Volatile compounds of arazá fruit (*Eugenia stipitata* McVaught)

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Palabras clave: *Eugenia stipitata*, Myrtaceae, arazá, compuestos volátiles, octanoato de etilo, decanoato de etilo, dodecanoato de etilo.
Key words: *Eugenia stipitata*, Myrtaceae, arazá, volatile compounds, ethyl octanoate, ethyl decanoate, ethyl dodecanoate.

RESUMEN. El arazá (*Eugenia stipitata* McVaugh) es nativo de la parte peruana de la selva amazónica. La fruta es una esfera, caracterizada por su intenso aroma y sabor ácido, así como color de la piel verde a amarillo al madurar. La parte comestible, una pulpa cremosa blanca se come fresca o es usada para preparar jugos, mermeladas, helados y licores. Los compuestos volátiles se aislaron del arazá mediante extracción líquida-líquida continua con el uso de pentano-diclorometano [1 : 1 (v/v)] durante 8 h y se analizaron por cromatografía de gases capilar con detector de ionización con llama de hidrógeno y cromatografía de gases-espectrometría de masas con el uso de columnas capilares del tipo HP-Innowax. El extracto concentrado obtenido mostró notas aromáticas similares al aroma de la fruta fresca, descrito como dulce-verdoso-frutal. Como resultado, se obtuvieron 7,9 mg de compuestos volátiles por kilogramo de fruta fresca. En total, se identificaron 27 ésteres, 20 terpenos, cinco alcoholes, seis compuestos carbonílicos, cinco ácidos, tres hidrocarburos, dos lactonas y dos compuestos azufrados. De los 70 constituyentes identificados, 53 se reportan por primera vez en esta fruta. Los ésteres (54,8 % del total de la composición) fueron la clase de compuestos más abundante. El octanoato de etilo, dodecanoato de etilo y decanoato de etilo fueron los componentes mayoritarios. Otros compuestos significativos fueron: el etanol, 1-hexanol, globulol, ácido 2-metilbutanoico, ácido hexanoico, ácido octanoico, 3-metil-2-buten-1-ol y 2-furfural.

ABSTRACT. The arazá (*Eugenia stipitata* McVaugh) is native from the Peruvian part of the Amazonian forest. The fruit is a sphere, characterized by its intense aroma and acid flavor and green to yellow peel at maturity. The edible part, a creamy-white pulp, is eaten fresh or is used to prepare juices, marmalades, ice creams and liquors. Volatile compounds were isolated from arazá by continuous liquid-liquid extraction using pentane-dichloromethane [1 : 1 (v/v)] for 8 h, and analyzed by GC-FID and GC-MS using HP-Innowax fused silica column. The concentrated extract showed aroma notes resembling the flavor of fresh fruit, described as sweet-green-fruity. A total amount of 7.9 mg of volatile compounds per kilogram of fresh fruit was obtained. In total, 27 esters, 20 terpenes, five alcohols, six carbonyls, five acids, three hydrocarbons, two lactones and two sulfur-compounds were identified. Of the 70 components identified, 53 are reported for the first time in this fruit. Esters (54.8 % of the total composition) were the most abundant compound class. Ethyl octanoate, ethyl dodecanoate and ethyl decanoate were found to be the major constituents. Other significant compounds were: ethanol, 1-hexanol, globulol, 2-methylbutanoic acid, hexanoic acid, octanoic acid, 3-methyl-2-buten-1-ol and 2-furfural.

INTRODUCTION

Colombia has a natural diversity of tropical fruits with distinctive exotic flavors appealing to the producer that they could be an important source of income. However, the volatile composition responsible for their flavors has not yet been characterized widely. Among them, arazá (*Eugenia stipitata* McVaught), belonging to the Myrtaceae family, is an indigenous Amazonian tree widespread in different regions of Colombia. This fruit is also known as araçaboi in Brazil or as pichi or sororia in Peru. The fruit, characterized by its intense aroma and acid flavor, is round, about 12-15 cm in diameter, 800 g maximum weight, and green to yellow peel at maturity. The edible part, a creamy-white pulp, is eaten fresh or is used to prepare juices, marmalades, ice creams and liquors.[1-3]

As far it is known, there are only two reports on the composition of the volatile compounds of this fruit.[4,5] In both works, 30 and 65 volatiles were identified, respectively.

The main purpose of this study was to identify additional arazá fruit (*Eugenia stipitata* McVaught) compounds that may contribute to its delicate flavor.

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MATERIALS AND METHODS

Fresh mature arazá fruits were picked from bushes grown in Caquetá, Colombia, and transported by airplane to the laboratory within 24 h after harvest. The fruits were allowed to ripen at room temperature. After separation of the skin and seeds the pulp was gently bended in a commercial blender. The blended pulp was immediately subjected to extraction.

Isolation of volatile compounds was made by the following procedure: an aliquot of blended pulp (1 kg) was diluted with distilled water (1 L) and centrifuged at 10 000 r /min for 20 min . Decanol (0.25 mg) was added as internal standard before the liquid-liquid extraction. The supernatant was continuously extracted with pentane-dichloromethane [1 : 1 (v/v)] for 8 h . The organic phase was dried over anhydrous sodium sulfate and concentrated to 0.2 mL on a Kuderna-Danish evaporator with a 15-cm Vigreux column. Extractions were made by triplicate.

An HP 6890 GC with a FID, equipped with an HP-Innowax fused silica column (60 m X 0.25 mm X 0.25 µm film thickness) was employed. The column temperature was programmed as follows: 50 °C hold 4 min, to 220 °C at 4 °C/min, then hold 10 min. Nitrogen carrier gas was used at a flow rate of 1 mL/min . The injector and detector were maintained at 230 °C . Sample injection volume was 1 µL with a split ratio of 1 : 10. Linear retention indices were calculated using n-paraffin standards.[6]

An HP 6890 Series II equipped with a mass selective detector HP-5973N and the same capillary column and temperature program as in GC-FID technique was used. Helium carrier gas was used at a flow rate of 1 mL/min . Mass spectra were recorded in the electron-impact mode at 70 eV by 1.8 scans/s . Detection was performed in the scan mode between 30 and 400 Daltons.

Compounds were identified by comparing their spectra to those of authentic standards, those in NIST library or literature[7-9] and also, in many cases, by comparison of their GC linear retention indices to those of standard compounds.

Quantitative analysis was made by the internal standard method from the electronic integration of the FID peak areas without the use of correction factors.

RESULTS AND DISCUSSION

The volatile compounds of arazá fruit were obtained by liquid-liquid extraction and analyzed by GC-FID and GC-MS. A valid aroma concentrate was prepared by using an established procedure with an acceptable extraction efficiency (> 80 % recovery) and low danger of artifact formation.[10-12] The concentrated extract showed aroma notes resembling the flavor of fresh fruit, described as sweet-green-fruity.

Table 1 presents identified compounds with their concentrations. Quantitations were based upon GC-FID peak integration data, so accuracy is potentially limited by a number of factors, including coelution of two or more components and differences in FID response factors among compounds. The quantitative data (Table 1) shows that totally 7.9 mg of volatile compounds per kilogram of fresh fruit were obtained.

In total, 27 esters, 20 terpenes, five alcohols, six carbonyls, five acids, three hydrocarbons, two lactones and two sulfur-compounds were identified. Of the 70 components identified, 53 are reported for the first time.

According to class of compounds, esters dominate the volatiles profile. These compounds that constitute over 54.8 % of the total volatiles include many ethyl and hexyl esters. Of them, ethyl octanoate, ethyl dodecanoate and ethyl decanoate were found to be the major ones. In one previous result about arazá fruit, the amount of esters was low,[4] whereas in the other report they were in significant amounts. These discrepancies may be related to the stage of ripeness of the fruit when sampled, different cultivars or geographical regions and the isolation method. Two identified lactones, δ-decalactone and γ-dodecalactone, were reported for the first time in arazá fruit.

In the terpene group, many monoterpene and sesquiterpenes were identified, with the major representatives being globulol and

Table 1. Volatile constituents of arazá fruit.

Compound	Identification[2]	RI[3]	Amount (µg/kg)
Ethyl acetate[1]	MS, GC	824	43
Ethanol[1]	MS, GC	898	566
α-Pinene	MS, GC	1012	t
Ethyl butanoate[1]	MS, GC	1021	10
Ethyl 2-methylbutanoate[1]	MS, GC	1040	14
β-Pinene	MS, GC	1115	t
Myrcene	MS, GC	1140	t
2-Methyl-2-pentenal[1]	MS	1152	60
Ethyl hexanoate[1]	MS, GC	1220	t
3-Methyl-2-buten-1-ol[1]	MS, GC	1231	295
(E)-β-Ocimene	MS, GC	1241	38
Hexyl acetate[1]	MS, GC	1261	150
Terpinolene	MS, GC	1270	t
3-Hydroxy-2-butanone[1]	MS, GC	1275	54
Hexyl propanoate	MS, GC	1321	54
Hexyl isobutanoate[1]	MS, GC	1325	32
1-Hexanol	MS, GC	1340	313
(Z)-3-Hexenol	MS, GC	1361	123
Methyl octanoate[1]	MS, GC	1378	25
1-Tetradecane[1]	MS, GC	1395	143
Hexyl 2-methylbutanoate[1]	MS, GC	1408	183
Ethyl octanoate	MS, GC	1421	1031
Ethyl 2-methylthioacetate[1]	MS	1425	162
2-Furfural[1]	MS, GC	1439	300
α-Copaene	MS, GC	1475	t
1-Pentadecane[1]	MS, GC	1499	28

Table 1. (continued)

Compound	Identification[2]	RI[3]	Amount (μg/kg)
Ethyl 3-hydroxybutanoate	MS, GC	1502	43
β-Bisabolene[1]	MS, GC	1508	t
Ethyl nonanoate[1]	MS, GC	1519	29
Ethyl (E)-2-octenoate[1]	MS, GC	1532	25
Ethyl 3-methylthiopropanoate[1]	GC	1535	25
5-Methyl-2-furfural[1]	MS, GC	1558	100
2-Methyloctanol[1]	MS, GC	1565	41
β-Caryophyllene	MS, GC	1571	t
Hexyl hexanoate[1]	MS, GC	1592	158
3-Hydroxy-2-methylpentanal[1]	MS	1602	t
Ethyl decanoate	MS, GC	1621	516
(Z)-3-Hexenyl hexanoate[1]	MS, GC	1638	25
Citronellyl acetate[1]	MS, GC	1658	t
α-Humulene	MS, GC	1689	t
2-Methylbutanoic acid[1]	MS, GC	1691	250
1-Heptadecane[1]	MS, GC	1699	26
Germacrene D	MS, GC	1710	t
γ-Muurolene[1]	MS, GC	1713	25
β-Himachalene[1]	MS, GC	1716	25
Ethyl undecanoate[1]	MS, GC	1721	16
(E,Z)-α-Farnesene[1]	MS, GC	1722	50
Hexyl octanoate[1]	MS, GC	1800	141
Ethyl dodecanoate[1]	MS, GC	1818	792
Hexanoic acid	MS, GC	1830	291
Furfuryl hexanoate[1]	MS, GC	1845	33
2-Hexanoyl furan[1]	GC	1847	33
2-Phenylethyl propanoate[1]	MS, GC	1852	300
2-Phenylpropyl acetate[1]	MS, GC	1926	45
Ethyl tetradecanoate[1]	MS, GC	2027	191
Octanoic acid	MS, GC	2045	208
2-Phenylethyl benzoate[1]	MS, GC	2056	79
Globulol[1]	MS, GC	2061	216
Spathulenol[1]	MS, GC	2070	25
(E)-2-Hexenyl benzoate[1]	MS, GC	2078	33
(E)-Cinnamyl acetate[1]	MS, GC	2099	100
γ-Eudesmol[1]	MS, GC	2135	t
T-Cadinol[1]	MS, GC	2138	83
δ-Decalactone[1]	MS, GC	2145	25
T-Muurolol[1]	MS, GC	2151	58
α-Muurolol[1]	MS, GC	2165	10
Decanoic acid[1]	MS, GC	2258	33
γ-Dodecalactone[1]	MS, GC	2316	55
Methyl (E)-9-octadecenoate[1]	MS	2438	85
Dodecanoic acid[1]	MS, GC	1638	41

[1] Reported for the first time in this fruit.
[2] Identification: MS mass spectra, GC comparison of retention indices with standards.
[3] Linear retention indices reported on HP-Innowax capillary column.
t Represents less than 10 μg/kg .

(*E*,*Z*)-α-farnesene. Germacrene D, reported in a previous study as the most abundant compound,[4] was only detected in traces in the present study.

Alcohols and carbonyls compounds represented 17.0 and 6.9 % of the total volatiles. Of them, ethanol, 1-hexanol and 3-methyl-2-buten-1-ol were the major alcohols, whereas 2-furfural was the most abundant carbonyl compound.

The presence of some acids (6.8 %) and n-paraffins (2.5 %) should not significantly contribute to fruit flavor, due to the high thresholds of these compounds.[13] Two sulfur-compounds not reported previously, ethyl 2-methylthioacetate and ethyl 3-methylthiopropanoate were identified. On the other hand, methyl 3-methylthipropanoate which was previously reported,[5] was not found in the present study.

Certainly, many of the found compounds (Table 1) should make important contributions to the overall arazá flavor, particularly the esters, with their relative low threshold.[13] Many of the esters found in arazá which seems to be strong contributors to tropical fruit aromas have also been found in a variety of other tropical and subtropical fruits. Ethyl and hexyl esters similar to those found in this study have been identified as important contributors of tropical fruit flavors in papaya,[14] passion fruit,[15] guava,[16] pineapple,[17] lulo fruit,[18] and mango.[19]

CONCLUSIONS

Volatile compounds were isolated from araza fruit (7.9 mg/kg of fresh fruit). In total, 27 esters, 20 terpenes, five alcohols, six carbonyls, five acids, three hydrocarbons, two lactones and two sulfur-compounds were identified. Of the 70 components identified, 53 are reported for the first time. Esters (54.8 % of the total composition) were the most abundant compound class. Ethyl octanoate, ethyl dodecanoate and ethyl decanoate were found to be the major constituents.

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