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Identifying Carotenoids and Phenolic Compounds In Naranjilla (*Solanum quitoense* Lam. Var. Puyo Hybrid), an Andean Fruit

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The naranjilla or lulo (*Solanum quitoense* Lam.) is a little known fruit that originated in the Andes. Commonly consumed as a fresh drink, it is particularly appreciated for its aroma. Besides its organoleptic qualities, the naranjilla also seems to have good antioxidant properties. We therefore studied the physicochemical characteristics of variety “Puyo hybrid”; determined its juice composition; identified its carotenoids and phenolic compounds, using HPLC-DAD and HPLC/ESI-MS, respectively, in each fruit part; and measured the antioxidant capacities of each part, using the ORAC and DPPH methods. We found the following bioactive compounds: *all-trans*-β-carotene, 13-*cis*-β-carotene, and 9-*cis*-β-carotene and the lutein (carotenoids); chlorogenic acids and their hexosides in the flesh and placental tissues, and flavonol glycosides in the skin (phenolic compounds); and many dihydrocaffeoyl spermidines in all three parts of the fruit. The naranjilla appeared to be a fruit with good nutritional potential that can provide the basis for a new fruit-drink flavor or other fruit derived-products.

KEYWORDS: ***Solanum quitoense*** **var. “Puyo hybrid”; carotenoids; phenolic compounds; dihydrocaffeoyl polyamines; antioxidant capacity; HPLC/ESI-MS**

INTRODUCTION

Growing demand in both developed and developing countries for diverse and novel foods is creating new markets for underutilized crops. These crops are cultivated on a very small scale and are recognized as having traditional uses in local areas such as highly nutritious food and/or medicinal remedies. One such crop is naranjilla (*Solanum quitoense* Lam.), a fruit also known as lulo.

The naranjilla belongs to the huge *Solanaceae* family (*1*). This 1−2.5 m high shrubby perennial is native to the Andes. The geographical distribution of *S. quitoense* stretches from Venezuela to Peru. It is generally cultivated between 1000 and 1900 m (*2, 3*). Two geographically separated varieties of *S. quitoense* Lam. are recognized: var. *quitoense*, a spineless form, found in southern Colombia and Ecuador, and var. *septentrionale,* a form with spines, that is found in central Colombia, Panama and Costa Rica (*3*).

In the 1980s, a local Ecuadorian farmer crossed *S. quitoense* with cocona (*S. sessiliflorum* Dunal) (*1*), resulting in the hybrid now known as the “Puyo hybrid”. It is vigorous and highly productive but the fruits are much smaller than those of the common naranjilla. The fruits of this hybrid can also be distinguished from pure naranjilla fruits by their lighter green pulp and lack of filled seeds. Other hybrids have been developed, such as the “Palora”. This hybrid produces fruits significantly bigger than those of the “Puyo hybrid” and also differs from the “Puyo hybrid” by giving orange rather than green juice. Although the “Palora hybrid” is now widely cultivated in Ecuador and southern Colombia for its higher productivity, consumers prefer the color of the “Puyo hybrid” and are willing to pay higher prices for it.

The naranjilla plant produces a spherical fruit with a diameter that may range from 3 to 8 cm (*4*). The skin (exocarp) is orange, giving the fruit its Spanish name *naranjilla* for “little orange”. Usually, the skin is covered with short, prickly, stiff hairs (or “spines”) that easily rub off. The skin is usually peeled and discarded in food preparation. The fruit’s internal structure is similar to that of the tomato: the yellow-green flesh (mesocarp and endocarp) forms four compartments separated by membranous partitions and filled with translucent green or yellowish, very juicy, slightly acid to acid, pulp (*5*). The naranjilla fruit is rarely eaten fresh, but is most commonly used to make flavored drinks, preserves and desserts. The fresh juice is also processed into frozen concentrates and can be fermented to make

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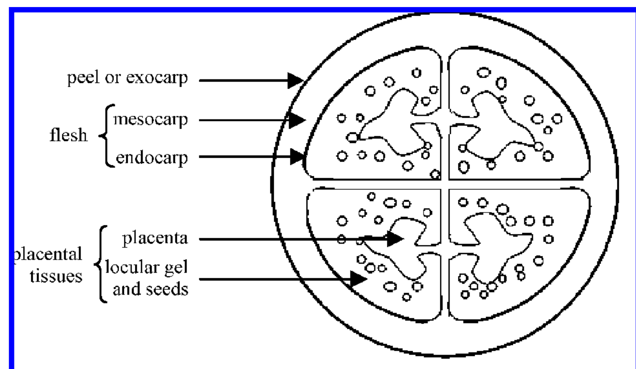

Figure 1. Scheme of the transverse section of the naranjilla fruit.

wine (*4, 5*). The fruit appears to be rich in vitamins, proteins and minerals that have considerable nutritional potential (*5, 6*).

For these reasons, interest in the naranjilla is growing. Studies are being conducted on improving the plant (*7*), its resistance to diseases and nematodes (*8, 9*), the aroma composition of its pulp, peel and leaves (*10, 11*), and postharvest treatment (*12*). Huyskens-Keil et al. (2001) (*12*), in their study on the effect of surface coating on preservation of fruit quality, refer to β-carotene as the main carotenoid in the naranjilla fruit. However, no other literature has been published on characterizing the carotenoids and phenolic compounds of naranjilla.

Our study therefore has two main objectives: to better describe the physicochemical characteristics of the naranjilla fruit such as weight, dimensions, total soluble solids, pH, and titratable acidity; and to identify the carotenoids and phenolic compounds present in each part of the fruit (i.e., exocarp, mesocarp, and placental tissues) and determine the antioxidant capacities of each part. We hope our study will further knowledge on naranjilla for use in future research, especially in a world that increasingly recognizes the cultural, economic and food value of indigenous biodiversity.

MATERIALS AND METHODS

Reagents. All organic solvents were of HPLC grade and purchased from Carlo Erba (Val de Reuil, France) except for methyl *tert*-butyl ether (MTBE) (Sigma-Aldrich, Steinheim, Germany). Folin-Ciocalteu reagent, magnesium hydroxide carbonate, sodium chloride, and formic acid were also from Carlo Erba (Val de Reuil, France). Ascorbic acid, sugars, organic acids, diphenylpicrylhydrazyl (DPPH), fluorescein, 6-hydroxy-2,5,7,8-tetramethyl-2-carboxylic acid (Trolox), and 2, 6-di-*tert*-butyl-4-methylphenol (BHT) were from Sigma-Aldrich (Steinheim, Germany). 2-2′-azobis(2-amidinopropane) dihydrochloride (AAPH) was purchased from Wako Chemicals (Richmond, VA). Standards used were purchased from Extrasynthese (Genay, France): β-carotene, lutein, 13-*cis*-β-carotene, gallic acid. Water was bidistillated.

Plant Materials. Ripe and frozen fruits of naranjilla (*Solanum quitoense* var. Puyo hybrid) came from the povince of Pichincha, Ecuador (latitude 00° 05′ 50″ N, longitude 78° 44′ 50″ W; 2506 masl). Fruits were randomly grouped into five batches of five. Results were expressed as the mean of the five lots.

Fruit Preparation. Whole fruits were weighed without their peduncles and their diameters and heights measured. The pulp (placentas, locular tissues, and seeds), flesh (mesocarp and endocarp) and peel (exocarp) were removed separately (**Figure 1**) and each part was weighted. For each batch, half of each part of each fruit was ground in liquid nitrogen and kept at −20 °C for the carotenoid analyses (5 batches × 3 parts). The other halves were ground, freeze-dried and kept at −20 °C for the phenolic compound analyses (5 batches × 3 parts).

Naranjilla juice was obtained as follows: 1 kg of fruits was cut into 8 pieces and refined in a juice extractor. Aliquots were kept at −20 °C for the determination of pH and titratable acidity. The remaining juice was freeze-dried for sugar, organic acid and, mineral analyses.

Fruit Color Measurement. The CIE L^*, a^*, and b^* parameters were determined with a Minolta Chroma Meter CR-300 (Minolta Co., Osaka, Japan) using the illuminant D65 diffused illumination standardized with a white porcelain calibration plate. The CIE L^*, a^*, and b^* parameters were defined as follow: CIE L^* = black (0) to white (100) scale; CIE a^* = red (+) to green (−) color scale; CIE b^* = yellow (+) to blue (−) color scale. Peel and flesh colors were measured on the fruit surface (3 measures × 4 areas × 5 fruits) before and after peeling respectively. Color of placental tissues was measured after assembling and mixing the five fruit pulps (3 measures × 5 areas) in a Petri box.

For each fruit part, the chroma value (C^*) and the hue angle (H^*) were calculated as follows:

$$C^* = (a^{*2} + b^{*2})^{1/2}$$

$$H^* = \tan^{-1}(b^*/a^*)$$

C^* indicates the saturation; H^* is a color indicator such as 0° corresponds to red, 90° to yellow, 180° to green, and 270° to blue.

Naranjilla Juice Composition. *Titratable Acidity.* Titratable acidity was estimated according to AOAC methods (1990) (*13*) and expressed as grams of citric acid equivalent per 100 grams fresh weight (FW).

Sugar and Organic Acid Content. Sugar and acid organic contents were determined by the SCA laboratory (CNRS, Vernaison, France). Briefly, 0.6 g of freeze-dried material was homogenized with 70 mL of water in an ultrasonic water bath. Analyses were performed with a Dionex DX 500 (Dionex Corporation, Sunnyvale, CA).

For the sugar analyses, an ED 40 amperometric detector, equipped with an Ag/AgCl reference electrode and a gold working electrode, was used. Sugars were separated in a CarboPac PA1 column (Dionex Corporation, Sunnyvale, CA), 5 μm particle size, 25 cm length, 4 mm i.d. The chromatographic conditions were as follows: flow rate at 1 mL/min; injection volume at 100 μL, and the eluent was NaOH at 200 mM.

For the organic acid analyses, separation was conducted in AS11 HC column (25 cm length, 4 mm i.d) (Dionex Corporation, Sunnyvale, CA) equipped with a carbonate trap (ATC-2). The electrolyzing current was 100 mA, and the chromatographic conditions were as follows: gradient from NaOH (5 mM) to NaOH (100 mM) at 1.5 mL/min. Detection was performed with an electrochemical detector (ED 40, conductivity cell) with Anion Self-Regenerating Suppressor (ASRS ULTRA II, 4 mm; Dionex Corporation).

Mineral Content. 500 mg of freeze-dried juice was placed in a quartz capsule, which itself was placed in a oven. The temperature was gradually raised to 500 °C and kept at this temperature for 2 h. After cooling, the ash was moistened with a few drops of water and 2 mL of 6 N HCl. The preparation was placed on a hotplate and evaporated until dried. After another 2 mL of 6 N HCl, was added, the preparation was left for 10 min before being filtered into 50-mL flasks. The residue was heated at 500 °C. Fluorhydric acid (1 to 2 mL) was added to the ashes and then evaporated. The residue was dissolved in 1 mL of 6 N HCl and filtered into the same 50-mL flasks. The solutions were adjusted to the gauge line, homogenized by manual agitation, and transferred to sample cups previously rinsed with the solution and marked with the sample number.

The elements in solution were assayed by a Varian Vista ICP spectrometer fitted with CCD detector (Varian Inc., Palo Alto, CA). This technique was used to analyze simultaneously the following elements: P, K, Ca, Mg, Na, Fe, Mn, Cu, Zn, Al, and B.

Fibers, Proteins and Lipids. Total, soluble, and insoluble fibers were estimated as described by Asp et al. (1983) (*14*). The protein content and lipid content were determined using the AOAC methods (2000) (*15*).

Total Phenolic Compounds and Ascorbic Acid. Total phenolic compounds and ascorbic acid contents were determined according to George et al. (2005) (*16*).

Preparation of Extracts. 500 mg of placental tissues, 500 mg of flesh, and 200 mg of peel (freeze-dried material) were extracted with 20 mL, 20 and 12 mL of acetone/water (7:3, v/v), respectively, stirring for 30 min. Supernatants of each mixture were then recovered, using filter papers (Whatman, U.K.). The filtrates constituted the raw extracts (REx). Distilled water was added to each aliquot of REx to reduce the

proportion of acetone to 7%. Two milliliters of diluted REx was settled on an Oasis cartridge (Waters, Milford, MA). The filtrate (interfering water-soluble components such as reducing sugars, ascorbic acid...) was recovered with 2 mL of distillated water. The recovered volume of this washing extract (WEx) was carefully measured. Aliquots of WEx were boiled at 80 °C for 2 h to remove the vitamin C (BWEx).

Folin-Ciocalteu Assay. All extracts were submitted to the Folin-Ciocalteu method, as described by George et al. (*16*), to estimate the contents of total phenolic compounds and acid ascorbic.

Expression of the Results. Total polyphenols, as determined by subtracting gallic acid equivalents (GAE) from REx from that of WEx, were expressed as milligrams of gallic acid per 100 grams of dried or fresh material. Ascorbic acid content was determined by subtracting ascorbic acid equivalents from WEx from that of BWEx, and expressed as milligrams of ascorbic acid per 100 grams of dried (DW) or fresh weight (FW).

Antioxidant Capacity. *DPPH Assay.* Scavenging free radical potentials were tested in methanolic solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH). That is, we mixed 1950 μL of methanolic DPPH solution (60 μM final) and 50 μL of the sample in a 2.5-mL spectrophotometer tub.

Juice samples were obtained by stirring 50 mg of dried fruit material dissolved in 2 mL of water and then centrifuging for 5 min at 14 000 rev/min. Several dilutions of the samples were then tested.

Results were expressed in ED_{50} = dilution (mg of freeze-dried material or fresh material per mL of tub medium) required for a 50% decrease of DPPH radicals.

ORAC Assay. ORAC assays were performed with a microplate spectrofluorimeter (Infinite 200 series, Tecan France S.A.S., Lyon, France) using 96-well polypropylene plates. The excitation and emission wavelengths were 485 ± 9 nm and 520 ± 20 nm, respectively. A maximum of 48 wells were used per observation. Solutions were prepared with 75 mM phosphate buffer (pH 7.4). Each well was filled with 160 μL of a 78.75 nM fluorescein (FL) solution (63 nM final in the well) and 20 μL of buffer (blank), or standard 0−50 μM Trolox solutions (0−5 μM final), or a sample of an appropriate dilution.

The plates were incubated at 37 °C during 20 min, and 20 μL of a 178 mM AAPH solution (17.8 mM final) was then added. (Fluorescein and Trolox solutions were made daily, using stock solutions at 787.5 μM and 500 μM, respectively, and kept in the dark at 4 °C). After adding the AAPH, the fluorescence decay was measured every minute for 240 min. The long period was needed because the plates were not temperature regulated.

Final values were calculated by using a regression equation between the Trolox concentration and the net area under the FL decay curve. The area under the curve (AUC) was calculated as follows:

$$AUC = 0.5 + f_1/f_0 + f_2/f_0 + f_3/f_0 + \ldots + f_i/f_0 + \ldots + f_{239}/f_0 + 0.5(f_{240}/f_0)$$

where f_0 is the initial fluorescence reading at 0 min and f_i the fluorescence reading at time i.

The net AUC was calculated as follows:

$$\text{net AUC} = AUC_{sample} - AUC_{blank}$$

The relative ORAC value was calculated as follows:

$$\text{relative ORAC value} = [(AUC_{sample} - AUC_{blank})/(AUC_{Trolox} - AUC_{blank})](\text{molarity of Trolox}/\text{molarity of the sample})$$

The ORAC value is expressed as micromoles of Trolox equivalents per gram of DW or FW.

Carotenoid Analysis. *Preparation of the Extracts.* The carotenoid extraction method was adapted from that described by Taungbodhitham et al. (1998) (*17*). We first stirred 10 g of puree (flesh or placental tissues), and 1 g of pureed peel, each for 5 min with 100 mg of $MgCO_3$ and 35 mL of extraction solvent (×2) (ethanol/hexane, 4:3 v/v, containing 0.1% of BHT as antioxidant). The residue was separated from the liquid phase using a filter funnel (porosity no. 2), and washed with 30 mL of ethanol and 30 mL of hexane. Organic phases were transferred to a separation funnel and successively washed with 50 mL of 10% sodium chloride and 50 mL of distilled water (×2). The aqueous layer was removed. For unsaponified extracts, the hexanic phase was dried under anhydrous sodium sulfate, filtered, and evaporated to dryness at 40 °C in a rotary evaporator. The residue was dissolved in 500 μL of dichloromethane and 500 μL of MTBE/methanol (80:20, v/v). Samples were placed in amber vials before HPLC analysis. For saponified extracts, the hexanic phase was evaporated to dryness with a rotary evaporator and redissolved with 20 mL of hexane, and placed in a 50 mL ambered vial to which were added 20 mL of 10% methanolic KOH. Saponification was carried out overnight in the dark at room temperature. The sample was shaken under nitrogen in the sealed vial. Sample was transferred to a separatory funnel to which 50 mL of distilled water was added to separate the layers. The hexanic layer was rinsed until free of alkali. The methanolic KOH layer was extracted with 3 × 15 mL of dichloromethane. The extracts were pooled and washed to remove alkali. Aqueous traces from organic extracts were removed with anhydrous sodium sulfate; then extracts were filtered and evaporated to dryness under vacuum and the residue was dissolved in 500 μL of dichloromethane and 500 μL of MTBE/methanol (80:20, v/v) for HPLC analysis.

HPLC Analysis. Unsaponified and saponified extracts of carotenoids were analyzed by reverse-phase high-performance liquid chromatography using an Agilent 1100 system (Agilent Technologies, Massy, France) according to the previously published method of Dhuique-Mayer et al. (2005) (*18*). Carotenoids were separated along a C_{30} column (250 × 4.6 mm, 5 μm particle size) (YMC EUROP GmbH, Dinslaken, Germany). The mobile phases were water as eluent A, methanol as eluent B, and MTBE as eluent C. Flow rate was fixed at 1 mL/min and the column temperature was set at 25 °C. A gradient program was performed: the initial condition was 40% A/60% B; 0−5 min, 20% A/80% B; 5−10 min, 4% A/81% B/15% C; 10−60 min, 4% A/11% B/85% C; 60−71 min, 100% B; 71−72 min, back to the initial conditions for reequilibration. The injection volume was 20 μL and the absorbance was followed at 290, 350, 450 and 470 nm using an Agilent photodiode array detector.

Carotenoids were identified using retention times, UV−visible spectra, and coinjection with authentic standards (β-carotene, lutein, and 13-*cis*-β-carotene). The spectral fine structure value, % III/II, was calculated as the percentage of the quotient between band III and band II (λ_{max}), taking the trough between the two bands as the baseline. The UV−visible spectra and % III/II were compared with those reported in the literature.

Quantitification of carotenoids was achieved using calibration curves with *all-trans*-β-carotene with five concentrations (correlation coefficient = 0.998). Results were expressed as micrograms of β-carotene equivalents per 100 grams of FW. Total carotenoids were estimated as the sum of all compounds present in the unsaponified extracts and expressed as milligrams of β-carotene equivalents per 100 grams of FW or DW. The concentrations of external solution (β-carotene) were determined using molar extinction coefficient (ε_{mol}) in appropriate solvent checked by spectrophotometry according to the method of Britton et al. (1995) (*19*).

The vitamin A value was calculated as retinol equivalents (RE), using the following conversion:

$$RE = (\mu g \text{ of } \beta\text{-carotene}/6) + (\mu g \text{ of other provitamin A carotenoid}/12)$$

In our case only β-carotene, 13-*cis*-β-carotene, and 9-*cis*-β-carotene contributed to vitamin A activity.

Phenolics Compounds Analysis. *Preparation of Extracts.* 500 mg of placental tissues, flesh or peel was extracted with 20 mL of acetone/water (7:3, v/v) during 30 min. Mixture supernatants were then recovered by filtration (Whatman, Maidstone, U.K.) and evaporated under vacuum at 40 °C until almost all the solvent was removed. The remaining extracts were purified with Amberlite XAD-7 resin (Rhom and Hass France SA, Lauterbourg, France) and then concentrated. They were then diluted with water in a 10-mL flask and filtered through a syringe filter (0.45 μm). These phenolic extracts were stored at −20 °C until injection.

Table 1. Weight, Dimensions, and Color (L^*, a^*, b^*, C^*, H^* Parameters) of the Placental Tissues, Flesh, and Peel of the Naranjilla Fruit

	unit	whole fruit	placental tissues	flesh	peel
fruit weight	g	65.7[a] (5.9)[b]	37.6 (2.4)	24.9 (3.6)	3.2 (0.2)
dimensions					
diameter	cm	5.4 (0.1)			
height	cm	4.7 (0.1)			
dry weight	%		9.2 (0.3)	10.8 (0.5)	32.4 (1.3)
color					
L^*			59.78 (1.69)	61.23 (2.58)	47.23 (2.11)
a^*			−5.24 (0.48)	−1.22 (1.83)	16.67 (1.89)
b^*			46.42 (1.45)	53.76 (5.45)	46.12 (4.04)
C^*			46.71 (1.48)	53.77 (5.41)	49.04 (3.78)
H^*			96.4 (0.5)	91.3 (2.1)	70.1 (2.8)

[a] Mean of five lots (a lot contains 5 fruits). [b] Standard deviation.

HPLC/ESI-MS Analysis. The injection volume was 10 μL and the detection was carried out between 200 and 600 nm. Separation of the polyphenols was conducted with a Surveyor Plus HPLC System (Thermo Electron Corporation, San Jose, CA) and an ACE C-18 column (5-μm particle size, 25 cm length, 4.6 mm i.d), (AIT, Houilles, France). The chromatographic conditions were as follows: 0.5 mL/min flow rate; 20 μL injection volume, and eluents, A (water/formic acid, 99.9:0.1, v/v) and B (acetonitrile/water/formic acid, 80:19.9:0.1, v/v). The gradient used for separation was as follows: 0 min, 3% B; 0−50 min linear gradient from 3 to 35% B; 50−55 min linear gradient from 35 to 50% B; 55−60 min linear gradient from 50 to 80% B; 60−65 min linear gradient from 80 to 100% B; 65−70 min 100% B; 70−72 min from 100 to 3% B; and 72−85 min 100% B. The initial conditions are maintained at least 5 min before a new run was conducted.

An MS^n analysis was carried out, using a Finnigan LCQ ion trap mass spectrometer, fitted with an electrospray interface (Thermo Finnigan, San Jose, CA). Scan range was 95−1000. The desolvation temperatures were 250 and 300 °C in the positive and negative ion modes, respectively. High spray voltage was set at 5 kV. Nitrogen was used as the dry gas at a flow rate of 75 mL/min. MS/MS and MS^3 were carried out using helium as the target gas and the collision energy was set at 30−40% and 50−60%, respectively. Identifications were achieved on the basis of the ion molecular mass, MS^n and UV−visible spectra.

Statistical Analyses. Results were expressed as the mean of the five lots of fruits. Standard deviations were calculated for all results.

RESULTS AND DISCUSSION

Physical Characterization of the Naranjilla Fruits. Table 1 presents the main physical traits of the naranjilla fruit var. "Puyo hybrid", together with the dry weight and color of each part. As previously described (*4*), the naranjilla is a small almost round fruit, slightly larger than high (5.4 versus 4.7 cm) and weighs ∼66 g. The fruit is composed of different parts: the peel (exocarp), the flesh (mesocarp and endocarp), and the placental tissues (placenta, locular gel and seeds) (**Figure 1**). The placental tissues, the flesh and the peel represent 57%, 38%, and 5%, respectively, of the whole fruit weight.

Each part has a different color (**Table 1**). The peel appears orange when ripe with a^* and b^* values both being positive. The corresponding H^* angle (70°) agrees with this result, as 0° corresponds to red and 90° to yellow. The flesh is yellow ($b^* > 0$ and $a^* \approx 0$), and the placental tissues have a green color ($b^* > 0$ and $a^* < 0$). Together, they make the juice yellowish green to green. In Latin America, this color in juice is particularly appreciated. For all fruit parts, chroma values C^* are positive, meaning that the colors are bright.

Physicochemical Characteristization of the Naranjilla Juice. Table 2 shows juice composition, including sugars, organic acids, and mineral contents. Total soluble solids content (TSS), pH, and titratable acidity were also determined.

The naranjilla fruit had a low TSS content (7.3), similar to that of the lemon (7.7−8.6) (*20*). Organic acids contributed ∼40% of this value. Its pH was low at 3.24, being similar to that of the mango (3.32) (*21*).

The titratable acidity of the naranjilla juice was ∼2.86 g of citric acid equivalents per 100 g of FW, being between the orange one (0.6−1.3%) (*22*) and lemon (5.84−6.52%) (*20*). This result agrees with the total organic acid content evaluated by HPLC (2.69 g per 100 g of FW). The high content of organic acid makes the naranjilla juice particularly acid. Indeed, citric acid represented more than 30% of DW and 97% of the total organic acids.

The content of total, soluble, and insoluble dietary fibers in naranjilla were similar to those of the grape (*23*). The soluble dietary fibers represented ∼22% of the total dietary fibers. Protein content (7.44 g per 100 g of DW or 0.63 g per 100 g of FW) corresponded to the highest value estimated by Morton in the naranjilla (1987) (*5*). Lipid content was 11.65 g per 100 g of DW.

Minerals represented ∼52 mg per 100 g of DW. Potassium was the major mineral in the naranjilla juice like in most fruit juices. K and P contents were similar to those obtained by Leterme et al. (2006) (*24*).

Total Phenolics, Carotenoids, and Antioxidant Capacities. Table 3 presents the composition in antioxidant compounds (phenolic compounds and carotenoids) and the antioxidant capacities (ORAC and DPPH values) in the placental tissues, flesh, and peel of naranjilla. All results were calculated for dried and fresh materials.

The peel had the highest content of total polyphenols. It contained 1.5 and 2.6 times more than the flesh and placental tissues, respectively. When expressed as mg of GAE per 100 g of FW, the ratios were even more significant (×5 and ×10). When comparing contents of total phenolic compounds in the placental tissues and flesh (which are the edible parts of the naranjilla fruit) with contents in other tropical fruits such as guava, dragon fruit, lychee, mango, or papaya, the naranjilla appeared to have intermediary amounts of phenolic compounds (*25*).

Total carotenoid content was much higher (23.0 mg of β-carotene equivalents per 100 g of DW) in naranjilla peel than in placental tissues (5.0) or flesh (7.4). When compared with other tropical fruits, contents for edible parts were similar to those of the cashew apple (5.3 μg of β-carotene equivalents per g of FW) and the orange cv. "pêra" (5.4) but lower than those of mango (18.0−25.0) and papaya (44.0−46.4) (*26*).

High ORAC value and low DPPH ED_{50} value (dilution required for a 50% decrease of DPPH radicals expressed as milligrams of freeze-dried material or fresh material per milliliters of tub medium) correspond to an important antioxidant capacity. Thus, the antioxidant capacity of the placental tissues, estimated with ORAC and DPPH methods, was higher than for the flesh, which, in its turn, was higher than for the peel. These results were inversely ranked when compared against the contents of total phenolic compounds and carotenoids that are known as good antioxidants. Other compounds such as ascorbic acid can contribute to the antioxidant capacity and explain this ranking. Hence, ascorbic acid content was assessed in each part from freeze-dried materials. Acid ascorbic contents of the three parts of the naranjilla fruit were 125, 69 and 20 mg per 100 g of DW for placental tissues, flesh, and peel respectively. The values of the placental tissues and flesh were lower than that found by Morton (1987) (*5*) for the edible part (31.2−83.7 mg ascorbic acid per 100 g of FW). The difference may be explained

Table 2. Nutrient composition of the edible part of the naranjilla fruit

	unit	value		unit	value
soluble solids	°brix	7.3 (0.4)	fibers		
pH		3.24 (0.06)	total dietary fiber	g/100 g DW	15.24
titratable acidity	g CAE[a]/100 g FW[b]	2.86 (0.16)	soluble dietary fiber	g/100 g DW	3.39
moisture	%	91.5	insoluble dietary fiber	g/100 g DW	11.85
sugars	% DW[c]	38.5	proteins	g/100 g DW	7.44 (0.1)
glucose	% DW	14.9	lipids	g/100 g DW	11.65 (0.13)
fructose	% DW	10.3	minerals		
sucrose	% DW	13.3	K	mg/g DW	31.58
organic acids	mg/g DW	316.2	N	mg/g DW	14.71
citrate	mg/g DW	307.0	P	mg/g DW	2.40
isocitrate	mg/g DW	5.8	Mg	mg/g DW	1.71
butyrate	μg/g DW	1624	Ca	mg/g DW	1.08
succinate	μg/g DW	610	Na	μg/g DW	64.9
propionate	μg/g DW	380	Fe	μg/g DW	19.3
oxalate	μg/g DW	315	Zn	μg/g DW	16.3
galacturonate	μg/g DW	157	Al	μg/g DW	15.1
acetate	μg/g DW	127	Mn	μg/g DW	11.3
cis-aconitate	μg/g DW	100	Cu	μg/g DW	7.9
citramalate	μg/g DW	65	B	μg/g DW	7.0
malate	μg/g DW	<30			

[a] Citric acid equivalent. [b] Fresh weight. [c] Dry weight.

Table 3. Total Phenolic Compounds, Total Carotenoids, and Antioxidant Capacity of the Placental Tissues, Flesh and Peel of Naranjilla Fruit

	placental tissues		flesh		peel	
	DW[a]	FW[b]	DW	FW	DW	FW
total phenolic compounds (mg of GAE[c]/100 g)	605[d] (60)[e]	56 (5)	1008 (58)	109 (6)	1559 (196)	505 (63)
total carotenoids (mg of β-carotene/100 g)	4.98 (0.54)	0.46 (0.05)	7.35 (0.46)	0.79 (0.05)	22.99 (0.15)	7.45 (0.05)
ORAC value (μmol of TE /g)	118 (13)	10.9 (1.2)	99 (14)	10.7 (1.5)	60 (12)	19.4 (3.9)
DPPH ED_{50} (mg /mL)	0.38 (0.01)	4.13 (0.11)	0.87 (0.02)	8.06 (0.19)	1.10 (0.09)	3.40 (0.27)

[a] Dry weight. [b] Fresh weight. [c] Gallic acid equivalent. [d] Mean of five lots (a lot contains 5 fruits). [e] Standard deviation.

by our having used freeze-dried, not fresh, materials. The ascorbic acid values ranked in the same order as the antioxidant estimates.

However, the antioxidant capacities of different parts of naranjilla could not be attributed to ascorbic acid only. Indeed, extracts were obtained by adding phosphate buffer on freeze-dried materials. Many hydrophilic molecules were solubilized, including sugars, organic acids, and phenolic compound. The antioxidant activities of these extracts could result from the interaction of all these compounds having antioxidant or pro-oxidant activities.

When compared with the ORAC values of other fruits obtained by similar extraction (*27*), the naranjilla placental tissues and flesh of naranjilla (∼11 μmol of TE per g of FW) exhibited good antioxidant capacities. Indeed, as pointed out by Wang et al. (1996) (*27*), only strawberry showed higher ORAC value (12.4 μmol of TE per g of FW).

Carotenoid Identification and Quantification. Extracts of unsaponified and saponified carotenoids from the placental tissues, flesh and peel of the naranjilla fruit were injected in HPLC-DAD for tentative identification and quantification. **Figure 2** shows the HPLC-DAD chromatograms of unsaponified extracts from each part of the fruit at 450 nm.

A tentative identification of carotenoids was made based on retention times, absorption spectra, % III/II, and coinjection with authentic standards (**Table 4**).

The main carotenoid characterized was the *all-trans-β*-carotene (peak **5**). Data found for this compound (**Table 4**) were in agreement with those obtained by de Rosso and Mercante (2007) (*28*). This tentative identification was confirmed by coinjection of the *all-trans-β*-carotene standard. Other carotenoids such as 13-*cis-β*-carotene and lutein were also identified based on the same pattern.

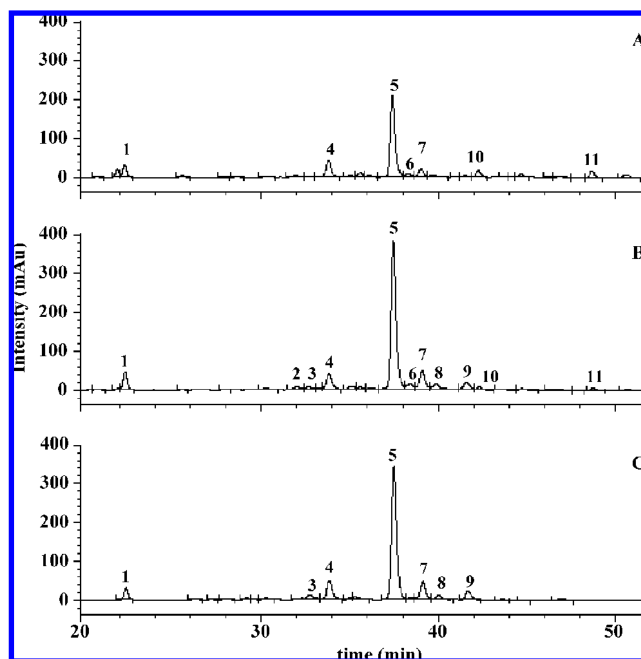

Figure 2. HPLC chromatrograms of carotenoids from naranjilla (detection at 450 nm): **A**, placental tissues; **B**, flesh (mesocarp and endocarp); **C**, peel (exocarp). (For compound identification see **Table 4**).

According to its retention time, its UV−vis spectrum, its %III/II value (∼20), and its relative position with the *all-trans-β*-carotene, we tentatively identified peak **7** as the 9-*cis-β*-carotene (*28, 29*). However we could not confirm this assignment by the injection of the standard because it was not available.

Table 4. Tentative Identification of Carotenoids by HPLC-DAD in the Naranjilla Placental Tissues, Flesh, and Peel

			UV−vis spectra (nm)					
no.	t_R[a]	fruit part	*cis*-peak	peak I	peak II	peak III	% III/II	tentative identification
1	22.3	pl,[b] fl,[c] pe[d]		420	444	472	54	lutein[e]
2	32.0	pl, fl		400	424	448	64	unknown
3	32.7	fl, pe	337	416	440	464	7	unknown
4	33.8	fl, pe	338	422	444	468	6	13-*cis*-β-carotene[e]
5	37.4	pl, fl, pe		428	452	478	19	*all-trans*-β-carotene[e]
6	38.4	pl, fl, pe		422	446	472	40	ester
7	39.0	pl, fl, pe	338	422	446	472	20	9-*cis*-β-carotene
8	39.9	fl, pe		422	446	472	36	ester
9	41.6	fl, pe		420	444	472	44	ester
10	42.3	pl, fl		418	440	470	78	ester
11	48.8	pl, fl		422	446	472	57	ester

[a] Retention time. [b] Placental tissues. [c] Flesh. [d] Peel. [e] Identified using authentic standards.

Table 5. Carotenoid Composition of the Naranjilla Fruit (μg of β-Carotene Equivalents/100 g FW)

compound	placental tissues	flesh	peel
all-trans-β-carotene	208[a] (8)[b]	380 (10)	3622 (60)
lutein	29 (1)	43 (1)	370 (40)
13-*cis*-β-carotene		55 (4)	630 (60)
9-*cis*-β-carotene	24 (3)	54 (6)	610 (60)
esters	54 (5)	52 (4)	380 (70)
others	144 (15)	210 (30)	1838 (40)

[a] Mean of five lots (a lot contains 5 fruits). [b] Standard deviation.

Esters (peaks **6**, **8**, **9**, **10**, and **11**) were identified comparing chromatograms of unsaponified and saponified extracts. According to the area augmentation of the lutein peak (peak **1**) after saponification (data not shown), peaks **6**, **8**, **9**, **10**, and **11** (**Figure 2**) could be esters of lutein.

Table 5 reports the carotenoid composition of the different parts of the naranjilla fruit. *all-trans*-β-carotene, the major carotenoid, represented ∼45% of total carotenoid contents. Of the three fruit parts, the peel had the highest content of β-carotene (3622 μg per 100 g of FW) followed by the flesh (380) and the placental tissues (208). These results agreed with the measured colors of the different parts (**Table 1**), where the peel appeared orange, the flesh yellow, and the placental tissues yellowish-green.

Compared with other fruit sources of β-carotene, the edible parts of the naranjilla fruit fell between mango (444 μg per 100 g of FW) and papaya (275 μg per 100 g of FW) according to USDA data (*30*). Peaks that were characterized as esters represented 12% of carotenoids in the placental tissues, 7% in the flesh, and 5% in the peel. Other minor carotenoids represented between 25 and 31% of the total contents.

The different fruit parts exhibited provitamin A activity at 37, 72, and 707 RE per 100 g of FW for the placental tissues, flesh, and peel, respectively. Although the peel is not consumed, it appeared to be a very good source of carotenoids with a high provitamin A activity close to that of the carrot (835 RE per 100 g of FW) (*30*).

Phenolic Compound Identification. Phenolic compounds of naranjilla were studied in placental tissues, the flesh and the peel. Total phenolic extracts were purified with XAD-7 resin before being injected for the HPLC/ESI-MS assay. The HPLC-DAD chromatograms are shown in **Figure 3**. **Table 6** shows the tentative identification of some of the peaks.

The chromatograms of the placental tissues (**Figure 3A**) and the flesh (**Figure 3B**) shared more peaks in common than with that of the peel (**Figure 3C**). While the placental tissues exhibited more very polar compounds (peaks **1**−**7**), the peel presented less polar compounds (peaks **23**, **24**, **26**, and **28**).

Caffeoylquinic Acids and Derivatives. Peaks **14** and **17** were present in all three parts of naranjilla fruit. Both peaks had a molecular mass of 354 and similar UV−visible spectra (**Table 6**). Compounds with such characteristics are known as chlorogenic acids. The MS/MS fragmentation in negative mode of the molecular ion ($[M - H]^- = 353$) of these peaks, carried out with 30% energy, produced different base peaks: *m/z* 191 for the compound **14** and *m/z* 179 for the compound **17**. According to Clifford et al. (2003) (*31*) and Nandutu et al. (2007) (*32*), peak **14** was identified as 5-*O*-caffeoylquinic acid and not as 3-*O*-caffeoylquinic. Although both these compounds produce an MS/MS fragment base peak at *m/z* 191, they can be distinguished on the basis of the relative intensity of the secondary ion *m/z* 179. For 5-*O*-caffeoylquinic acid the secondary ion at *m/z* 179 is very weak or undetectable, whereas, for 3-*O*-caffeoylquinic acid, the relative intensity of the secondary ion at *m/z* 179 is ∼50% or more. Based on the elution order and the absence of *m/z* 191, component **17** should be the 4-*O*-caffeoylquinic acid.

Although compounds **2**, **3**, and **7** produced a molecular ion at *m/z* 515, they were not identified as dicaffeoylquinic acids. Indeed, even though our HPLC conditions were different from those of Clifford et al. (2007) (*33*), the dicaffeoylquinic acids should have eluted after the caffeoylquinic acids. On the contrary, peaks **2**, **3**, and **7** were eluted before the caffeoylquinic acids, suggesting caffeoylquinic acid glycosides (*33*). At MS/MS, both compounds **3** and **7** produced *m/z* 353 base peak that could correspond to [caffeoylquinic acid $- H^+]^-$ ion and therefore to the loss of a hexose. The MS^3 fragmentation of MS/MS *m/z* 353 base peak provided fragment ions at *m/z* 191 for compound **3** and *m/z* 179 for compound **7** (**Table 6**). Thus, as previously described for compounds **14** and **17**, the *m/z* 353 base peaks of compounds **3** and **7** could be identified as [5-*O*-caffeoylquinic $- H^+]^-$ and [4-*O*-caffeoylquinic $- H^+]^-$ ions. Otherwise, the MS/MS fragmentation (**Table 6**) of *m/z* 515 of component **2** produced *m/z* 341 and *m/z* 179 (base peak), suggesting another 4-*O*-caffeoylquinic acid glycoside (*33*). These three caffeoylquinic acid glycosides were found in placental tissues. Compound **3** was also present in flesh.

Flavonol Glycosides. The UV spectra of peaks **9**, **10**, **23**, **24**, **28**, and **30** were similar to those of quercetin glycosides, whereas peaks **12**, **19**, and **26** showed UV spectra similar to those of kaempferol derivatives (**Table 6**). All these peaks were exclusively present in naranjilla peel. Such tissue-specific accumulation agreed with findings by Stewart et al. (2000) which showed ∼98% of the flavonols (quercetin- and kaempferol-glycosides) to be located in peel tissue (*34*).

On the basis of their fragmentation patterns, peaks **9**, **23**, and **24** were identified as quercetin glycosides, although peaks **10**, **28**, and **30** were identified as isorhamnetin glycosides. Indeed, the MS^2 or MS^3 fragmentation permitted discrimination between both compounds class derivatives of quercetin, producing a fragment ion at *m/z* 301, although isorhamnetin glycosides produce fragment ions at *m/z* 315 and *m/z* 301. Molecular weights of quercetin and ishoramnetin are, respectively, 302 and 316, with isorhamnetin having the same structure as quercetin with an additional methyl group. A MS full scan of compound **24** showed an $[M - H]^-$ ion at *m/z* 609 with an MS/MS fragmentation pattern matching that of rutin (quercetin-3-rutinoside) (*34*).

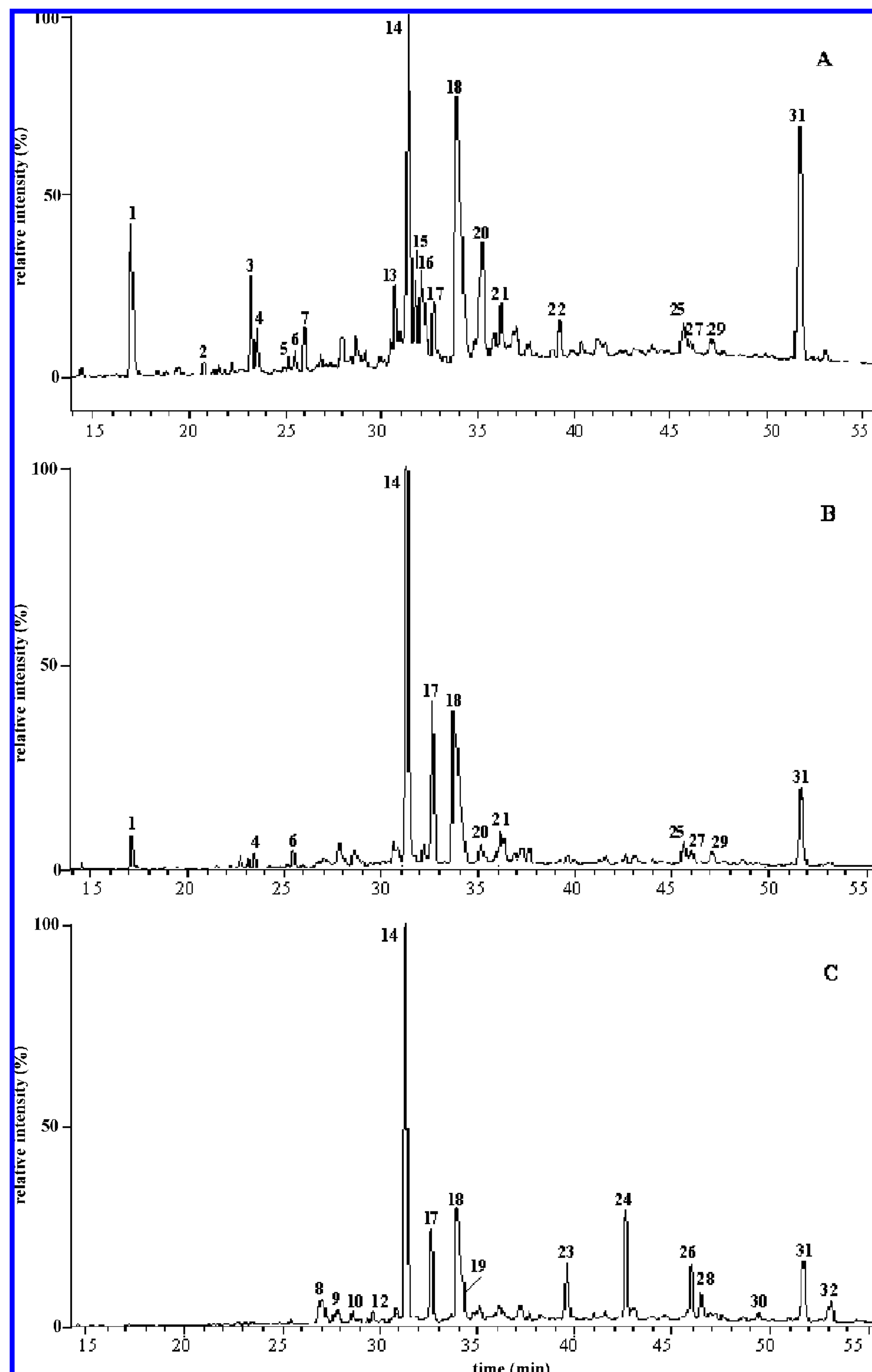

Figure 3. HPLC chromatograms of phenolic extracts from naranjilla (UV detection at 280 nm): **A**, placental tissues; **B**, flesh (mesocarp and endocarp); **C**, peel (exocarp). (For compound identification see **Table 6**).

Dihydrocaffeoyl Polyamines and Derivatives. The tentative identification of components **13**, **16**, **18**, **21**, **25**, **27**, **29** and **31** was based on their UV spectra, molecular masses and HPLC/ESI-MS data.

Compounds **18** and **21** produced the same molecular ion $[M - H]^-/[M + H]^+$ at 473/474 and the same MS/MS fragment ions in negative mode *m/z* 351 and *m/z* 308 but with different relative intensities (**Table 6**), indicating that they were probably isomers. The MS/MS fragmentation in positive mode of both components provided the same fragment ions (e.g., *m/z* 457, *m/z* 293, *m/z* 236, *m/z* 222, and *m/z* 165; data not shown) as those obtained by Parr et al. (2005) for the *N*,*N′*- bis(dihydrocaffeoyl) spermidine, a dihydrocaffeoyl polyamine (*35*). According to this identification and Roshani and Duroy (2006) (*36*), *m/z* 351 and *m/z* 308 fragments ions could be explained by the loss of $-C_7H_7O_2$ and −dihydrocaffeoyl moieties, respectively. Both compounds could be tentatively identified as N^1,N^4- bis(dihydrocaffeoyl) spermidine or N^4,N^8- bis(dihydrocaffeoyl) spermidine for peak **18** and N^1,N^8- bis(dihydrocaffeoyl) spermidine for peak **21** (**Figure 4**).

Table 6. Identification of Phenolic Compounds by HPLC/ESI-MS in the Naranjilla Placental Tissues, Flesh and Peel

no.	t_R[a]	fruit part	UV−vis spectra (nm)	$[M-H]^-$ / $[M+H]^+$	negative MS^2	negative MS^3	tentative identification
1	17	pl,[b] fl[c]	276, 300sh	−/−			
2	20.7	pl	318	515/517	341 (52) 179 (100)		4-*O*-caffeoylquinic acid hexoside
3	23.2	pl, fl	291, 316	515/517	353 (100) 191 (40)	191 (100)	5-*O*-caffeoylquinic acid hexoside
4	23.5	pl, fl	293, 318	−/−			
5	25.2	pl, fl	307	−/−			
6	25.5	pl, fl	300, 325sh	−/−			
7	26	pl	291, 316sh	515/517	353 (100) 341 (15) 179 (67)	173 (100) 179 (86)	4-*O*-caffeoylquinic acid hexoside
8	27	pe[d]	285	471/473	453 (70) 257 (65) 241 (100)		
9	27.7	pe	254, 266sh, 353	771/773	609 (100) 463 (18) 301 (2)	301 (100)	rutin hexoside
10	28.6	pe	252, 266, 346	639/-	477 (100) 315 (10)		isorhamnetin dihexoside
11	28.7	pl, fl	267	797/799	635 (100) 473 (12)		*N*,*N*′-bis(dihydrocaffeoyl) spermidine dihexoside
12	29.7	pe	266, 233sh, 347	755/757	593 (100)	429 (26) 285 (100)	kaempferol rutinoside hexoside
13	30.7	pl, fl	273	635/637	473 (100)	351 (100) 308 (90)	N^1,N^4 or N^4,N^8-bis(dihydrocaffeoyl) spermidine hexoside
14	31.4	pl, fl, pe	300sh, 324	353/355	191 (100) 179 (8)		5-*O*-caffeoylquinic acid
15	31.8	pl	288, 335	−/−			
16	32	pl, fl	279	635/637	473 (100)	351 (100) 308 (98)	N^1,N^8 -bis(dihydrocaffeoyl) spermidine hexoside
17	32.7	pl, fl, pe	300sh, 326	353/355	191 (4) 179 (100) 173 (98)		4-*O*-caffeoylquinic acid
18	33.9	pl, fl, pe	281	473/474	351 (100) 308 (98)	308 (100)	N^1,N^4 or N^4,N^8-bis(dihydrocaffeoyl) spermidine
19	34.2	pe	265, 324sh, 347	609/611	447 (100) 285 (10)	285 (100)	kaempferol dihexoside
20	35.2	pl, fl	330	599/601	563 (100)		
21	36.2	pl, fl, pe	265,320sh	473/474	351 (52) 309 (100)		N^1,N^8-bis(dihydrocaffeoyl) spermidine
22	39.3	pl	289, 321	−/−			
23	39.6	pe	255, 263sh, 353	755/757	609 (20) 591 (40) 301 (100)	301 (100)	rutin pentoside
24	42.6	pe	254, 265sh, 354	609/611	301 (100)		rutin
25	45.7	pl, fl	280, 320sh	799/800	637 (100)	515 (5) 473 (100)	N^1,N^4,N^8-tris(dihydrocaffeoyl) spermidine hexoside
26	46	pe	265, 345	593/595	429 (65) 285 (100)		kaempferol rutinoside
27	46.1	pl, fl	281, 319sh	799/800	637 (100)	473 (100)	N^1,N^4,N^8-tris(dihydrocaffeoyl) spermidine hexoside
28	46.5	pe	253, 266, 353	623/625	459 (45) 315 (100) 300 (24)	301 (100)	isorhamnetin dihexoside
29	47.1	pl, fl	281, 319sh	799/800	637 (100)	473 (100)	N^1,N^4,N^8-tris(dihydrocaffeoyl) spermidine hexoside
30	49.4	pe	255, 267sh, 354	623/625	315 (100) 300 (15)	301 (100)	isorhamnetin dihexoside
31	51.7	pl, fl, pe	281	637/638	473 (100)	351 (70) 308 (100)	N^1,N^4,N^8-tris(dihydrocaffeoyl) spermidine
32	53.1	pe	283, 327sh	−/−			

[a] Retention time. [b] Placental tissues. [c] Flesh (mesocarp and endocarp). [d] Peel (exocarp).

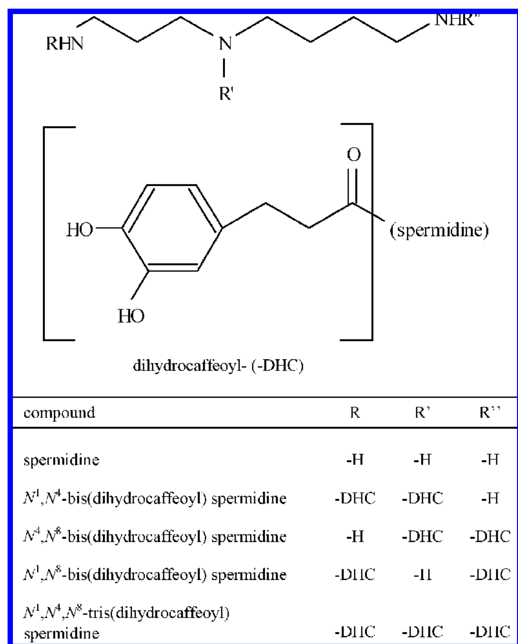

Figure 4. Structure of the dihydrocaffeoyl spermidines.

Following the same scheme and according to Parr et al. (2005) (*35*), component **31** ($[M-H]^-/[M+H]^+$ at 637/638) was identified as tris(dihydrocaffeoyl) spermidine.

Two components with molecular ions of $[M-H]^-/[M+H]^+$ at 635/636 (peaks **13** and **16**) and three others with molecular ions of $[M-H]^-/[M+H]^+$ at 799/800 (peaks **25, 27** and **29**) were also found in the chromatogram (**Figure 3**), with retention time that was lower than that of bis(dihydrocaffeoyl) spermidine and tris(dihydrocaffeoyl) spermidine, respectively. The MS/MS fragmentation of these compounds produced base peaks of 473 and 637, which may correspond to the loss of a hexose. Parr et al. (2005) had already mentioned the presence of a putative *N*,*N*′,*N*″-tris(dihydrocaffeoyl) spermidine glycoside ($[M+H]^+$ at 800 with a major loss of *m*/*z* 162, retention time of ∼3 min less than for the aglycon) in the potato (*35*). Based on the same hypothesis, we could identify the peaks **25, 27** and **29** as N^1,N^4,N^8-tris(dihydrocaffeoyl) spermidine glycosides and peaks **13** and **16** as *N*,*N*′-bis(dihydrocaffeoyl) spermidine glycosides.

Polyamines are present in food, especially in breast milk and meat but also in plants where they can be free or conjugated with compounds such as hydroxycinnamic acids (*37*). Theses polyamines have been studied for their properties, as they play an important role in several activities such as cell proliferation, gene expression, and cell signaling. They are known to have biological effects, particularly in the differentiation of immune cells and regulation of the inflammatory reactions. Larqué et al. (2007) explained that diets with a high polyamine content could play an important role in the recovery of intestinal microflora and gut mucosa because of their influence on tissue repair processes (*38*). They added that the administration of spermidine might improve treatment of traumas. In contrast, polyamine-free diets may be crucial for reducing tumorous growth (*39*). Hence, the naranjilla fruit may provide a good source of spermidine, as all the polyamines present in this fruit are spermidine derivatives.

Unidentified Peaks. Some peaks (**1**, **4**, **5**, **6**, **8**, **15**, **20** and **22**) remained unidentified by the HPLC-DAD and HPLC/ESI-MS methods (**Table 6**). These peaks were found in the placental

tissues and flesh of naranjilla. Unidentified compound 32, however, was present only in the peel.

Isolation and NMR identification are needed to unequivocally elucidate, from a structural viewpoint, all the unidentified peaks.

Further analyses, such as acid hydrolysis, are needed to determine the identity of sugars in the glycosylated compounds, although we suspect glucose as hexose and rhamnose as pentose.

Finally, our study is the first to attempt to characterize the underutilized specie, *Solanum quitoense* var. "Puyo hybrid", especially with regard to its carotenoids and phenolic compounds. The main chlorogenic acids and dihydrocaffeoyl spermidine were found in all parts of the naranjilla fruit. Glycosylated chlorogenic acids and dihydrocaffeoyl spermidines appeared to be located mainly in the placental tissues and flesh, whereas flavonol glycosides were exclusively present in the peel. Although Parr et al. (2005) (*35*) have already reported N^1,N^4,N^8-tris(dihydrocaffeoyl) spermidine glycosides in potato, our study is the first to report *N*,*N*′-bis(dihydrocaffeoyl) spermidine glycosides in a fruit.

Thus, besides its original organoleptic qualities, the naranjilla appears to be a fruit with good nutritional potential and thereby deserves to be well-known. This fruit can provide the basis for a new fruit-drink flavor or other fruit derived-products that could become popular in North America, Japan, Europe, and similar areas. But further research is needed, especially on improving storage conditions, which remain the limiting factor to this tropical fruit's development.

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