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Volatile compounds captured through purge and trap technique in caja-umbu (*Spondias* sp.) fruits during maturation

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Abstract

This work identifies the volatile compounds present in the pulp of caja-umbu (*Spondias* sp.) fruits harvested at two different stages (half-ripe and ripe) of maturation. The volatiles were captured through purge and trap technique. The half-ripe caja-umbu fruit pulp contained 67 components among which the principal compounds, representing an area of 71.7% of chromatogram, were identified as β-caryophyllene (22.2%), 2-methyl butanal (19.3%), 2-hexanol (18.6%), ethyl butyrate (7.6%) and α-caryophyllene (3.9%). However, in the ripe caja-umbu fruit pulp, 70 compounds were detected among which 2-methyl butanal (28.4%), 2-hexanol (15.0%), β-caryophyllene (14.1%), ethyl butyrate (6.1%) and α-caryophyllene (2.4%) were prominent compounds. There were notable quantitative differences in prominent compounds such as β-caryophyllene and 2-hexanol which were quantitatively higher in half-ripe fruits while 2-methyl butanal known to possess characteristic pungent fresh fruit aroma increased with maturation, being relatively higher in its content in ripe fruits.

Keywords: Dynamic headspace; Volatiles; Flavor; Aroma; Gas chromatography; Mass spectrometry

1. Introdution

The northeast region of Brazil is known for large scale production of various tropical and sub-tropical fruits as in this region, the growth conditions are favorable for their cultivation such as higher temperatures, light effects and adequate humidity. Among the exotic fruits pertaining to the genus *Spondias*, which are very much appreciated in the region are yellow mombin (*Spondias mombin* L.), umbu (*Spondias tuberosa* Arruda Camara) and caja-umbu fruits.

Although the fruit's origin is unknown, caja-umbu is considered to be a natural hybrid between cajá or yellow mombin (*S. mombin* L.) and umbu (*S. tuberosa* Arruda Camara) fruits (Giacometti, 1993). It possesses some xerophytic characters and is widely spread in some northeastern Brazilian states such Rio Grande do Norte, Ceará, Piauí, Pernambuco e Bahia. In some earlier reports, the fruit was cited as umbu-cajá (Franco & Janzantti, 2005; Franco & Shibamoto, 2000; Lima, Lima, Aldrigue, & Gondim, 2002), however, of late, the fruit is standardized for citation as cajá-umbu (Lira Junior et al., 2005). Furthermore, the use of *Spondias cytherea*, characterizing specie of the caja-umbu fruit, is misnomer as it represents the fruit ambarella (Leon & Shaw, 1990).

The caja-umbu production, although unquantified in Brazil, is considered to be of minor scale. The fruit is known for its attractive appearance, nutritional quality, pleasing aroma and flavor characteristics which are very much appreciated for its consumption as a fresh fruit or in processed form such as pulp, juice, nectars and ice-cream products (Souza, 1998). There is very little work done on post-harvest aspects of caja-umbu fruits. Lima et al. (2002) assembled data on physical, physico-chemical and chemical characteristics of fruits at different stages of mat-

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uration. However, they did not report any data on volatile aroma compounds present in the fruit.

In order to avail full potential of commercialization of caja-umbu fruits it is important to know the maturation and ripening process during which changes occur in their color, texture and flavor specially in its volatile compounds. There is only one work published on the identification of volatile compounds in caja-umbu fruit pulp wherein Franco and Shibamoto (2000) identified only 26 volatile compounds utilizing the dynamic headspace isolation technique. They reported a volatile profile representing a large majority (87%) of terpenic compounds along with 5% esters. However, their work was limited to mature ripe fruits. The objective of this work was also to use the dynamic headspace technique, being in particular, the purge and trap concentration of volatiles and to identify the compounds present in pulp of caja-umbu fruit at two different maturation (half-ripe and ripe) stages.

2. Material and methods

2.1. Fruits and other materials

Fresh half-ripe and ripe caja-umbu fruits were obtained from a Experimental Station Farm, administered by IPA (*Empresa Pernambucana de Pesquisa Agropecuária*), situated in the city of Itambé, in the Pernambuco state of Brazil. Fruits at half-ripe stage of maturation were classified as those possessing either predominant or total yellow color while those at ripe stage possessed totally orange–yellow color. The fruits were transported to the laboratory in the city of João Pessoa in small cardboard boxes and did not have any application whatsoever of inhibitor or accelerator for the control of maturation. Fruits free from any apparent skin damage were selected for analysis. The solvents and authentic standard flavor compounds used in volatiles identification were of pure grade (purity >97.7%) of Merck and Sigma–Aldrich companies, respectively.

2.2. Volatiles isolation

The fruit, after being washed with distilled water, were cooled to 2 °C by submerging it in ice-cooled water. The skin and kernel were separated manually by using a stainless steel knife and the pulp macerated. The capture of volatile components was undertaken in a dynamic headspace system consisting of purge and trap concentrator (Make Tekmar, model 3000). The trap contained a polymer mixture of tenax/silica gel/charcoal (Trap No. 3 of Tekmar). Fifteen millilitres of fruit pulp was taken in the fritless sparger which served as sampler unit and its heating was programmed with an initial temperature of 15 °C for 15 min, followed by heating until 80 °C at which temperature it was maintained for 35 min. Helium gas was utilized as a purge flowing at 40 ml/min. The other analytical conditions were:

Trap temperature: purge 30 °C; desorption 180 °C; bake 225 °C.
Time: purge 50 min; injection 1 min; desorption 1.5 min; trap bake 20 min.

The purge and trap concentrator was interfaced with a system containing a gas chromatograph coupled with a mass spectrometer.

2.3. High-resolution gas chromatography/mass spectrometry

A combined system of Varian gas chromatograph (GC 3800) coupled with mass spectrometer (Saturn 2000R) was used and the analytical data were processed by using software "Saturn GC/MS Workstation, version 5.5" (Varian Inc., Palo Alto, USA). Capillary GC investigations were carried out on a 30 m (length) × 0.25 mm (internal diameter) innophase bondable polyethylene glycol polar capillary column (HP-INNOWax; 0.25 μm film thickness; Hewlett–Packard, Inc., Palo Alto, USA) (Narain & Galvão, 2004). The carrier gas used was helium and column head pressure was maintained at 11.5 psi having a flow rate of 1 ml/min. The oven temperature was programmed: initiation at 30 °C for 5 min, increased at 7 °C/min to 100 °C, maintained at 100 °C for 5 min, increased at 1 °C/min to 130 °C, increased at 10 °C/min to 195 °C wherein maintained for 45 min. The temperatures of the injection port and the GC/MS interface were 175 °C and 195 °C, respectively. The mass spectrometer was operated in the electron ionization mode with an electrical energy of 70 eV and an ion source temperature of 250 °C. The mass spectrum was scanned between 35 and 450 a.m.u. at 0.31 s intervals.

2.4. Compound identification

The linear retention index (RI) values for unknowns were determined based on retention time data obtained by analyzing a series of normal alkanes (C_8–C_{21}). Volatile components were positively identified by matching their RI values and mass spectra with those of standards, also run under identical chromatographic conditions in the laboratory. The identification was also based on matching an unknown mass spectrum with a spectrum available on the National Institute of Standards and Technology, USA (NIST) mass spectral data system or the literature (Adams, 1995; Jennings & Shibamoto, 1980; Kondjoyan & Berdagué, 1996).

3. Results and discussion

Table 1 lists the principal volatile compounds identified in the pulp of caja-umbu fruits at two different stages (half-ripe and ripe) of maturation while Table 2 presents the principal compounds which were found to have major differences between the fruits of half-ripe and ripe stages. The data lists the retention indices and peak area percent values

Table 1
Volatile compounds in caja-umbu fruits

No.	Compound	RI[b]		Area (%)	
		Reference	Sample	Half-ripe	Ripe
1	NI[a]		620		0.01
2	NI		653	0.26	0.76
3	NI		670	0.09	0.04
4	NI		681	0.08	
5	NI		698	0.05	0.05
6	NI		730	0.04	0.05
7	NI		762	0.51	0.17
8	NI		806	0.01	0.01
9	NI		821	0.05	0.05
10	Ethyl acetate		824		0.04
11	Isopropyl formate[c]	838	840	0.15	0.20
12	2-Methyl butanal[c]	906	903	19.26	28.35
13	3-Methyl butanal[c]	910	909	0.06	0.02
14	NI		939	0.08	
15	NI		947	0.25	
16	Isomethyl butanoate[c]	913	916		0.01
17	2,5-Dimethyl furan	938	939		1.30
18	2-Ethyl furan	936	945		7.64
19	2,4-Dimethyl furan	949	954	0.19	0.02
20	Propyl acetate	971	973	0.22	0.08
21	NI		980	0.10	0.02
22	2-Pentanone	983	983		0.06
23	α-Pinene	1007	1007	1.22	0.70
24	1-Penten-3-one	1015	1017	0.38	0.05
25	Ethyl butyrate	1022	1037	7.64	6.13
26	NI		1045	0.02	
27	NI		1047	0.03	
28	Camphene[c]	1050	1049		1.85
29	NI		1053	0.10	
30	1-Hexanal	1069	1068		0.03
31	Butyl acetate	1070	1070	0.30	0.23
32	3-Hexanone	1072	1075	0.05	0.02
33	3-Methyl-2-butenal[c]		1081	0.21	0.17
34	NI		1083	0.03	
35	3-Methyl-2-butanol	1089	1091	0.13	0.03
36	NI		1105	0.06	
37	2-Methyl-2-pentanol	1101	1101		0.15
38	3-Pentanol	1109	1111	0.03	0.08
39	NI		1131	0.10	
40	*p*-Xylene	1120	1120		0.01
41	4-Methyl-3-penten-2-one	1128	1127		0.04
42	NI		1134	0.05	0.08
43	1-Undecene	1136	1139	1.51	0.88
44	3-Carene[c]	1144	1148		0.60
45	β-Myrcene	1145	1143	0.28	0.09
46	NI		1159	5.20	
47	3-Methyl-2-butanoate[c]	1150	1153		0.04
48	*m*-Xylene	1158	1161		0.03
49	1,2-Diethyl-benzene	1160	1162	0.36	0.05
50	NI		1164	0.30	
51	*o*-Xylene	1175	1171		3.12
52	NI		1171	0.01	
53	NI		1174	0.05	
54	NI		1177	0.09	
55	1-Methyl-4-(1-methyl)-1,3-cyclohexadiene[c]	1179	1178	0.01	0.01
56	2-Methyl cyclopentanone	1177	1180		0.44
57	NI		1192	0.01	
58	4-Hexen-3-one	1197	1197		0.76
59	NI		1200	3.66	
60	2-Hexanol	1222	1219	18.56	14.95
61	β-*cis*-Ocimene[c]	1228	1223	2.01	2.68
62	NI		1235	0.03	
63	Cyclopentanone	1239	1238		0.62

Table 1 (*continued*)

No.	Compound	RI[b]		Area (%)	
		Reference	Sample	Half-ripe	Ripe
64	NI		1243	0.35	
65	NI		1249	0.01	
66	3-Hexen-2-one[c]	1252	1250		0.06
67	Hexyl acetate	1268	1258		0.10
69	3-Methyl-3-buten-1-ol	1274	1272	3.50	3.17
68	Methyl pyrazine	1279	1280		0.09
70	3-Hydroxy-2-butanone	1282	1278		0.05
71	NI		1296	0.02	
72	4-Penten-1-ol	1300	1299	0.12	0.15
73	1-Hexanol	1350	1346		0.58
74	4-Methyl-cyclohexanone	1348	1348	0.52	0.17
75	NI		1359	0.01	
76	3-Hexen-1-ol	1378	1379	0.55	0.85
77	2-Nonanone	1388	1392	0.07	0.06
78	2-Hexyl-furan[c]		1394	0.08	0.06
79	2-Cyclohexen-1-one	1410	1412	0.75	0.59
80	NI		1422	0.07	
81	1-Heptanol	1440	1436	0.01	0.05
82	3-Methyl-2-cylopentanol[c]	1448	1446	0.01	0.02
83	NI		1455	0.20	
84	1,2,3,4-Tetramethyl-benzene	1464	1462		0.13
85	2-Acetyl-furan	1510	1509		1.02
86	Linalool	1537	1538	1.83	0.73
87	β-Caryophyllene	1585	1580	22.15	14.08
88	α-Caryophyllene	1642	1642	3.90	2.41
89	NI		1650	0.17	0.19
90	1-Nonanol	1660	1652	0.16	0.54
91	4,4-Dimethyl-cyclopentene[c]	1679	1674		0.15
92	NI		1687	0.58	0.95
93	NI		1694	1.14	1.39

[a] Not identified.
[b] Retention index.
[c] Identified tentatively based on spectrum verification from the NIST mass library or the literature retention indices (Adams, 1995; Jennings & Shibamoto, 1980; Kondjoyan & Berdagué, 1996; our own database of standards).

Table 2
Principal volatile compounds identified in pulp of caja-umbu fruit at two maturation (half-ripe and ripe) stages

Item	Compound name	Class	Retention index	Area (%)	
				Half-ripe	Ripe
1	β-Caryophyllene	Terpene	1567	22.15	14.08
2	2-Methyl butanal	Aldehyde	903	19.26	28.35
3	2-Hexanol	Alcohol	1219	18.56	14.95
4	Ethyl butyrate	Ester	1037	7.64	6.13
5	α-Caryophyllene	Terpene	1642	3.90	2.41
6	3-Methyl-3-buten-1-ol	Alcohol	1221	3.50	3.17
7	β-*cis*-Ocimene	Terpene	1223	2.01	2.68
8	1-Undecene	Alkene	1139	1.51	0.88
9	α-Pinene	Terpene	1007	1.22	0.70
10	2-Ethyl-furan	Furan	945	Nd[a]	7.64
11	*o*-Xylene	Aromatic	1171	Nd	3.12
12	Camphene	Terpene	1049	Nd	1.85
13	2,5-Dimethyl furan	Furan	939	Nd	1.30
14	2-Acetyl furan	Furan	1509	Nd	1.02

[a] Nd, not detected.

for prominent compounds identified and in particular, emphasis is given to the compounds, which had major quantitative changes in fruits of two maturation stages.

Out of a total number of 67 components separated in the half-ripe fruit pulp, representing a total area of about 79% in chromatograms, 24 compounds were positively identified, 8 tentatively identified while 35 compounds could not be identified due to the lack of standard organic compounds. Among the identified components were 10 alcohols, 5 ketones, 4 esters, 5 terpenes. The major classes of total volatiles pertained to terpenes (26.1%), alcohols (22.1%) and aldehydes (20.4%). The major components identified in half-ripe caja-umbu pulp were β-caryophyllene (22.2%), 2-methyl-butanal (19.3%), 2-hexanol (18.6%) and ethyl butyrate (7.6%).

The pulp of ripe caja-umbu fruits when captured through purge and trap technique of volatiles revealed the presence of 70 volatile components out of which 43 were positively identified, 14 tentatively and 13 compounds could not be identified. Of the identified compounds, 12 were classified as ketones, 12 as alcohols, 8 esters, 7 terpenes, 5 aromatic hydrocarbons, 5 furans, 3 aldehyde and 3 alkenes. The aldehyde class represented a higher total area (28.6%) in volatiles captured from ripe fruits when compared with those obtained from half-ripe fruits

(19.5%). The presence of esters ethyl acetate, ethyl butyrate, butyl acetate and hexyl acetate, and terpenes such as β-caryophyllene, α-pinene, β-myrcene, β-trans-ocimene and α-caryophyllene identified in this study were reported earlier by Franco and Shibamoto (2000) who utilized the dynamic headspace technique, using a different polymer, Porapak Q and in their methodology, the volatiles were eluted with hexane. They reported a volatile profile representing 87% of terpenic compounds and 5% of esters. The major compounds identified were (*Z*)-β-ocimene (36%), β-caryophyllene (27%), (*E*)-ocimene (7.4%), D-limonene (7.1%) and D-humulene (4.5%). The difference in volatile profile could be due to a different polymer (Porapak Q) used in the trap, followed by a subsequent elution with hexane. Furthermore, they used only the mature ripe fruits and hence no comparison can be made on variations in volatile compounds profile in fruits at different stages of maturation. In this work, however, we found the presence of (*Z*)-β-ocimene to be only in 2.7% and β-caryophyllene be 14.1% as compared to 36% and 27%, respectively, reported by Franco and Shibamoto (2000). In a study performed on aroma of ambarella (*Spondias cytherea*) fruit by static cryogenic headspace isolation, Fraga and Rezende (2001) identified six aroma impact compounds, being ethyl-2-methyl butyrate (fruity), ethyl isovalerate (fruity and cheese-like), ethyl propionate (fruity), ethyl butyrate (fruity and refreshing), linalool (floral) and (*E*)-pinocarveol (herbaceous). Among these esters identified in ambarella fruit, in this study, only ethyl butyrate, which possesses strong fruity aroma was found to be present.

The total area contributed by the organic compounds as per class such as aldehydes (half-ripe 19.5% and ripe 28.6%), aromatics (half-ripe 0.4% and ripe 3.4%); ketones (half-ripe 1.8% and ripe 2.5%) and furans (half-ripe 0.3% and ripe 10.0%) increased with maturation, representing higher values in the pulp of ripe fruits as compared to that of half-ripe stage. However, during maturation (from half-ripe fruits to ripe fruits) there was a decrease in the concentration of compounds pertaining to classes such as terpenes (half-ripe 31.4% and ripe 23.2%), alcohols (half-ripe 23.2% and ripe 20.6%) and esters (half-ripe 8.3% and ripe 6.9%) was observed. One of the main volatile compounds which had a major effect during maturation was 2-methyl butanal. Its area increased from half-ripe stage of 19.3% to ripe stage of 28.4%. The compounds 2-ethyl furan (7.6%), *o*-xylene (3.1%), camphene (1.9%), 2,5-dimethyl furan (1.3%) and 2-acetyl furan (1.0%) were present only in the pulp of ripe caja-umbu fruits However, the compound numbers 46 and 59 (Table 1), which were represented by 5.2% and 3.7%, respectively, in the pulp of half-ripe fruits and which could not be identified were absent in ripe fruits.

Although the main purpose of this study was to verify the differences in volatiles profile in half-ripe and ripe stages of caja-umbu fruits, the compounds β-caryophyllene and 2-hexanol decreased with maturation while 2-methyl butanal, known to possess characteristic pungent fresh fruit aroma increased with maturation, being relatively higher in content in ripe fruits. The presence of ethyl butyrate, which is characterized as a responsible aroma compound for pineapple fruits was observed in the pulp of fruits of both stages of maturation although to a lesser extent in ripe caja-umbu fruits. Besides the esters, the presence of terpinic compounds are also related to the exotic aroma of the fruit.

4. Conclusions

This work reports for the first time the volatiles profile of caja-umbu fruits at two stages (half-ripe and ripe) of its maturation. There were notable quantitative differences in prominent compounds such as β-caryophyllene and 2-hexanol which decreased with maturation while 2-methyl butanal known to possess characteristic pungent fresh fruit aroma increased with maturation, being relatively higher in content in ripe fruits. In the total volatiles profile, the compounds belonging to the terpene and alcohol classes decreased during maturation of caja-umbu fruit from half-ripe to ripe stage. Besides the major compounds such as β-caryophyllene, 2-methyl butanal, 2-hexanol, ethyl butyrate, α-caryophyllene and β-*cis*-ocimene, some compounds such as isomethyl butanoate, 2,5-dimethyl furan, 2-ethyl furan, 2-methyl-2-pentanol, 3-carene and 1-hexanol were found to be present only in fully ripe stage of fruits and these may contribute to the over-all aroma of ripe cajá-umbu fruits.

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