

Changes in volatile constituents during the ripening of cocona (*Solanum sessiliflorum* Dunal) fruit

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Recibido: 14 de mayo de 2005. Aceptado: 10 de febrero de 2006.

Palabras clave: cocona, *Solanum sessiliflorum*, maduración, compuestos volátiles, CG-EM.
Key words: cocona, *Solanum sessiliflorum*, maturation, volatile compounds, GC-MS.

RESUMEN. La cocona (*Solanum sessiliflorum* Dunal) es un arbusto nativo de la región del Alto Orinoco en la cuenca del Amazonas, el cultivo se ha extendido y tecnificado debido a su fruto comestible, el cual ha comenzado a comercializarse, es muy apetecido por su exquisito sabor y aroma. En este estudio se evaluó la composición de los constituyentes volátiles en la pulpa de cocona durante la maduración de la fruta. Tres estados de madurez fueron estudiados: verde, pintón y maduro. Los compuestos volátiles se aislaron por extracción líquido-líquido con pentano-diclorometano 1 : 1 (v/v) en forma continua y se analizaron por cromatografía de gases con detector de llama de hidrógeno y por cromatografía de gases acoplada a espectrometría de masas. Un total de 76 compuestos se identificaron en la fruta de ellos, 38 constituyentes en estado verde, 67 en estado pintón y 66 en estado maduro, la mayoría reportados por primera vez en esta fruta. Durante la maduración, se observó un incremento en la concentración de los ésteres y alcoholes, así como una disminución respecto a los compuestos carbonílicos. Los constituyentes mayoritarios son similares en los tres estados de maduración, pero el salicilato de metilo es el compuesto que presentó la mayor concentración en el estado de madurez junto con el α -terpineol y en menor proporción el (Z)-3-hexenol, mientras que los aldehídos como el (Z)-3-hexenal, (Z)-2-hexenal, (E)-2-hexenal y hexanal disminuyeron su contenido con la maduración.

ABSTRACT. Cocona (*Solanum sessiliflorum* Dunal) is a shrub native from the upper Orinoco region of the Amazon basin, recently his culture has extended and technified due to its edible fruits, which has begun to commercialize itself very it is desired by its exquisite flavor and aroma. In this study was evaluated the composition of the volatile compounds in pulp cocona during the ripening fruit. Three stages of maturation were studied: green, mature and ripe. The volatiles were isolated by continuous liquid-liquid extraction with pentane-dichloromethane 1 : 1 (v/v) and researched by GC-FID and GC-MS. A total of 76 compounds were found in this fruits, 40 in green fruits, while up to 67 were present in mature and 66 in ripe fruits, most of them reported for the first time. During the maturation an increase in concentration of esters and alcohols, and decrease in carbonyl compounds were observed. Similar compounds were found in the three maturation stages, but higher concentration of methyl salicylate together with α -terpineol and smaller proportion (Z)-3-hexenol were found, while aldehydes as (Z)-3-hexenal, (Z)-2-hexenal, (E)-2-hexenal and hexanal decreased with maturation.

INTRODUCTION

Solanum sessiliflorum Dunal is a shrub native from the upper Orinoco region of the Amazon basin, previously cultivated by natives because of its edible fruits, which are rarely used nowadays.^{1,2} It is commonly named cocona, coconilla or naranjilla in Colombia, and cibu in Brazil.

The cocona plant is a highly branched, herbaceous shrub which reaches a height up to 2 m. It has a downy stem, densely white-hairy twigs, and ovate leaves, which are oblique at the base, scalloped on the margins, downy on the upper surface, prominently veined beneath. The leaves are about 45 cm long and 38 cm wide. The flowers, in clusters of 2 or more in the leaf axils, are 2.5 cm wide, with 5 pale greenish-yellow petals, 5 yellow stamens, and a dark-green 5-pointed calyx. The thin, tough skin is coated with a slightly prickly, peach-like fuzz until the fruit turns fully ripe, then it is smooth, golden- to orange-yellow, burnt-orange, red, red-brown or deep purple-red, and has a bitter taste. Inside the fruit is found a 6 to 10 mm layer of cream-colored, firm flesh enclosing the yellow, jelly-like central pulp. The cut-open fruit has

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a faint, tomato-like aroma. The pulp has a mild flavor faintly suggestive of tomato, while the pulp has a pleasant, lime-like acidity.² The fruits is prized for making jam, marmalade, paste, and jelly, and is sometimes pickled or candied. It is also often processed as nectar or juice which, sweetened with sugar, is a popular cold beverage.

The chemical composition of the aroma of *Solanum quitoense* L.⁴ and *Solanum vestissimum* Dunal,⁵ have been reported. Despite the pleasant aroma of cocona fruit, to date its volatile compounds have only been studied for Brazilian fruits,⁶ identifying 20 volatile constituents. Although this fruit is not yet commercially cultivated in Colombia its distinctive exotic flavor makes it promising as a raw material for the food industry.

The objective of this study was to establish a relationship between the compositions of the volatile during three maturation stages of cocona (*Solanum sessiliflorum* Dunal) fruits grown in Colombia.

MATERIALS AND METHODS

Fruits

Fresh green, mature and ripe fruits were picked from the same bushes grown in Caquetá, Colombia. The fruits were collected, provided and identified by Colombian Institute of Agricultural (ICA). This fruits were transported by airplane, immediately after arrival they were checked and tested, so that the isolation of volatile compounds was concluded within 24 h after harvest. Fruit puree was prepared in a commercial blender for analysis.

Quality analysis

Soluble solids were determined by refractometer at 20 °C and were expressed as °Brix. Measurement of pH was accomplished with a potentiometer and physical hardness was determined with an Effesi mod. FT 327 testing manual machine with a 1 cm diameter cylindrical probe. Samples were punctured to 2 cm depth. Three fruits from each ripening stage were evaluated for hardness in the equatorial part of the fruit.

Isolation of volatile compounds

One kilogram fruits of each maturation stage (peeled and without seeds) was mixed with 1.5 L of distilled water, blended in a commercial blender for 10 min and then centrifuged at 10 000 r/min, 5 °C for 20 min .

An internal standard (0.45 mg of n-decanol) was added to the supernatant, which was immediately subjected to a continuous liquid-liquid extraction used as mixture solvents with 250 mL of pentane-dichloromethane 1 : 1 (v/v)⁷ for 8 h . The extracts were dried over anhydrous sodium sulfate and concentrated to 0.2 mL with a Kuderna-Danish apparatus with a Vigreux column (40 °C) to 0.2 mL . All the isolations were made by duplicated.

Gas chromatography (GC-FID)

An HP 6890 GC with FID equipped with a fused silica HP-Innowax capillary column (60 m X 0.25 mm i.d. X 0.25 mm film thickness) was used. The temperature program was 4 min isothermal at 50 °C and then 40 - 220 °C at 4 °C/min . The carrier flow rate (nitrogen) was 1 mL/min . Injector and detector temperatures were kept at 220 °C . Volumes of 1 mL were injected with a split ratio (1:10). Retention indices were calculated for compounds relative to a C₈ - C₂₅ n-alkanes mixture.

Gas chromatography-mass spectrometry (GC-MS)

An HP 6890 Series II coupled to a HP-5973N mass detector and with a similar column and temperature program as for the GC-FID technique was used. Mass spectra were obtained by electron impact ionization at 70 eV .

Qualitative and quantitative analysis of volatile compounds

Constituents were identified by comparison of their mass spectra with those in NBS, NIST or our FLAVORLIB data base and confirmed in many compounds by their relative retention indexes. Mass spectra from the literature,⁸⁻¹⁰ were also compared.

Quantitative determinations were calculated approximate concentrations of volatile compounds from GC-FID peak areas according to the internal standard method using n-decanol as reference sub-

stance with considering calibration factors, that is $F = 1$ for all compounds.. Results were compared by ANOVA and Duncan' test.

RESULTS AND DISCUSSION

The maturity of cocona fruit is related to changes in the carbohydrates, nonvolatile organic acids, volatile compounds, pigment and pectin content. Table 1 shows the quality measurements of fruits from green, mature and ripe stages. With respect to the content of soluble solids, the green fruits show a lower value than the mature and ripe fruits. The pH values were slightly superior in mature and ripe fruits than green fruits due to a decrease of organic acids. The hardness of fruits decreased obviously with maturation, probably due to the solubilization of pectin.

The volatile compounds from three different stages of maturity of cocona fruits were isolated by liquid-liquid extraction. The final extracts had different odor characteristics; those extracts from green fruits had typical herbal notes, while mature fruit extract had a predominantly sweet odor and the extract from ripe fruits possessed a sweet fruity odor with lower herbal notes.

Table 2 presents the identified compounds and their quantitative distribution. They were identified by comparing mass spectra and GC retention indexes. In total, 76 volatile compounds were identified, corresponding to 29 esters, 13 terpenes, 12 carbonyls, 10 alcohols, 5 acids, 3 lactones, 2 phenols and 2 hydrocarbons. In the extract from green fruits 39 compounds were identified, while in the other two maturation stages up to 70 volatiles were found. Among the identified compounds, 73 were reported for the first time in this fruit.

Comparing qualitative results with the reported composition of other *Solanum* species,^{3,4} some constituents seems to be common in this plant family, like (Z)-3-hexenol, linalool and α -terpineol. The identi-

Table 1. Quality measurement of cocona fruit at three maturation stage.

Quality item	Green	Mature	Ripe
External color	green	reddish orange	red purple
Soluble solids (°Brix)	3.7 a	4.0 a	8.2 b
pH	3.8 a	4.0 b	4.1 c
Hardness (kgf/cm ²)	9.0 a	7.2 b	5.4 c

Different letters on the same row indicate significant differences at $p < 0.05$.

Table 2. Quantitative comparison (mg/kg) of volatile components from different maturation stages of cocona fruits.

Compound	RI	Green	Mature	Ripe
ethyl acetate ⁺	825	54a	78b	125c
3-methylbutanal ⁺	902	35a	25a	23a
2-pentanone ⁺	975	26a	–b	–b
methyl 3-methylbutanoate ⁺	1 020	45a	60b	85c
hexanal ⁺	1 025	356a	156b	52c
ethyl butanoate ⁺	1 030	15a	20a	36b
1-propanol ⁺	1 035	45a	36b	25c
ethyl 2-methylbutanoate ⁺	1 045	2a0	35b	47c
3- <i>Z</i> hexenal ⁺	1 070	484a	426b	402c
butyl acetate ⁺	1 073	–a	125b	165c
2- <i>Z</i> pentenol ⁺	1 112	58a	63a	72a
1-butanol ⁺	1 135	85a	32b	13c
heptanal ⁺	1 165	–a	32b	21b
2- <i>Z</i> hexenal ⁺	1 185	905a	586b	352c
1-dodecane ⁺	1 199	24a	–b	–b
2- <i>E</i> hexenal ⁺	1 218	287a	153b	79c
4- <i>Z</i> heptenal ⁺	1 225	168a	–b	–b
cyclopentanone ⁺	1 236	42a	–b	–b
(<i>E</i>)- β -ocimene ⁺	1 241	–a	25b	138c
cyclopentanol ⁺	1 280	–a	12b	57c
hexyl acetate ⁺	1 303	–a	26b	57c
2- <i>Z</i> hexenyl acetate ⁺	1 320	45a	56a	85b
3- <i>Z</i> hexenyl acetate ⁺	1 335	–c	35b	45c
1-hexanol	1 356	58a	110b	135c
isopropyl hexanoate ⁺	1 385	–a	8b	12b
3- <i>Z</i> hexenol ⁺	1 391	85a	158b	259c
butyl hexanoate ⁺	1 399	45a	58b	53b
<i>cis</i> -linalool oxide (5-membered) ⁺	1 418	–a	25b	42c
acetic acid ⁺	1 425	31a	52b	63c
ethyl octanoate ⁺	1 430	–a	53b	35c
hexyl 3-methylbutanoate ⁺	1 432	–a	25b	58c
pentyl butanoate ⁺	1 440	–a	–a	25
2-furfural ⁺	1 445	10a	25b	38c
octyl acetate ⁺	1 454	–a	46b	56b
camphor ⁺	1 485	–a	21b	35b
benzaldehyde ⁺	1 490	13a	25b	35c
2-octyl acetate ⁺	1 493	–a	30b	35b
linalool ⁺	1 503	36a	125b	185c
ethyl 3-hydroxybutanoate ⁺	1 521	–a	56b	85c
hexyl butanoate ⁺	1 530	25a	35a	–b
butyl hexanoate ⁺	1 535	–a	85	98
1-octanol ⁺	1 550	–a	27b	34b
<i>trans</i> -linalool oxide (5-membered) ⁺	1 555	15a	28b	48c
ethyl nonanoate ⁺	1 568	–a	–a	26b
methyl benzoate ⁺	1 590	–a	25b	12c
hexyl hexanoate ⁺	1 593	125a	158b	170c
2- <i>E</i> ,4- <i>E</i> octadienal ⁺	1 599	34a	–b	–b
citronellyl acetate ⁺	1 603	–a	13b	25c

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fied lactones γ -octalactone, γ -decalactone and δ -undecalactone, and the identified phenols 4-vinylguaicol and eugenol are reported for the first time in *Solanum* species.

The quantitative analysis showed a total amount of 3.53, 5.27 and 6.61 mg/kg of pulp from green, mature and ripe fruit, respectively. Carbonyl compounds (2.36 mg/kg) presented the highest concentration in green fruit, whereas esters showed the highest content in mature and ripe fruits (2.18 and 2.68 mg/kg, respectively). It is interesting to note that the amount of C₆-aldehydes, including (*Z*)-3-hexenal, (*Z*)-2-hexenal, (*E*)-2-hexenal and hexanal could be related to the maturity of the fruit by a significant decrease of their concentrations. The amount of terpenes, alcohols, acids, phenols and lactones increased with maturation of the fruit.

The major volatile constituents in green fruit were (*Z*)-2-hexenal (0.90 mg/kg), (*Z*)-3-hexenal (0.48 mg/kg), hexanal (0.36 mg/kg) and (*E*)-2-hexenal (0.29 mg/kg). Due to their green notes, it can be supposed that the hexenals have the major impact on the flavor of green fruits. On the other hand, the most abundant volatile were methyl salicylate (0.76 mg/kg), (*Z*)-2-hexenal (0.59 mg/kg) and (*Z*)-3-hexenal (0.43 mg/kg); whereas methyl salicylate (0.85 mg/kg), α -terpineol (0.42 mg/kg), (*Z*)-3-hexenal (0.40 mg/kg) and (*Z*)-2-hexenal (0.35 mg/kg) show the highest concentration in the ripe fruits.

Methyl salicylate has pungent-sweet and fruity-rooty odor; also the term minty is often used as description of the odor of this ester, while the odor of α -terpineol is delicately floral and sweet of Lilac type.¹¹ Due to their characteristics, and their large amounts in mature and ripe fruits, the esters might have an impact on the aroma of cocona fruits.

In general, the significant increase in concentrations of (*Z*)-3-hexenol, α -terpineol and the esters was in agreement with the results reported during maturation of *S. vesstisimun* fruits.¹² (Suárez & Duque, 1992).

ACKNOWLEDGMENTS

Grateful acknowledgements are expressed to the Faculty of Sciences of the University of the Andes for the financial support. We thank Jaime Campos for supplying the fruits used in this study.

Table 1. (Continued)

Compound	RI	Green	Mature	Ripe
benzoic acid ⁺	1 618	15a	12a	13a
ethyl benzoate ⁺	1 642	-a	30b	25b
α -farnesene ⁺	1 658	-a	50b	72c
ethyl 3-hydroxyhexanoate ⁺	1 673	-a	65b	-a
α -terpineol ⁺	1 681	25a	156b	425c
benzyl acetate ⁺	1 689	-a	101b	178c
1-heptadecane ⁺	1 701	-a	14b	-a
geranyl acetate ⁺	1 712	-a	135b	258c
4-vinylguaiaicol ⁺	1 728	-a	25b	45c
phenylethanediol ⁺	1 735	-a	35b	-a
β -selinene ⁺	1 725	-a	-a	145b
methyl salicylate	1 751	137a	758b	850c
geranyl acetone ⁺	1 794	-a	-a	25b
hexyl octanoate ⁺	1 800	10a	78b	125c
ethyl dodecanoate ⁺	1 835	-a	52b	75c
hexanoic acid ⁺	1 849	54a	43b	12c
benzyl alcohol ⁺	1 965	12a	18a	21a
γ -octalactone ⁺	1 886	-a	28b	35c
β -ionone ⁺	1 913	-a	18b	27c
octanoic acid ⁺	2 035	-a	35b	25b
hexyl benzoate ⁺	2 056	21a	42b	54c
γ -decalactone ⁺	2 100	-a	35b	56c
eugenol	2 120	-a	85b	156c
farnesyl acetate ⁺	2 222	23a	45b	85c
ethyl hexadecanoate ⁺	2 248	-a	65b	142c
δ -undecalactone ⁺	2 218	15a	56b	85c
decanoic acid ⁺	2 358	-a	47b	-a
<i>E</i> -phytol*	2 568	25a	35b	153c

RI Retention indices on Innowax capillary column.

Different letters on the same row indicate significant differences at $p < 0.05$.

* Identified for the first time. - Not detected.

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