Volatile Composition of Some Brazilian Fruits: Umbu-caja (*Spondias citherea*), Camu-camu (*Myrciaria dubia*), Araça-boi (*Eugenia stipitata*), and Cupuaçu (*Theobroma grandiflorum*)

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Twenty-one volatile compounds were identified for the first time by GC-MS in umbu-caja and in camu-camu, plus 30 volatile compounds were identified in araça-boi samples. Terpenic compounds predominated among the volatile compounds in these fruit samples, with the major compounds being identified as *cis*-*β*-ocimene and caryophyllene in the northeastern fruit; α-pinene and *d*-limonene were the most abundant volatile compounds in the headspace of the Amazonian fruit camu-camu. Sesquiterpenes were the most abundant compounds in the araça-boi sample, with germacrene D presenting a higher relative percentage. The chemical class of esters predominated in the cupuaçu sample. Ethyl butyrate and hexanoate were the major compounds in the headspace of this Amazonian fruit.

Keywords: *Volatile compounds; headspace; identification; chromatography−mass spectrometry; tropical fruits*

INTRODUCTION

Brazil has a natural abundance of tropical fruits with distinctive exotic flavors appealing to the foreign consumer. However, the flavors of the majority of these fruits have not yet been characterized. Characterization of the volatile compounds would allow for the delineation of a processing procedure that would retain a high quality of aroma and flavor in the finished product.

Umbu-caja, camu-camu, araça-boi, and cupuaçu were the fruits selected for this study because of their economic potential.

Araça-boi is a round fruit, about 12 cm in diameter, with a yellow skin. The edible part, a creamy-white pulp, has an acid flavor. This Amazonian fruit has an excellent economic potential because the tree grows easily and begins to produce within two years. The fruits have a high percentage of pulp, presenting an attractive aroma and flavor, adequate for the manufacture of juices, ice creams, and desserts.

Camu-camu is also a round fruit (2−2.5 cm in diameter), with a red skin and pink pulp. Because of its acid flavor it is consumed mainly as juice. It is also appreciated for its high content of vitamin C.

Cupuaçu fruits are 12−25 cm in length and 10−12 cm in diameter. They are oblong fruits with a hard skin. The creamy-white pulp has an attractive and characteristic aroma and flavor. Cupuaçu is a tree native to the state of Para, and the fruits are consumed mainly as juice.

Umbu-caja, a small round fruit (∼3 cm in diameter) with a yellow skin and a refreshing aroma and sour flavor, is native to the northeastern region of Brazil. It is also mainly consumed as juice.

To date, there is no published scientific information in the literature on the volatile compositions of these fruits, except for cupuaçu.

Alves and Jennings studied canned cupuaçu pulp (1979) using a Nickerson−Lickens simultaneous distillation−extraction apparatus and found that esters were important contributors to the cupuaçu aroma. Ethyl butanoate and hexanoate were the major volatile compounds. Methyl *trans*-2-hexenoate, methyl crotonate, and hexanoic acid were the major compounds when cupuaçu pulp was studied by a solid-phase extraction technique (Fischer et al., 1995).

MATERIALS AND METHODS

Selection of Raw Material. Ripe umbu-caja fruits were bought in January 1997 from a market in Recife, Pernambuco. They were immediately frozen in a 500 g polyethylene bag and sent by airplane to Campinas, São Paulo. Fresh ripe camu-camu and araça-boi fruits were acquired at a market in Manaus, Amazonas, in January 1997 and transported by airplane to Campinas in a 1 kg bag. Commercial frozen cupuaçu pulp was acquired at a market in Campinas in January 1997.

Isolation of the Volatile Compounds. On arrival at the laboratory, the volatile compounds from the headspace of umbu-caja, camu-camu, araça-boi, and cupuaçu were swept by vacuum to a Porapak Q trap for 2 h and then eluted with 300 μL of hexane or, in the case of cupuaçu samples, methanol (Franco and Rodriguez-Amaya, 1983). All solvents employed were pure for chromatography (Lichrosolv Merck). A 100 g aliquot of frozen fruits or 200 g of frozen pulp was homogenized with distilled water at a proportion of 1:2 in a Waring blender. After the addition of 30% w/w NaCl to 300 g of the juice obtained, the solution was put into a volatile collecting apparatus. The salt was previously heated at 200 °C for 2 h. Four samples were prepared for each fruit, which were sealed in ampules and transported to the United States by airplane

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Table 1. Volatile Composition of the Umbu-caja Sample

compound	Kovats index	% area
NI[a]	725	0.42
ethyl acetate	824	1.71
NI	900	0.21
NI	925	0.20
NI	932	0.23
α-pinene	1010	1.48
NI	1038	0.29
ethyl butyrate	1043	1.90
toluene	1055	3.60
butyl acetate	1100	0.72
β-pinene	1100	0.43
β-myrcene	1154	1.29
d-limonene	1184	7.09
β-phellandrene	1192	tr[c]
cis-*β*-ocimene	1236	36.30
trans-*β*-ocimene	1250	7.45
ethyl hexanoate	1252	0.77
hexyl acetate	1289	0.20
1,5,5,6-tetramethyl-1,3-cyclohexadiene[b]	1365	0.62
ethyl octanoate	1442	tr
α-copaene	1450	0.59
β-caryophyllene	1556	26.8
α-caryophyllene	1606	4.49
β-selinene	1679	1.22
1,2,3,4,4a,5,6,8a-octahydro-4a,8-dimethylnaphthalene[b]	1685	1.65
δ-cadinene		0.32

[a] NI, not identified. [b] Tentative identification: based on only mass spectra data. [c] Traces.

in a small insulated box. (U.S. federal laws prohibit the entrance of raw material into the country.)

Gas Chromatographic Analysis. The mixture of volatile compounds was separated on a DB-Wax bonded phase, fused silica capillary column (30 m in length and 0.2 mm i.d.) in an HP gas chromatograph, model 5890, equipped with an FID detector and a Spectra-Physics integrator, model 4290. The chromatographic parameters used were as follows: type of injection, split (1:15); linear velocity of the carrier gas (helium), 25 cm/s at 100 °C; injector and detector temperatures, 250 °C; makeup gas (nitrogen), 30 mL/min. The temperature program used for the column was as follows: initial temperature, 50 °C, held for 8 min, and then programmed to increase at 3 °C/min to a maximum of 180 °C. This final temperature was held for 15 min in the case of the cupuaçu samples.

Gas Chromatography−Mass Spectrometry. Volatile compounds were identified in an HP gas chromatograph, model 5890 series II, equipped with a mass detector, HP model 5971, and an automatic sampler. A 2.0 *μ*L volume was injected into a splitless injector. The fused silica column and programmed temperature were the same as described for the separation of the volatile compounds.

Kovats Indices. A standard mixture of paraffin homologues (C_7−C_9, C_{11}−C_{28}) was prepared using hexane GC Resolv (Fisher Scientific) as solvent. Co-injection of the sample and standard mixture of hydrocarbons gave Kovats indices under the same chromatographic conditions as used previously for the separation of the volatile compounds.

Assignment of Structures. Identification of the volatile compounds was based on the comparison of mass spectra of unknown compounds against NIST library data for the GC-MS and comparison of experimental and theoretical Kovats indices. Identification was considered tentative when it was based on only mass spectra data.

RESULTS AND DISCUSSION

The volatile compositions of umbu-caja, camu-camu, araça-boi, and cupuaçu are shown in Tables 1, 2, 3, and 4, respectively.

Twenty-six compounds were detected in the umbu-caja sample by high-resolution gas chromatography.

Table 2. Volatile Composition of the Camu-camu Sample

compound	Kovats index	% area
ethyl acetate	820	0.17
α-pinene	1009	66.2
α-fenchene	1029	0.09
ethyl butyrate	1048	0.16
camphene	1052	0.20
NI[a]	1065	tr[b]
β-pinene	1102	0.48
car-3-ene	1142	tr
β-myrcene	1155	1.11
α-phellandrene	1160	0.27
NI	1162	0.33
α-terpinene	1169	0.11
d-limonene	1195	23.72
β-phellandrene	1200	0.29
eucalyptol	1208	tr
γ-terpinene	1238	0.58
p-cimene	1267	0.31
terpinolene	1271	0.40
fenchol	1554	tr
β-caryophyllene	1563	4.61
4-terpineol	1574	tr
humulene	1606	tr
NI	1636	0.20
NI	1744	0.16

[a] NI, not identified. [b] Traces.

There was an inversion in the order of elution of ethyl hexanoate and *trans*-*β*-ocimene when performed by gas chromatography. However, the sequence of elution of these compounds in the total ion current chromatogram (obtained by mass detection) was the same as indicated by their theoretical Kovats indices.

The volatile compounds of umbu-caja were predominantly terpenic compounds (87.5%), followed by esters. Nevertheless, this class of compounds accounted for only 5.3% of the total relative percentage. *cis*-*β*-Ocimene (36%), a monoterpene hydrocarbon, and *β*-caryophyllene (27%), a sesquiterpene, were by far the most abundant compounds in the umbu-caja sample, followed by *trans*-ocimene (7.4%), *d*-limonene (7.1%), and α-caryophyllene (4.5%).

The majority of the compounds identified in camu-camu were terpenes (98%). α-Pinene predominated in the headspace of this Amazonian fruit (66%), followed by *d*-limonene (24%). Among the sesquiterpenes, *β*-caryophyllene presented the major relative abundance (4.6%).

Araça-boi was characterized by a complex pattern of sesquiterpenes. These compounds predominated in this Amazonian fruit, with germacrene D being the major compound (38%).

Twenty-one volatile compounds were detected in the headspace of the cupuaçu sample by high-resolution gas chromatography. The chemical class of compounds that predominated in the cupuaçu samples was the esters. Ethyl butanoate and ethyl hexanoate were the major compounds with 42 and 22%, respectively, of the relative area percentages, followed by hexadecanoic acid, with 12% of the total area.

Ethyl butyrate, ethyl 2-methylbutyrate, butyl 2-methylbutyrate, and ethyl hexanoate had already been detected in canned cupuaçu pulp by using the Nickerson−Likens technique (Alves and Jennings, 1979). Ethyl butanoate and hexanoate were also the major volatile compounds, and the authors concluded that esters were important contributors to the cupuaçu aroma.

Ethyl butyrate, ethyl 2-methylbutyrate, 1-butanol, ethyl hexanoate, 3-hydroxy-2-butanone, ethyl octanoate, acid acetic, linalool, and palmitic and oleic acid had

Table 3. Volatile Composition of the Araça-boi Sample

compound	Kovats index	% area
α-pinene	935	10.4
toluene	994	0.7
β-pinene	1104	15.2
sabinene	1118	0.4
β-myrcene	1158	1.6
α-phellandrene	1169	tr[a]
d-limonene	1188	0.9
β-phellandrene	1200	tr
cis-β-ocimene	1236	tr
trans-ocimene	1250	0.6
terpinolene	1270	tr
hexyl acetate	1290	0.8
cis-3-hexenyl acetate	1337	0.5
n-hexyl proprionate	1353	tr
1-hexanol	1369	0.4
n-hexyl butanoate	1427	0.4
NI[b]	1431	tr
α-cubebene[c]	1435	tr
(3*R*-*trans*)-4-ethenyl-4-methyl-3-(1-methylethenyl)-1-(1-methylethyl)cyclohexene[c]	1445	1.6
copaene	1453	1.3
[3a*S*-(3aα,3bβ,4β,7α]octahydro-7-methyl-3-methylene-4-(1-methylethyl)-1*H*-cyclopentane[1,3]cyclopropane[1,2]benzene[c]	1496	0.4
(−)-1,7-dimethyl-7-(4-methyl-1,3-pentenyl)-tricyclo[2.2.1.0(2,6)]heptane[c]	1535	0.8
[1a*R*-(1aα,7α,7aα,7bα)]-1a,2,3,5,6,7,7a,7b-octa-hydro-1,1,7,7a-tetramethyl-1*H*-cyclopropa[a]naphthalene[c]	1544	tr
NI	1551	1.5
β-caryophyllene	1558	2.0
NI	1566	0.3
(*S*)-6-ethenyl-6-methyl-1-(1-methylethyl)-3-(1-methylethylidene)cyclohexene[c]	1579	0.7
(1*S*-*exo*)-2-methyl-3-methylene-2-(4-methyl-1,3-pentenyl)bicyclo[2.2.1]heptane[c]	1600	tr
NI	1611	0.5
α-caryophyllene	1632	0.5
NI	1652	2.3
germacrene D	1683	38.3
germacrene B[c]	1700	1.5
NI	1705	12.6
δ-cadinene	1725	0.3
α-farnesene[c]	1732	0.8
NI	1737	0.3
NI	1749	0.4
NI		0.6

[a] Traces. [b] NI, not identified. [c] Tentative identification: based on only mass spectra data.

already been identified in cupuaçu pulp by an SPE technique (Fischer et al., 1995). Methyl *trans*-2-hexenoate, methyl crotonate, and hexanoic acid were the most abundant compounds, with 16, 15, and 6%, respectively, of the total percentage. In that study, ethyl butanoate and ethyl hexanoate (the major compounds in this study) were detected with relative abundances of only 2 and 0.6%, respectively.

Comparison between Umbu-caja, Camu-camu, Araça-boi, and Cupuaçu Volatile Compounds. Terpenic compounds predominated among the volatile compounds of these tropical fruits, except for the cupuaçu samples. Umbu-caja presented 88% of this class of compounds, camu-camu 98% of the total area, and araça-boi 91% of the relative abundance. A higher predominance of terpenic compounds seems to be a characteristic of tropical fruits.

A monoterpene hydrocarbon, *cis*-β-ocimene (36%), was the major compound in the northeastern fruit followed by a sesquiterpene compound, β-caryophyllene (29%). The Amazonian fruit camu-camu presented a higher relative abundance of two monoterpene hydrocarbons, α-pinene (66%) and *d*-limonene (24%). Camu-camu also showed three terpene alcohols, eucalyptol, fenchol, and 4-terpineol. Araça-boi was characterized by a higher relative abundance of sesquiterpene compounds, and germacrene D was the most abundant compound, with 38% of the total relative area.

Table 4. Volatile Composition of the Cupuaçu Sample

compound	Kovats index	% area
2-methyl-3-buten-2-ol	1064	1.62
ethyl butanoate	1086	42.2
ethyl 2-methylbutyrate	1107	tr[a]
butyl acetate	1134	tr
NI[b]	1162	0.71
1-butanol	1176	9.17
NI	1240	0.85
butyl butyrate	1243	2.80
butyl 2-methylbutanoate	1253	3.27
ethyl hexanoate	1259	21.19
(*E*)-ocimene	1287	1.15
butyl 3-methylbutanoate	1295	tr
3-hydroxy-2-butanone	1320	3.42
butyl hexanoate	1428	1.05
ethyl octanoate	1449	tr
acetic acid	1465	0.64
2,3-butanodiol	1566	3.29
linalool	1579	2.21
1,3-butanodiol	1619	0.71
hexadecanoic acid	2460	12.5
oleic acid	2717	0.73

[a] Traces. [b] NI, not identified.

The detection of esters in these fruits was low. However, cupuaçu samples exhibited a completely different pattern of volatile compounds. Esters predominated in the headspace of this Amazonian fruit (70%), followed by alcohols (15%) and acids (14%). Terpenic compounds were also found in the cupuaçu samples, but only (*E*)-ocimene and linalool were detected among the compounds identified and in low relative percentages. Ethyl butanoate (42%) and hexanoate (22%) were the principal esters found in the headspace of this Amazonian fruit.

Umbu-caja presented as distinctive volatile compounds 1,3-cyclohexadien-1,5,5,6-tetramethyl-1,3-cyclohexadiene, β-selinene and 1,2,3,4,4a,5,6,8a-octahydro-4a,8-dimethylnapthalene.

Camu-camu was qualitatively characterized by α-fenchene, car-3-ene, γ-terpinene, and *p*-cimene and by the presence of the monoterpene alcohols eucalyptol, fenchol, and terpineol.

Araça-boi was characterized by the presence of complex sesquiterpenes and cupuaçu by esters, alcohols, three acids, and a ketone, 3-hydroxy-2-butanone.

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