eicosane	1996	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
54b	(*E*)-Cinnamaldehyde	2014	0.71	1270	HS-SPME-ap-GC–MS	
55b	Ethyl Tetradecanoate	2032	–	1795	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Boulanger et al. (1999)
56b	*n*-Heneicosane	2096	–	–	$HSSE_{Dual}$	
57b	1-Tetradecanol	2152	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
58b	*n*-Docosane	2195	–	–	$HSSE_{Dual}$	
59b	Hydroxydihydromaltol	2206	–	–	$HSSE_{PDMS}$	
60b	Ethyl palmitate	2233	–	1995	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$	
61b	Ethyl hexadecanoate	2235	–	–	$HSSE_{Dual}$	Boulanger et al. (1999)
62b	*n*-Tricosane	2294	–	–	$HSSE_{Dual}$	
63b	1-Hexadecanol	2358	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
64b	Ethyl oleate	2461	0.05	2168	HS-SPME-ap-GC–MS	
65b	Toluene	–	–	805	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
66b	*n*-Hexanal	–	–	823	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
67b	(*E*)-2-Hexenal	–	–	863	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
68b	(*Z*)-3-Hexen-1-ol	–	–	866	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
69b	Methyl hexanoate	–	–	925	HS-SPME-ap-GC–MS	Borges and Rezende (2000)
70b	Geranic oxide	–	–	969	HS-SPME-ap-GC–MS	
71b	1-Heptanol	–	–	972	HS-SPME-ap-GC–MS/ *HS-SPME-GCXGC-qMS*	
72b	Phenol	–	–	984	HS-SPME-ap-GC–MS	
73b	Butyl butanoate	–	–	997	HS-SPME-ap-GC–MS	

(*continued on next page*)

Table 2 (*continued*)

Peak #	Compound	Solgel-Wax		Mega-SE52	Other techniques	Ref.
		LRI	Peak (%)	LRI		
74b	Ethyl hexanoate	–	–	1001	HS-SPME-ap-GC–MS	Borges and Rezende (2000), Boulanger et al. (1999)
75b	p-Cymene	–	–	1022	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
76b	2-Nonanone	–	–	1093	HS-SPME-ap-GC–MS	Boulanger et al. (1999), Alves and Jennings (1979)
77b	(*E*)-Rose oxide	–	–	1127	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
78b	Nerol oxide	–	–	1155	HS-SPME-ap-GC–MS	
79b	3-Ethylphenol	–	–	1168	HS-SPME-ap-GC–MS	
80b	Ethyl octanoate	–	–	1199	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
81b	2-Phenoxyethanol	–	–	1220	HS-SPME-ap-GC–MS	
82b	(2*E*)-Decenal	–	–	1262	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
83b	Butyl benzoate	–	–	1373	HS-SPME-ap-GC–MS	
84b	Ethyl decanoate	–	–	1397	HS-SPME-ap-GC–MS/ *HS-SPME-GCXGC-qMS*	
85b	*n*-Tetradecane	–	–	1399	HS-SPME-ap-GC–MS	
86b	*n*-Dodecanal	–	–	1409	HS-SPME-ap-GC–MS	
87b	(*E*)-α-Bergamotene	–	–	1435	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
88b	*n*-Pentadecane	–	–	1499	HS-SPME-ap-GC–MS	
89b	Ethyl dodecanoate	–	–	1596	HS-SPME-ap-GC–MS	Boulanger et al. (1999)
90b	Methyl oleate	–	–	2101	HS-SPME-ap-GC–MS	
91b	Palmitic acid	2844	–	–	$HSSE_{PDMS}$	Borges and Rezende (2000)

b- for bacuri; LRI – Linear Retention Index; Peak%:% area calculated on HS-SPME-GC-polar column-MS pattern; Ref.: literature reference of identified compounds; (–): compounds not found with the method mentioned at the head of the column; dual: PDMS-Carbopack B; ap: apolar. Components identified by HS-SPME-GCxGC-qMS are in Italics.

Table 3
List of volatiles identified in the headspace of sapodilla fruits sampled with HS-SPME and HSSE combined with GC–MS ordered in function of their elution sequence on polar column.

Peak #	Compound	Solgel-Wax		Mega-SE52	Other techniques	Ref.
		LRI	Peak (%)	LRI		
1s	Ethyl butyrate	1047	0.93	825	HS-SPME-ap-GC–MS	
2s	Isobutanol	1086	3.39	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
3s	Isoamyl acetate	1104	11.61	882	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	
4s	1-Butanol	1130	0.55	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	MacLeod and Troconis (1983), Pino et al. (2003)
5s	*n*-Heptanal	1143	–	–	$HSSE_{PDMS}$	
6s	Limonene	1172	0.65	1026	HS-SPME-ap-GC–MS	
7s	3-Methyl-1-butanol	1193	12.70	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	MacLeod and Troconis (1983), Pino et al. (2003)
8s	Ethyl hexanoate	1217	2.60	1001	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$	
9s	3-Methyl-3-buten-1-ol	1222	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
10s	Styrene	1237	2.20	–	–	MacLeod and Troconis (1983), Pino et al. (2003)
11s	3-Hydroxy-2-butanone	1261	2.37	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	MacLeod and Troconis (1983), Pino et al. (2003)
12s	Hydroxypropanone	1280	–	–	$HSSE_{Dual}$	
13s	6-Methyl-5-hepten-2-one/ *Ethyl lactate*	1320	0.21	–	$HSSE_{PDMS}$/ *HS-SPME-GCXGC-qMS*	
14s	1-Hexanol	1341	1.59	876	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	MacLeod and Troconis (1983)
15s	*n*-Nonanal	1380	0.08	1105	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	
16s	Ethyl octanoate/ *Z-Linalool oxide*	1422	0.43	1199	HS-SPME-ap-GC–MS, $HSSE_{Dual}$/*HS-SPME-GCXGC-qMS*	
17s	Acetic acid	1432	27.88	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	Pino et al. (2003), Laohakunjit et al. (2007)
18s	2-Ethylhexanol/*i-Menthone*	1478	4.42	1030	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$/ *HS-SPME-GCXGC-qMS*	
19s	Propanoic acid	1515	–	–	$HSSE_{Dual}$	
20s	Linalyl acetate	1534	–	–	$HSSE_{Dual}$	
21s	Linalool	1536	2.26	1101	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	
22s	1-Octanol	1542	–	–	$HSSE_{PDMS}$	
23s	Terpinen-4-ol	1578	0.83	1176	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Pino et al. (2003)
24s	Butyric acid	1603	–	–	$HSSE_{Dual}$	
25s	Acetophenone	1622	0.98	1065	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Pino et al. (2003)
26s	(*Z*)-2-Decenal	1623	–	–	$HSSE_{PDMS}$	
27s	Ethyl decanoate	1627	0.41	1398	HS-SPME-ap-GC–MS, $HSSE_{Dual}$	
28s	Ethyl benzoate	1636	7.32	1170	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	MacLeod and Troconis (1983), Pino et al. (2003)
29s	Borneol	1669	0.14	–	–	
30s	α-Terpineol	1676	0.06	1190	HS-SPME-ap-GC–MS	
31s	*n*-Dodecanal	1695	0.26	–	–	
32s	1-Undecanol	1710	-	–	$HSSE_{PDMS}$	
33s	1-Decanol	1751	0.05	–	–	
34s	Phenethyl acetate	1783	0.60	1258	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$	
35s	*n*-Tridecanal	1797	–	–	$HSSE_{PDMS}$	
36s	Caproic acid	1819	–	–	$HSSE_{Dual}$	Pino et al. (2003)

Table 3 (*continued*)

Peak #	Compound	Solgel-Wax		Mega-SE52	Other techniques	Ref.
		LRI	Peak (%)	LRI		
37s	Geranylacetone	1829	–	1454	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	
38s	Butyl Benzoate	1830	2.75	1374	HS-SPME-ap-GC–MS	MacLeod and Troconis (1983), Pino et al. (2003)
39s	Benzyl alcohol	1842	2.70	1034	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	MacLeod and Troconis (1983), Pino et al. (2003), Laohakunjit et al. (2007)
40s	2-Phenylethanol	1875	5.73	1113	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	
41s	1-Dodecanol	1955	0.03	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
42s	*n*-Eicosane	1999	–	–	$HSSE_{PDMS}$	
43s	Ethyl Tetradecanoate	2037	0.05	1796	HS-SPME-ap-GC–MS	Pino et al. (2003)
44s	Eugenol	2127	0.18	1358	HS-SPME-ap-GC–MS, $HSSE_{PDMS}$, $HSSE_{Dual}$	Pino et al. (2003)
45s	1-Tetradecanol	2155	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	
46s	2,3-Dihydro-3,5-dihydroxy-6-methyl- 4H-pyran-4-one	2207	–	–	$HSSE_{Dual}$	
47s	Ethyl palmitate	2238	–	1996	HS-SPME-ap-GC–MS, $HSSE_{Dual}$	
48s	*n*-Tricosane	2298	–	–	$HSSE_{Dual}$	
49s	1-Hexadecanol	2359	–	–	$HSSE_{Dual}$	
50s	Ethyl oleate	2461	0.02	2169	HS-SPME-ap-GC–MS	Pino et al. (2003)
51s	Dodecanoic acid	2482	–	–	$HSSE_{PDMS}$	Pino et al. (2003)
52s	Ethyl linoleate	2505	0.04	2163	HS-SPME-ap-GC–MS	
53s	Toluene	–	–	805	HS-SPME-ap-GC–MS	MacLeod and Troconis (1983)
54s	Isobutyl acetate	–	–	810	HS-SPME-ap-GC–MS	
55s	Butyl acetate	–	–	834	HS-SPME-ap-GC–MS	
56s	2-Methylbutyl acetate	–	–	884	HS-SPME-ap-GC–MS	
57s	Phenol	–	–	984	HS-SPME-ap-GC–MS	
58s	Hexyl acetate	–	–	1016	HS-SPME-ap-GC–MS	MacLeod and Troconis (1983)
59s	*n*-Decanal	–	–	1206	HS-SPME-ap-GC–MS, $HSSE_{Dual}$	
60s	2-Phenoxyethanol	–	–	1220	HS-SPME-ap-GC–MS	
61s	Hydrocinnamic alcohol	–	–	1232	HS-SPME-ap-GC–MS	MacLeod and Troconis (1983), Pino et al. (2003)
62s	(*E*)-Cinnamaldehyde	–	–	1270	HS-SPME-ap-GC–MS	
63s	Ethyl dihydrocinnamate	–	–	1350	HS-SPME-ap-GC–MS	Pino et al. (2003)
64s	Methyl eugenol	–	–	1406	HS-SPME-ap-GC–MS	MacLeod and Troconis (1983), Pino et al. (2003)
65s	β-Caryophyllene	–	–	1418	HS-SPME-ap-GC–MS	MacLeod and Troconis (1983), Pino et al. (2003)
66s	Ethyl cinnamate	–	–	1466	HS-SPME-ap-GC–MS	Pino et al. (2003)
67s	Ethyl Dodecanoate	–	–	1596	HS-SPME-ap-GC–MS	Pino et al. (2003)
68s	Benzophenone	–	–	1626	HS-SPME-ap-GC–MS	
69s	Ethyl 9-hexadecenoate	–	–	1974	HS-SPME-ap-GC–MS	
70s	*n*-Tridecanoic acid	2656	–	–	$HSSE_{Dual}$	
71s	Myristic acid	2722	–	–	$HSSE_{Dual}$	Pino et al. (2003)
72s	Palmitic acid	2858	–	–	$HSSE_{PDMS}$, $HSSE_{Dual}$	Pino et al. (2003)

s- sapodilla; LRI – Linear Retention Index; Peak%:% area calculated on HS-SPME-GC-polar column-MS pattern; Ref.: literature reference of identified compounds; (–): compounds not found with the method mentioned at the head of the column; dual: PDMS-Carbopack B; ap: apolar. Components identified by HS-SPME-GCxGC-qMS are in Italics.

3.1. Chemical composition of murici pulp (*Byrsonima crassifolia L.*)

Fig. 1 reports the HS-SPME-GC–MS profile of the volatile fraction of murici pulp with a polar column. Table 1 shows the compounds identified in the headspace of murici pulp.

Sixty-five compounds were identified in murici pulp by HS-SPME-GC–MS, with 54 of them through polar column-GC–MS and 41 with apolar column-GC–MS; 24 of them were specifically detected by polar column-GC–MS and 10 by apolar column-GC–MS. Most of the compounds identified with the polar column were

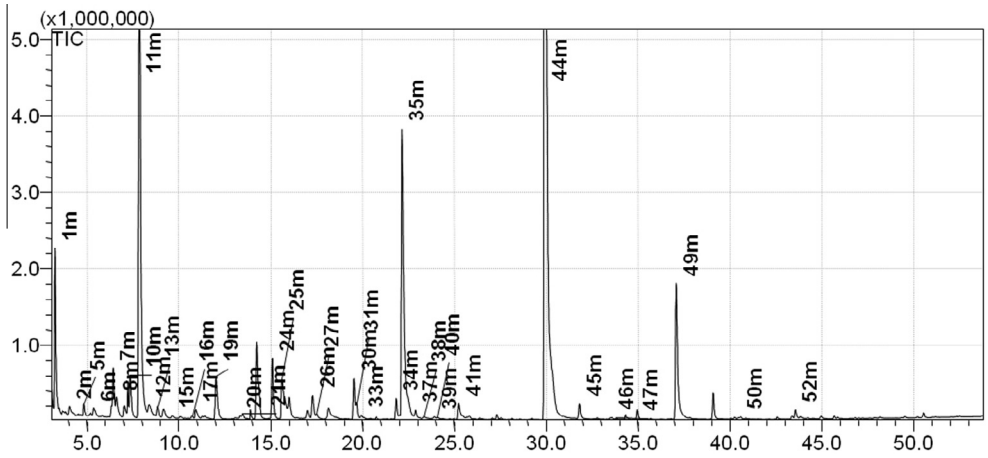

Fig. 1. HS-SPME-GC–MS with polar column pattern of the volatile fraction of murici pulp (time expanded total ion chromatogram).

esters (38% of total identified compounds), carboxylic acids (19%), alcohols (14%), and aldehydes (11%) and approximately 13% consisted of terpenoids and sulfur compounds. The most abundant components were caproic acid (**44m**), (area%: 44%), ethyl hexanoate (**11m**) (area%: 26%), and butyric acid (**35m**), (area%: 11%). These compounds were also identified by other authors (Alves & Franco, 2003; Franco & Janzantti, 2005; Rezende & Fraga, 2003; Sgorbini et al., 2009). The compounds identified for the first time in this fruit are limonene (**8m**), *n*-octanal (**15m**), 6-methyl-5-hepten-2-one (**17m**), *n*-nonanal (**21m**), 2-ethylhexanol (**26m**), *n*-decanal (**27m**), 1-octanol (**33m**), isovaleric acid (**39m**), phenylethyl butyrate (**46m**) and heptanoic acid (**47m**). HS-SPME-GC–MS with apolar column afforded to identify another 15 volatiles for the first time, in particular, pentadecane (**29m**), *n*-dodecanal (**42m**), toluene (**53m**), (2*E*)-heptenal (**56m**), 2-phenoxyethanol (**58m**), isopentyl hexanoate (**59m**), (*E*)-cinnamaldehyde (**60m**), butyl benzoate (**61m**) and tetradecane (**62m**).

Thirty-six compounds were identified with HSSE-GC–MS, 20 of which were already identified by HS-SPME-GC–MS with polar columns. Fourteen compounds were identified with PDMS twister and nine with PDMS-Carbopack B; the most abundant were 3-methyl-1-butanol (**9m**) and 3-hydroxy-2-butanone (**14m**). 1-Dodecanol (**48m**), 1-tetradecanol (**51m**), 1-hexadecanol (**64m**) and tridecanoic acid (**65m**) are reported here for the first time in this fruit.

Other authors studied the volatile fraction of murici pulp. Alves and Jennings found a large number of esters in the pulp diluted with water after SDE extraction (Alves & Jennings, 1979). Alves and Franco identified 46 volatile compounds in murici pulp diluted with water by dynamic headspace with Porapak Q as a trapping material; 31 of them have also been found in the present study (Tienpont et al., 2000). Rezende and Fraga identified 19 compounds in the SDE extracts of murici pulp (Rezende & Fraga, 2003), ten of which were also found here in the HS-SPME-GC–MS profile.

Sulphur compounds even in low concentrations frequently influence the sensory properties of the investigated fruits (Rezende & Fraga, 2003), although their isolation and identification are often an analytical challenge (McGorrin et al., 2011). The sulfur compounds here identified in murici pulp and in previous studies were ethyl-3-methyl-thio-propionate (**31m**) and methionol (**41m**) Alves & Jennings, 1979; Alves & Franco, 2003. The presence of sulfur compounds was confirmed only by PDMS twister and not by PDMS-Carbopack B, likely because of the irreversible interaction of sulfur compounds with Carbopack B (Bicchi et al., 2005).

The aroma of murici was described as presenting cheesy, pineapple and cherry notes. In a previous study with GC-AEDA analysis, Rezende and Fraga identified ethyl butyrate (fruity, sweet), ethyl hexanoate (fruity), 1-octen-3-ol (mushroom, cheese) and 2-phenylethanol (floral) as characteristic odorants in the SDE extract of murici (Rezende & Fraga, 2003). These compounds were also identified in this study by using both HS-SPME-GC–MS and HSSE-GC–MS; 1-octen-3-ol was only found with HS-SPME-GC–MS.

3.2. Chemical composition of bacuri fruits (*Platonia insignis*)

Ninety-one compounds were identified in bacuri pulp by HS-SPME-GC–MS (Table 2), 66 of which were identified with the polar column-GC–MS and 26 with the apolar column-GC–MS. Most of the compounds identified with the polar column were terpenoids (41% of the total identified compounds), followed by non-terpenic alcohols (24%), esters (15%), ketones (9%), and aldehydes (6%), while approximately 3% were carboxylic acids. The major component is linalool (**30b**) (54%), while ethyl butyrate (**1b**), isobutanol (**2b**), isoamyl acetate (**3b**), 1-penten-3-ol (**5b**), (3*E*)-4,8-dimethyl-1,3,7-nonatriene (**16b**), 6-methyl-5-hepten-2-one (**17b**), *n*-nonanal (**21b**), 2-butoxy-etanol (**22b**), acetic acid (**25b**), 2-ethylhexanol (**27b**), acetophenone (**35b**), phenethyl acetate (**42b**), (*E*)-cinnamaldehyde (**54b**), and ethyl oleate (**64b**) are here reported for the first time in this fruit. With HS-SPME apolar column-GC–MS, another 26 volatiles have been found for the first time in this fruit, in particular, *n*-decanal (**28b**), *n*-hexadecane (**34b**), geranylacetone (**46b**), ethyl palmitate (**60b**), geranic oxide (**70b**), 1-heptanol (**71b**), phenol (**72b**), 3-ethylphenol (**79b**), 2-phenoxyethanol (**81b**), butyl benzoate (**83b**), *n*-tetradecane (**85b**), *n*-dodecanal (**86b**), *n*-pentadecane (**88b**) and methyl oleate (**90b**). Fig. 2 reports the HS-SPME-GC–MS with polar column profile of the volatile fraction of bacuri pulp.

Forty-three compounds were identified with HSSE-GC–MS, 27 of which have already been found by HS-SPME-GC–MS with polar columns. Twenty-two compounds were identified with PDMS and 18 with PDMS-Carbopack B twisters (eight of them with both twisters), the most abundant being geraniol (**45b**), 1-butanol (**4b**), styrene (**12b**), propanoic acid (**30b**), *n*-heptadecane (**38b**), *n*-octadecane (**43b**), 1-dodecanol (**51b**), *n*-eicosane (**53b**), *n*-heneicosane (**56b**), 1-tetradecanol (**57b**), *n*-docosane (**58b**), hydroxydihydromaltol (**59b**), *n*-tricosane (**62b**) and 1-hexadecanol (**63b**) are reported here for the first time in this fruit.

Alves and Jennings investigated the volatile profile of bacuri pulp suspended in water after SDE extraction and identified 12 compounds, four of them were also found in this study with HS-SPME (Belliardo et al., 2006). With the same approach, Borges and Rezende identified 23 compounds, the main one of them being linalool; seven of them were also identified in the present study (Borges & Rezende, 2000). Boulanger et al. analyzed the pulp of bacuri diluted with water followed by XAD-2 fractionation with a GC–MS and identified 74 components, only 16 of which found in the present study HS-SPME (Boulanger et al., 1999).

Some compounds detected in this study are known to be responsible of some specific bacuri sensory notes, such as 2,6-dimethyl-octa-3,7-dien-2,6-diol (**95b**), that can be transformed in hotrienol and nerol oxide under mild acid conditions by non-enzymatic rearrangement, or 1-hexanol (**19b**) and (*Z*)-3-hexen-1-ol (**68b**) that can contribute to the herbaceous odor, and geraniol (**45b**) and geranylacetone (**46b**) for the floral aroma (Borges &

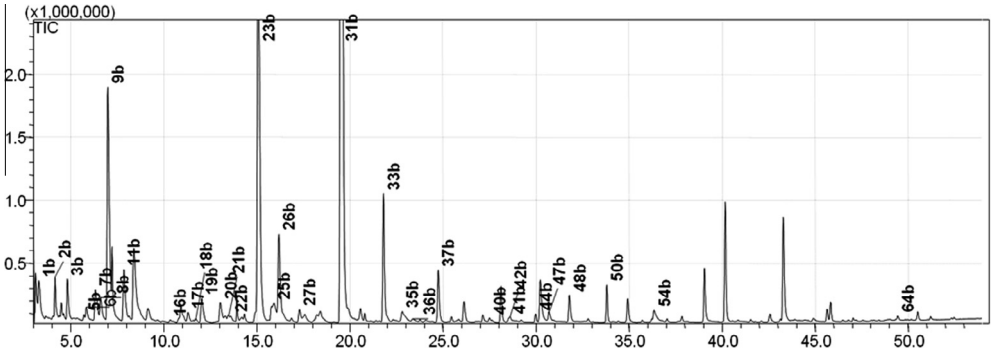

Fig. 2. HS-SPME-GC–MS with polar column profile of the volatile fraction of bacuri pulp (time expanded total ion chromatogram).

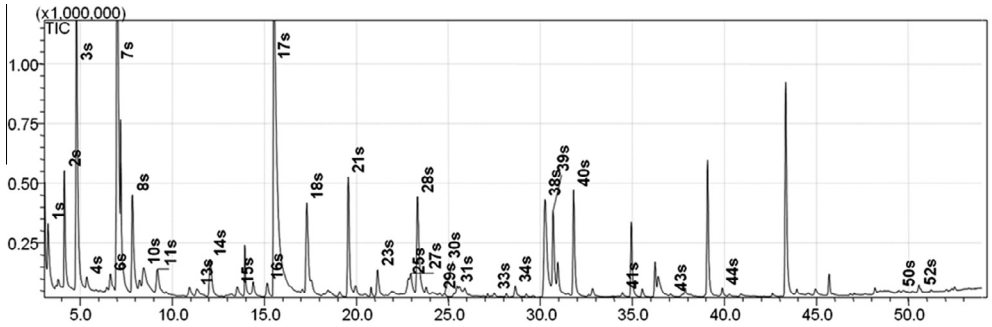

Fig. 3. HS-SPME-GC–MS with polar column pattern of the volatile fraction of sapodilla pulp (time expanded total ion chromatogram).

Rezende, 2000; Preininger et al., 2009; Čechovská, Cejpek, Konečný, & Velíšek, 2011).

In a study by GC-olfactometry in combination with AEDA, Bicas et al. found that the characteristic floral aroma was due to linalool and that the fruity note had to be attributed to methyl hexanoate (Bicas et al., 2011).

3.3. Chemical composition of Sapodilla fruits (Achras sapota L.)

Seventy-two volatile compounds were identified in the headspace of sapodilla fruits with the same techniques mentioned above. Fig. 3 reports the HS-SPME-GC–MS with the polar column profile of the volatile fraction of sapodilla pulp. The list of identified compounds from the sapodilla headspace is reported in Table 3.

HS-SPME-GC–MS applied to sapodilla pulp enabled to identify 72 compounds, 55 with polar column-GC–MS and 17 with apolar column-GC–MS. Most of the identified compounds with polar column were esters (33% of the identified compounds), alcohols (27%), terpenoids (18%), and ketones (9%) and approximately 12% were aldehydes, carboxylic acids and hydrocarbons. The most abundant component is acetic acid (**17s**) (27%), also found by other authors (Laohakunjit et al., 2007; MacLeod & Troconis, 1983; Pino et al., 2003). Ethyl butyrate (**1s**), isoamyl acetate (**3s**), limonene (**6s**), ethyl hexanoate (**8s**), 6-methyl-5-hepten-2-one (**13s**), *n*-nonanal (**15s**), ethyl octanoate (**16s**), 2-ethylhexanol (**18s**), linalool (**21s**), ethyl decanoate (**27s**), borneol (**29s**), α-terpineol (**30s**), *n*-dodecanal (**31s**), 1-decanol (**33s**), phenethyl acetate (**34s**), 1-dodecanol (**41s**) and ethyl linoleate (**52s**) were identified for the first time in this fruit. Another 17 volatiles reported for the first time in this fruit were found by apolar column-GC–MS; in particular, geranylacetone (**37s**), ethyl palmitate (**47s**), isobutyl acetate (**54s**), butyl acetate (**55s**), 2-methylbutyl acetate (**56s**), phenol (**57s**), *n*-decanal (**59s**), hydrocinnamic alcohol (**61s**), (*E*)-cinnamaldehyde (**62s**), ethyl dihydrocinnamate (**63s**), benzophenone (**68s**) and ethyl 9-hexadecenoate (**69s**).

A mean of 39 compounds were found with HSSE-GC–MS, 21 of which were already identified by HS-SPME-GC–MS with polar columns. Eleven compounds were identified with both PDMS and PDMS-Carbopack B twisters; the most abundant being palmitic acid (**72s**) followed by 3-methyl-3-buten-1-ol (**9s**) and geranylacetone (**37s**). *n*-Heptanal (**5s**), hydroxypropanone (**12s**), propanoic acid (**19s**), linalyl acetate (**20s**), 1-octanol (**22s**), butyric acid (**24s**), (*Z*)-2-decenal (**26s**), 1-undecanol (**32s**), *n*-tridecanal (**35s**), *n*-eicosane (**42s**), 1-tetradecanol (**45s**), *n*-tricosane (**48s**), 1-hexadecanol (**49s**) and 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one (**46s**) are reported for the first time in this fruit.

According to the literature, sapodilla aroma volatiles are mostly benzyl-derivatives, in addition to alkyl benzoates and methyl salicylate. MacLeod and Troconis analyzed a SDE extract of sapodilla diluted with water and identified 50 compounds; only seven of them were also found in this study with HS-SPME-GC–MS with a polar column. The major component was benzaldehyde, not found in this study (MacLeod & Troconis, 1983). Pino et al. analyzed a SDE extract of sapodilla with GC–MS with a polar column, and they obtained 34 compounds, only eight of them also found in this study. The major component was methanethiol, not detected in the present study.(Pino et al., 2003) Laohakunjit et al. identified 23 compounds in sapodilla pulp from Thailand and Central America by HS-SPME, only two also found in this study, although the same sampling approach was used. The most abundant components were acetaldehyde and ethyl acetate, not identified in this study. As also suggested by Laohakunjit et al., differences in composition can be related to the fruit variety and agricultural practices (Laohakunjit et al., 2007).

3.4. HS-SPME-GC × GC-qMS analysis of the investigated fruits

Comprehensive two-dimensional Gas Chromatography combined with mass spectrometry (GC × GC-qMS) was here applied because it provides an increase in peak capacity and sensitivity, and it can be very helpful in separating co-eluting peaks in the complex matrices under investigation (Chin, Eyres, & Marriot, 2011; Tran et al., 2006).

Some co-elutions in HS-SPME-1D-GC–MS have been overcome by applying HS-SPME-GC × GC-qMS, and new compounds potentially impacting the aroma have been identified. This is the case of 1-hexyl acetate a component with a typical fruit odor co-eluting with 3-hydroxy-2-butanone (**14m**) and ethyl-2-hexenoate with 1-hexanol (**19m**) with murici pulp (Alves & Franco, 2003; Alves & Jennings, 1979; Franco & Janzantti, 2005; Rezende & Fraga, 2003). In bacuri pulp, 5 acetate (**3b**) and 3-hexen-1-ol acetate, acetic acid (**25b**) and 1-heptanol (**71b**), and ethyl decanoate (**84b**) and geranylacetone (**46b**) were unequivocally separated and identified. In the sapodilla volatile fraction, the co-elutions of 6-methyl-5-hepten-2-one (**13s**) and ethyl lactate, ethyl octanoate (**16s**) and (*Z*)-linalool oxide, and 2-ethylhexanol (**18s**) and isomenthone were unequivocally overcome only when HS-SPME-GC × GC-qMS was applied. Ethyl lactate, (*Z*)-linalool oxide and isomenthone were identified for the first time in this fruit. Ethyl lactate is described in the literature as sweet, fruity, acidic ethereal and with a brown nuance; it was also found in murici fruit in this study; (*Z*)-linalool oxide was also found in soursop and bacuri fruits, and isomenthone occurs in several essential oils such as those of peppermint, geranium and bergamot (Franco & Janzantti, 2005).

The reported results clearly show how the study of the composition of the volatile fraction of a fruit can take advantage of the concurrent and complementary application of more than one sampling and analysis techniques and conditions. The adoption of this

strategy in the study of the volatile fraction of the above three fruits enabled not only to increase substantially the number of compounds identified but also to characterize components that because of their sensory properties strongly influence the aroma of the fruits investigated.

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Appendix A. Supplementary data

Supplementary figures 4, 5 and 6 present figures of murici, bacuri and sapodilla fruits. Supplementary figure 7 reports the H S-SPME–GC×GC–MS patterns from murici pulp with highlighted co-elutions. Supplementary figure 8 reports the HS-SPME–GC×G C–MS patterns from bacuri pulp with the co-elutions highlighted. Supplementary figure 9 reports the HS-SPME–GC×GC–MS patterns from sapodilla pulp with the co-elutions highlighted. This material is available free of charge at the journal webpage. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2016.09.098.

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