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Abstract. This work is a contribution to knowledge of the phenolic composition, antioxidant capacity and volatile profile of licuri (*Syagrus coronata* (Martius) Beccari) fruits. Samples of raw

and roasted licuri were provided by an agricultural cooperative in the state of Bahia (Brazil). The phenolic composition was both estimated by spectrophotometric assays (by measuring the content of total phenolics, total flavonoids, and condensed tannins) and quantified by HPLC-MS. Antioxidant capacity was evaluated by ABTS and DPPH radical scavenging assays, while volatiles were determined by HS-SPME-GC/MS. An increase of total phenolics, total flavonoids and total condensed tannins was observed after the roasting process. Similarly, the antioxidant capacity of roasted seeds was higher than that of raw samples. Among phenolic compounds (+)-catechin, (-)-epicatechin, procyanidins B1 and B2, myricetin, quercetin, quercetin-3-O-glucoside, quercetin-3-O-rhamnoside, quercetin-3-O-rutinoside and luteolin were identified. The majority of these phenolics significantly increased during the roasting process. Among volatiles, carboxylic acids such as octanoic and hexanoic acids prevailed in raw licuri seeds. However, after roasting, these compounds decreased and Strecker aldehydes, δ-lactones and alkyl pyrazines, (all with high odour activity), became the most abundant.

Keywords: Licuri, phenolic compounds, antioxidants, volatile compounds, HPLC-MS, HS-SPME-GC/MS

Highlights

The phenolic composition, antioxidant capacity and volatile profile of licuri seeds, a typical Brazilian product, and their change due to roasting process were shown for the first time.
The licuri seeds showed a high quantity of bioactive compounds - therefore the valorization of its health property is possible.

The traditional roasting process can positively affect the phytochemical composition of licuri seeds.

1. Introduction

Syagrus coronata (Martius) Beccari is a member of the palm family (Arecaceae, sub-family Arecoideae), typical of semi-arid regions which, in Brazil, comprises part of the Minas Gerais, Bahia, Sergipe and Alagoas states (Teixeira da Silva de La Salles et al., 2010). The species is popularly known as "licuri" or "ouricuri". It produces pulpy fruit bunches (1450 small nuts each; Figure 1) which dry during maturation to become edible (Brasil, 2006). Fruits are available all year, with maximum yields in March, June and July (Crepaldi, Almeida-Muradian, Rios, Vuono Camargo Penteado & Salatino, 2001; Noblick, 1986). Licuri holds great significance for both its socio-economical and nutritional value (seeds: 49.2 % of lipids, 9.7 % of total carbohydrates and 11.5 % proteins; $2.6x10^6$ J/100 g) (Crepaldi, Almeida-Muradian, Rios, Vuono Camargo Penteado & Salatino, 2001; Brasil, 2006). Thus, local people are organized into consortia for the handling of the harvest, processing and commercialization. The fruit harvest involves the whole community - men, women and children - and is carried out manually. The removal of the nut from the husk is carried out manually (taking one hour per bunch) or with a mechanical clamp which accelerates the process (Brasil, 2006). Once extracted, the seeds can be consumed both dry (raw) and cooked/grated (roasted). Raw kernels are first desiccated, traditionally by sunlight, and, if necessary, stored by freezing for no more than one year. This type of seed is widely used by local cooks as an aromatic ingredient in regional dishes. Licuri oil, obtained by cold pressing raw seeds, is mainly used for cooking, due to its particular sensory profile (Pereira, Oliveira, Medeiros, Costa, Bomfim & Queiroga, 2009). The flavor of licuri seeds and oil is similar to that of the common coconut (*Cocus nucifera*) reaching few shades of taste and aroma of the almonds

(*Prunus dulcis*). Most licuri nuts undergo the roasting process, as a way to extend their shelf-life. The roasting process is carried out traditionally, placing seeds in a wood stove for 1 hour at 170-190 °C. In some cases, the seeds are placed in terracotta or aluminum pans and roasted directly on a low heat for 15-20 minutes, or cooked in artisan ovens at 60 °C for 6 hours. Roasted kernels are mainly used in confectionary and bakery products, where they are particularly appreciated for their taste and aroma. The main traditional foods obtained with roasted licuri seeds and available in local markets are represented in Figure 2.

Like other Brazilian fruits, licuri is little-known abroad, and commercially available strictly at a local level. Despite this, licuri seeds could be an important source of income for local community, if appropriately valorized. However, apart from gross composition and vitamins (Crepaldi, Almeida-Muradian, Rios, Vuono Camargo Penteado & Salatino, 2001), data on the phenolic or volatile composition and antioxidant activity of raw or roasted licuri seeds are not yet available in literature. Phenolic compounds represent an extremely large and variegate group of secondary plant metabolites, and constitute the majority of dietary antioxidants Moreover, as already mentioned, licuri is particularly appreciated by local consumers for its characteristic odour and aroma. However, to the best of our knowledge, nothing is currently available in literature about the compounds responsible for its peculiar aroma, and their modifications during the roasting process. Therefore, the aim of this work was to define the volatile and phenolic composition as well as the antioxidant activity of raw licuri seeds as affected by the roasting process, locally carried out with the traditional method on a wood stove.

2. Material and methods

2.1 Chemicals

n-Hexane, acetone, ethanol, absolute ethanol, methanol, formic acid, gallic acid, procyanidin B1, (+)-catechin, procyanidin B2, (-)-epigallocatechingallate, (-)-epicatechin, (-)-epicatechingallate, quercetin-3-*O*-glucoside, rutin, myricetin, quercetin-3-*O*-rhamnoside, quercetin, luteolin, apigenin, vanillin, 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,2'-azino-bis-(3-ethylbenzothiazolin-6-sulfonic acid) diammonium salt (ABTS), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), Folin-Ciocalteu reagent, sodium carbonate, sodium nitrite, aluminum chloride, potassium persulfate, formic acid, hydrochloric acid and sodium hydroxide were purchased from Sigma-Aldrich (Milan, Italy). When available, reference volatile compounds were purchased from Sigma Aldrich (Milan, Italy). All chemicals were of high purity. Methanol and formic acid were suitable for high performance liquid chromatography (HPLC). Ultra-pure water was produced with a Milli-Q System (Millipore, Milan, Italy).

2.2 Preparation of samples

Licuri seeds (raw and roasted, three lots of each product) were furnished by the Cooperativa de Produção da Região do Piemonte da Diamantina-COOPES (Capim Grosso, Bahia, Brazil). They were harvested in 2010 in the Capim Grosso region (Bahia, Brazil). Roasting was carried out in a wood stove for 1 h at 170-190 °C.

Raw and roasted licuri seeds were separately frozen in liquid nitrogen and ground by a high-speed mill (IKA A11 Basic, Germany). The obtained powder (about 500 μm) was immediately used for the volatile composition determination or defatted for 6 h with *n*-hexane in a Soxhlet apparatus, dried in a rotary evaporator (Büchi R-210 Flawil, Switzerland) under vacuum for 30 min at 45 °C, lyophilized (LIO-5P, Cinquepascal, Milan, Italy) and used for the preparation of phenolic extracts.

2.3 Preparation of phenolic extracts

Extraction of phenolics was performed as described by Xu & Chang (2007) with modifications. Briefly, 0.5 g of powder was placed in a 50 mL test tube, and combined with 5 mL of a fresh mixture of acetone/water/formic acid (70:29.5:0.5, v/v/v) and two internal standards (IS), (-)-epicatechingallate and apigenin at 1000 and 2000 μg/l (final concentration) respectively. The suspension was shaken on an orbital shaker at 3 rpm in the dark at room temperature for 3 h, and then was centrifuged for 10 min at 10000 rpm. The supernatant was collected in an amber vial and frozen. The residue was re-extracted for an additional 12 h and extracts were combined. Acetone was evaporated under a nitrogen flux with stirring (Glas-Col®, Terre Haute, IN, USA) and extracts were diluted to 3 mL with a methanol/water/formic acid solution (50:49:1, v/v/v) and filtered (0.45 μm). Each sample was prepared in triplicate, then used for the determination of the total phenolic content, total flavonoids, total condensed tannins, antioxidant capacity and LC-MS analysis.

2.4 Total phenolic content

The amount of total phenolics was assayed spectrophotometrically by means of a modified Folin–Ciocalteu method (Singleton & Rossi, 1965; Singleton, Orthofer & Lamuela-Raventos, 1999). 0.5 mL of phenolic extract was mixed with 2.5 mL of water-diluted Folin-Ciocalteu reagent (1:10, v/v). The mixture was incubated for 3 min at room temperature, and 2 mL of 7.5% (p/v) aqueous sodium carbonate solution was added. The mixture was incubated for 15 min at 45 °C and finally cooled in a water-ice bath. The specific absorbance at 765 nm was immediately measured with a UV-Visible spectrophotometer (UV-1700 PharmaSpec, Shimadzu, Milan, Italy) (Pinelo, Rubilar, Jerez, Sineiro & Núñez, 2005). A mixture of solvent and reagents was used as a blank. The total

phenolic content was expressed as gallic acid equivalents (GAE) per gram of defatted sample, using a gallic acid standard curve (0-250 mg/l).

2.5 Total flavonoids

Total flavonoids were evaluated according to the method described by Dewanto, Wu, Adom & Liu (2002). Briefly, 0.25 mL of phenolic extract or (+)-catechin standard solution was mixed with 1.25 mL of distilled water in a test tube and then combined with 75 µL of a 5 % (p/v) sodium nitrite solution. Six minutes later, 150 µL of 10 % (p/v) aluminum chloride solution was added and allowed to stand for 5 min before adding 0.5 mL of 1 M sodium hydroxide solution. The mixture was brought to 2.5 mL with distilled water and mixed well. The absorbance was measured immediately against the blank (the same mixture without the sample) at 510 nm. The results were calculated and expressed as mg of (+)-catechin equivalents (CE) per gram of defatted sample. Ethanolic solutions of (+)-catechin were used for calibration (10-1000 µg/mL).

2.6 Total condensed tannin

Evaluation of total condensed tannin was carried out as proposed by Xu & Chang (2007). Aliquots of 50 µL of the extracts were placed in two separate test tubes (one for the sample and one for the blank). Afterwards, 3 mL of a 4 % methanol vanillin solution and 1.5 mL of concentrated hydrochloric acid were added to the sample, and 3 mL of pure methanol and 1.5 mL of concentrated hydrochloric acid were added to the blank. The mixtures were kept for 15 min in the dark at room temperature, and the absorbances were measured at 500 nm. Calibration was performed, as described previously, with (+)-catechin stock solutions. The results were calculated and expressed as mg (+)-catechin equivalents (CE) per gram of defatted sample.

2.7 Antioxidant capacity

2.7.1 TEAC assay

The Trolox equivalent antioxidant capacity (TEAC) of licuri extracts was estimated according to the original analytical procedure described by Re, Pellegrini, Proteggente, Pannala, Yang & Rice-Evans (1999), with slight modifications. ABTS radical cation ($ABTS^{\bullet+}$) was produced by reacting 7 mM ABTS stock solution with 2.45 mM potassium persulphate (final concentration). The mixture was allowed to stand in the dark at room temperature for 12-16 h before use. The radical was stable in this form for more than two days when protected from light and stored at room temperature. Just before analysis, the $ABTS^{\bullet+}$ stock solution was diluted with ethanol to an absorbance of 0.70 (± 0.02) at 734 nm, and equilibrated at 30 °C. Sample solutions (or standard) (30 µl) were mixed with $ABTS^{\bullet+}$ solution (3 mL). Absorbance readings were taken at 30 °C exactly 6 min later than initial mixing. Appropriate solvent blank was obtained by mixing absolute ethanol (30 µl) with $ABTS^{\bullet+}$ solution (3 mL) and absorbance was monitored after 6 min. The $ABTS^{\bullet+}$ scavenging effect (% Inhibition) was calculated by the equation:

$$\% \text{ Inhibition} = [(A_{734\text{blank}} - A_{734\text{sample}})/A_{734\text{blank}}] \times 100$$

where $A_{734\text{blank}}$ and $A_{734\text{sample}}$ are the absorbances of $ABTS^{\bullet+}$ solution at 734 nm before and after sample addition. Results were expressed as µM Trolox equivalent (TE) per gram of defatted sample, by means of a dose-response curve for Trolox (0-350 µM).

2.7.2 DPPH assay

The hydrogen atom or electron donation abilities of the licuri phenolic extracts were measured from the discoloration of the purple colored methanol solution of the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical. The spectrophotometric assay was conducted according to the method reported by von Gadow, Joubert & Hansmann (1997). Briefly, 75 µl of sample extract

was added to 3 mL of 6.1 x 10^{-5} M DPPH$^{\bullet}$ methanol solution. The decrease of absorbance at 515 nm was recorded, at room temperature, until stable values were reached (1 h). All operations were done in the dark or dim light (Sharma & Bhat, 2009). For control purpose, the absorbance of the DPPH$^{\bullet}$ without samples was measured. The inhibition percentage (IP) of the DPPH$^{\bullet}$ by licuri extracts was calculated according to the formula

$$IP = [(A_{0min} - A_{60min})/A_{0min}] \times 100$$

where A_{0min} is the absorbance of control at t = 0 min, and A_{60min} is the absorbance of samples at 60 min. Results were expressed as µM Trolox equivalent (TE) per gram of defatted sample, by means of a dose-response curve for Trolox (0-350 µM).

2.8 LC-MS analysis

A Thermo-Finnigan Spectra-System high-performance liquid chromatography (HPLC) system (Thermo-Finnigan, Waltham, USA), equipped with a P2000 binary gradient pump system, a SCM 1000 degasser, an AS 3000 automatic injector and a Finnigan MAT LCQ ion trap mass spectrometer with an electrospray ionization (ESI) source was used. The software for control of the equipment, acquisition and treatment of data was Xcalibur, version 1.2 (Thermo-Finnigan, Waltham, USA). The separation was achieved on a Luna C18 column (150 × 2.0 mm, 5 µm; Phenomenex, Castel Maggiore, Italy). The mobile phase was composed of a mixture of 2 % (v/v) formic acid aqueous solution (solvent A) and methanol (solvent B). Flow rate was 0.2 mL/min and injection volume 20 µl. Elution program was as follows: linear gradient from 80 % A to 70 % A, 0.0-6.0 min; isocratic elution 70 % A, 6.0-20.0 min; linear gradient from 70 % A to 50 % A, 20.0-22.0 min; linear gradient from 50 % A to 30 % A, 22.0-50.0 min; linear gradient from 30 % A to 0 % A, 50.0-55.0 min; isocratic elution 0 % A, 55.0-58.0 min; linear gradient from 0 % A to 80 % A, 58.0-60.0 min; isocratic elution 80 % A, 60.0-70.0 min. The interface conditions were:

negative ionization mode, capillary temperature 200 °C and spray voltage 3.5 kV. The negative masses were monitored in the selected ion mode in 6 segments: *m/z* 289, 457, 577 from retention time (Rt) 0 to 11 min; *m/z* 441 from Rt 11 to 15 min; *m/z* 463 and 609 from Rt 15 to 30 min; *m/z* 317 and 447 from Rt 30 to 34 min; *m/z* 301 and 285 from Rt 34 to 38 min; *m/z* 269 from Rt 38 to 44 min. Identification of the phenolic compounds was carried out by comparing retention time, mass spectrum (MS) and MS^2 with those of authentic standards. MS^2 experiments were carried out using helium as collision gas, with an isolation width of 1 *m/z* for parent mass and normalized collision energy of 24 % for procyanidin B1, procyanidin B2, (+)-catechin, (-)-epicatechin, 25 % for quercetin-3-*O*-rhamnoside, 27 % for (-)-epigallocatechingallate, (-)-epicatechingallate, quercetin-3-*O*-glucoside and rutin, 32 % for myricetin and quercetin, 38 % for apigenin and 41 % for luteolin. The calibration curves were constructed by plotting the peak area ratios of each analyte/IS vs. analyte concentration. The limit of detection (LOD) was determined by using a signal-to-noise ratio of 3, while limit of quantification (LOQ) was calculated by using a signal-to-noise ratio of 10.

2.9 HS-SPME-GC/MS analysis

The volatile fraction of raw and roasted licuri seeds was extracted by headspace sampling (HS), using a solid-phase micro-extraction technique (SPME) and analyzed by GC-MS.

For each analysis, 0.5 g of powder sample was placed in a 10 mL screw-cap glass vial fitted with silicone-PTFE septum. Vials were placed in a water bath at 30 °C for 15 min to equilibrate the headspace, then the fibre was exposed to the headspace for a sampling period of 60 min at 30 °C. The fibre was then removed and immediately inserted into the GC-MS injector set in splitless mode at 260 °C for 5 min. All the analyses were performed in triplicate.

A divinylbenzene/carboxen/polydimethylsiloxane (Supelco, Bellefonte, PA, USA) 50/30 μm film thickness and 2 cm long fibre was used (Krist, Unterweger, Bandion, & Buchbauer, 2004). Exposure time was lengthy, in order to extract a wide range of molecules of different polarities (Mebazaa, Mahmoudi, Fouchet, Dos Santos, Kamissoko, Nafti, et al., 2009).

GC/MS analysis was performed with a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu QP-2010 Plus quadrupole mass spectrometer (Shimadzu Corporation, Kyoto, Japan) and a DB-WAXETR capillary column (30 m × 0.25 mm, 0.25 μm film thickness, J&W Scientific Inc., Folsom, CA, USA). The temperature program started at 35 °C, increased at a rate of 1 °C/ min to 40 °C (held for 5 min), then at 10 °C/min to 230 °C (held for 5 min). The carrier gas (He) flow-rate was 1 mL/ min. The injection port temperature was 260 °C, the ion source temperature was 240 °C and the interface temperature was 230 °C. The detection was carried out by electron impact mass spectrometry in total ion current (TIC) mode, using an ionization energy of 70 eV. The mass acquisition range was *m/z* 30–330.

Volatile compound identification was achieved by comparing their mass spectra and corresponding linear retention indices (LRI) with those of authentic standards when available, or tentatively by comparison with literature data (Acree & Arn, 2012) or NIST05 library. LRI were calculated by linear interpolation relative to retention times of *n*-alkanes as external references (a mixture of a homologous series of C5-C28 was used). For each analysis, each compound was expressed as peak area by integration from the total ion current.

2.10 Statistical analysis

Conventional statistical methods were used to obtain a statistical evaluation

of the chemical data. Analysis of Variance (ANOVA) was applied using STATISTICA for Windows Release 7.1 (StatSoft Inc., Tulsa, OK, USA) to determine differences between raw and roasted licuri seeds.

3 Results

3.1 Phenolic content and antioxidant capacity

Values of total phenolics (TP), total flavonoids (TF), total condensed tannins (TCT), and antioxidant capacity, determined with DPPH and ABTS assays, of licuri seeds are presented in Table 1.

The TP contents of raw and roasted licuri, expressed as mg of gallic acid equivalents (GAE) per gram of defatted samples, were 1.21±0.01 and 2.78±0.39 respectively. Both TF and TCT content, expressed as mg of catechin per gram of defatted sample, were more abundant in roasted licuri (2.12±0.59 and 2.02±0.06 mg CE/g, respectively) than in raw licuri (1.16±0.09 and 1.17±0.09 mg CE/g, respectively).

As regards DPPH and ABTS radical scavenging activity, expressed as micromoles of Trolox equivalent per gram of defatted sample, higher values were shown for roasted licuri than for raw licuri. In particular, values obtained from DPPH assay were 7.01±0.23 μM TE/g for roasted seeds and 5.88±0.16 μM TE/g for raw seeds, while values obtained from ABTS assay were 5.31±0.74 μM TE/g for roasted seeds and 4.07±0.17 μM TE/g for raw products.

3.2 LC-MS analysis

The LC-MS analysis allowed the detection of 13 compounds, 10 of which were unequivocally identified (Table 2). The identification was achieved by comparing retention times, MS spectra

and MS^2 with those of authentic standards (Table 3). Identified compounds can be classified into four groups: flavanols ((+)-catechin, (-)-epicatechin), procyanidins (procyanidin B1 and procyanidin B2), flavonols (myricetin, quercetin, quercetin-3-O-glucoside, quercetin-3-O-rhamnoside, quercetin-3-O-rutinoside) and flavones (luteolin). Procyanidin dimmers 1 (Rt: 4.6 min) and 2 (Rt: 8.5 min) were tentatively identified as, similarly to procyanidin dimmers, they had $[M-H]^-$ at *m/z* 577 and MS^2 fragmentation at 289 *m/z* (Tomás-Barberán, Gil, Cremin, Waterhouse, Hess-Pierce & Kader, 2001; Jakopic, Petkovsek, Likozar, Solar, Stampar & Veberic, 2011). In addition, a currently unidentifiedcompound with $[M-H]^-$ at *m/z* 457 was also detected at Rt= 8.9 min.

All compounds were equally detected in raw and roasted *S. coronata* seeds (Table 2). Catechins, procyanidins and unknown compounds were found to be the most abundant of both raw and roasted licuri. Their content, expressed as mg per 100 g of defatted samples, ranged from 0.95±0.01 mg/100 g of procyanidin dimmer 1 in raw licuri to 7.71±0.72 mg/100 g of (-)-epicatechin in roasted nuts.

Among flavonols, quercetin was the most abundant in roasted seed (1.34±0.35 mg/100 g), while quercetin-3-O-rutinoside was found at the lowest amount in raw licuri (0.06±0.01 mg/100 g). Procyanidin dimmers 2 and luteolin did not result quantifiable in raw licuri and both raw and roasted licuri, respectively.

Flavanols, procyanidins, quercetin-3-O-glucoside, quercetin-3-O-rutinoside and quercetin significantly increased when licuri was roasted.

3.3 HS-SPME-GC/MS analysis

A total of 59 volatile compounds were identified in licuri (34 in raw and 55 in roasted) belonging to 8 chemical classes (Table 4). Among these, 30 compounds were found in both raw and roasted licuri.

In raw licuri seed, the free carboxylic acids were the most abundant volatile compounds, representing approximately 80 % of the total. Octanoic acid was the most important (44.28 %), followed by hexanoic acid (19.28 %) and acetic acid (13.12 %). Instead, propionic and isobutyric acids were identified only in roasted products. The total of acids significantly decreased (30.79 %) after roasting, with a considerable reduction of octanoic and hexanoic acids. Only acetic acid slightly increased with the roasting process. The second more abundant class of volatile compounds in raw seeds was represented by alcohols, making up 9.29 % of the total volatiles. The most important was 2-heptanol (3.51 %), present in both types of seeds. After the roasting process, alcohols increased to 22.73 % with production of new compounds such as 1-octanol and 2-furanmethanol, not present in the volatile fraction of raw product. Aldehydes (19.56 %) and ketones (15.93 %) also greatly contributed to the volatile fraction of licuri, especially 3-methylbutanal (9 %), 2-methylbutanal (5.16 %) and 2-heptanone (5.46 %). These compounds significantly increased with roasting. Esters were present above all in the volatile fraction of raw licuri seeds (2.79 %) and their presence decreased in the roasted products (1.24 %). Otherwise, the sum of lactones varied from 2.76 % of raw seeds to 6.03 % of roasted seeds. Among them, δ-decalactone was the most abundant and representative lactone in both raw and roasted licuri. This compound was also detected in other palm products such as coconut fruit and water, both characterized by a delta C8 lactone (Lin & Wilkens, 1970; Prades, Assa, Dornier, Pain & Boulanger, 2012). Licuri seeds also showed the presence of monoterpenes (2.41 %), especially limonene (1.39 %), also found in the fat fraction of coconut fruits (Santos, Villarino, Zosa, & Dayrit, 2011). These compounds significantly decreased during the roasting process. The azotate

heterocyclic compounds were absent in raw seeds, while they accounted for 3.29 % of roasted seeds.

4. Discussion

4.1 Phenolic composition and antioxidant capacity

Data on the phenolic composition and antioxidant capacity of *S. coronata* fruits, both raw and roasted, were not previously available in literature. In addition, in this work analyses were carried out on defatted materials and, consequently, all data were expressed as mg per g of defatted fruit. Therefore, we made a comparison, when possible, with other nuts (raw and roasted), which were equally defatted. Concerning raw nuts, Chandrasekara & Shahidi (2011) reported a TP value for cashew of 1.14 mg GAE per gram of defatted product, while Pelvan, Alasalvar & Uzman (2012) registered TP values for hazelnut ranging from 1.78 to 7.27 mg GAE per gram of defatted product. From the same literature sources, it has been reported that after roasting, the TP of cashew nuts increased (4.89-5.28 mg GAE/g defatted product) (Chandrasekara & Shahidi, 2011), while for hazelnuts it greatly diminished (0.50-1.95 mg GAE/g of defatted product) (Pelvan, Alasalvar & Uzman, 2012). Comparison of TP values for these three nuts (licuri, cashew and hazelnut) showed an increasing trend with roasted hazelnut (Turkish Tombul cultivar) < raw cashew < roasted hazelnut (Turkish Mincane cultivar) < raw licuri < raw hazelnut (Turkish Foşa cultivar) < roasted licuri < roasted cashew < raw hazelnut (Palaz cultivar).

As regards TCT content, raw hazelnuts showed values within the range 9.41-31.63 mg of CE/g defatted product (Pelvan, Alasalvar & Uzman, 2012) while for raw cashews TCT was reported to be 0.11 mg CE/g defatted material (Chandrasekara & Shahidi, 2011). Similarly to TP, the TCT of hazelnuts demonstrated a considerable decrease after roasting, due mainly to the removal of skin in which the majority of condensed tannins are located, with values in the range of 0.49-8.24 mg

of CE/g defatted nuts, while TCT of cashews did not change significantly during roasting. Also for TCT, it is then possible to highlight a trend with raw cashew = roasted cashew < roasted hazelnut (Turkish Çakıldak cultivar) < raw licuri < roasted licuri < roasted hazelnut (Turkish Palaz cultivar) < raw hazelnut.

Similarly to results obtained in this work, Chandrasekara & Shahidi (2011) noticed an increase of antioxidant activity, measured by ABTS assay, after the roasting of cashew nuts. In particular, ABTS values obtained for both raw and roasted cashew kernel (38.9 and 880 μmol TE/g of defatted material, respectively) were higher than those registered for raw and roasted licuri (4.07 and 5.31 μmol TE/g of defatted material, respectively).

An increase of TP, TF, TCT and antioxidant capacity of licuri was observed after roasting, probably because a greater extraction of phenolic compounds occurs with the increase of temperature (Ioannou & Ghoul, 2012). However, the reaction occurring during roasting between protein and sugars naturally present in licuri seeds (Crepaldi, Almeida-Muradian, Rios, Vuono Camargo Penteado & Salatino, 2001), could result in the formation of Maillard reaction products which can react with Folin-Ciocalteau reagent and DPPH and ABTS radicals as well as phenolic compounds. Thus, in addition to phenolics, other compounds could contribute to increasing the value of TP of roasted licuri as compared to raw fruits. Similarly, vanillin (which is used to estimate the content of condensed tannins) reacts not only with condensed tannins, but also with catechin monomer (Hagerman, 2002). Thus, the increase of TCT could also be due to the rise in catechin levels during roasting. This is probably due to the release of licuri phenolics from bounded forms.

The effect of roasting on phenolic composition of some edible nuts, such as cashew and hazelnut, was also investigated by other authors. In particular, similarly to our results, Chandrasekara & Shahidi (2011) showed that the (-)-epicatechin and (+)-catechin contents were almost 3 times

higher in cashew kernels processed at low (70 °C for 6 hours) and high (130 °C for 33 minutes) temperatures than in raw kernels. On the other hand, Schmitzer, Slatnar, Veberic, Stampar & Solar, (2011) reported that the hazelnut content of catechins and procyanidins was significantly reduced after roasting at 140 °C for 15 minutes, probably due to a chemical degradation.

4.2 Volatile composition

As with phenolic compounds, no bibliographic data have been reported on volatile compounds of licuri seeds. Only studies on the volatile fraction of other palm fruits such as coconut (*Cocos nucifera* L.) belonging to the family Arecaceae (Lin & Wilkens,1970; Jayalekshmy, Narayanan, & Mathew, 1991; Santos, Villarino, Zosa, & Dayrit, 2011; Prades, Assa, Dornier, Pain, & Boulanger, 2012) are available. These researches highlighted that δ-lactones, aldehydes, alcohols, methyl ketones and fatty acids are the most important compounds for volatile profile in coconut oil (Santos, Villarino, Zosa, & Dayrit, 2011) and in coconut water (Prades, Assa, Dornier, Pain, & Boulanger, 2012).

In raw licuri seeds, the main volatile compounds are the short chain carboxylic acids and particularly octanoic and hexanoic acids. Octanoic acid was found to be the main volatile compound also in fermented commercial virgin coconut oils produced by fermentation without heat (Santos, Villarino, Zosa, & Dayrit, 2011). Moreover, similarly to the volatile fraction of coconut oil and water (Santos, Villarino, Zosa, & Dayrit, 2011; Prades, Assa, Dornier, Pain, Boulanger, 2012), the volatile fraction of raw licuri seeds is also characterized by γ- and δ-lactones, deriving from the fatty acid anabolism pathway via 4- and 5-hydroxycarbobylic acids (C8 to C16), by the elimination of water, and responsible for the coconut-like aroma, whose odour threshold decreases with the increasing of molecular weight (Belitz, Grosch, & Schieberle, 2009). Unlike the coconut fruit, δ C10 and C11 lactones were found in raw licuri. Probably the

concurrent presence of lactones and alcohols as 2-heptanol, the main volatile compound in the profile of licuri seeds with a citrus-like odour (Frauendorfer & Schieberle, 2008), 3-methyl-1-butanol and 1-hexanol with a high relative percentage in roasted seeds could account for the coconut-like aroma of this fruit. In fact, it is known that lactones combined with 1-hexanol are responsible for the typical coconut aroma (Dufossè, Latrasse, & Spinnler, 1994).

In the volatile profile of raw licuri seeds, a low percentage of linear aldehydes are present. These compounds are produced from a degradative oxidation of unsaturated fatty acids and particularly oleic, linoleic and linolenic acids but since unsaturated fatty acids are only 14% of licuri fatty acids with 12% of oleic acid and 3% of linoleic acid (Teixeira da Silva de La Salles et al., 2010) this degradation process is not significant.

After the roasting process, the volatile profile of licuri seeds is characterized by potent aroma-active compounds produced by the amino acids degradation, such as 2-methyl-propanal, 2- and 3-methylbutanal, characterized by very low odour thresholds and a malty/cocoa odour (Belitz et al., 2009) and detected also in the oil of roasted nuts such as sesame (Bail, Stuebiger, Unterweger, Buchbauer, & Krist, 2009). The roasting process also led to the production of nitrogen-containing heterocyclic odorants, six alkyl pyrazines and one pyrrole from the Maillard reaction, not present in raw products but highlighted also in roasted coconut (Jayalekshmy, Narayanan, & Mathew, 1991). Alkyl pyrazine derivatives and, above all, methyl pyrazine and 2,6-dimethylpyrazine are associated with toasty, nutty, cocoa and woody odours and show high aroma activity (Belitz, Grosch, & Schieberle, 2009; Sabik, Fortin, & Martin, 2012).

5. Conclusions

In this work, the antioxidant capacity and the phenolic bioactive compounds of licuri seeds were determined and quantified for the first time. Results showed that the traditional roasting technique

enhanced the nutritional value of licuri by increasing the amount of phenolic compounds and the antioxidant capacity. In particular, phenolics belonging to flavan-3-ols class greatly increased in roasted products.

The volatile composition of licuri was determined in this work for the first time. The roasting process caused significant change in the volatile composition with the production of molecules connected to high odour activity i.e. Strecker aldehydes, δ-lactones or alkyl pyrazines, and the development of coconut, malty and roasted aroma. At the same time, there is a decrease of carboxylic acids with rancid aroma.

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Table 1

Total phenolics (TP), total flavonoids (TF), total condensed tannins (TCT), antioxidant capacity (DPPH and ABTS) and results of ANOVA analysis (*p*) for raw and roasted Licuri seeds[a].

	Raw licuri seed	Roasted licuri seed	*p*
TP (mg GAE/g)	1.21±0.01	2.78±0.39	**
TF (mg catechin/g)	1.16±0.09	2.12±0.59	*
TCT (mg catechin/g)	1.17±0.09	2.02±0.06	***
DPPH (mmol TE/g)	5.88±0.16	7.01±0.23	**
ABTS (mmol TE/g)	4.07±0.17	5.31±0.74	*

[a]Data were expressed as means (n=9) ± standard deviations on a defatted weight basis.

*, **, *** Significantly different at $p \leq 0.05$, $p \leq 0.01$ and $p \leq 0.001$, respectively.

Table 2

Content (mg/100 g) of phenolic compounds identified in raw and roasted licuri seeds[a] and results of ANOVA analysis (*p*)

Phenolic compounds	Raw Licuri seed	Roasted Licuri seed	*p*
Procyanidin B1	1.63±0.50	3.08±0.47	*
Procyanidin dimmer 1 (Mw=578)[α]	0.95±0.01	1.34±0.16	**
(+)-Catechin	2.57±0.04	4.95±0.79	**
Procyanidin B2	2.60±0.19	3.64±0.52	*
Procyanidin dimmer 2 (Mw=578)[α]	nq	0.59±0.09	-
Unknown (Mw=458)[α]	2.79±0.41	1.09±0.10	***
(-)-Epicatechin	2.16±0.23	7.71±0.72	***
Quercetin-3-*O*-glucoside	0.57±0.06	0.86±0.14	**
Rutin	0.06±0.01	0.14±0.02	***
Myricetin	0.34±0.06	0.33±0.07	ns
Quercetin-3-*O*-rhamnoside	1.71±0.34	1.21±0.18	*
Quercetin	0.74±0.09	1.34±0.35	**
Luteolin	nq	nq	-

[a]Data were expressed as means (n=9) ± standard deviations on a defatted weight basis; nq = not quantifiable.
[α]Procyanidin dimmer 1 was quantified as Procyanidin B1, Procyanidin dimmer 2 as Procyanidin B2 and Unknown as (-)-Epigallocatechingallate.

*, **, *** Significantly different at $p \leq 0.05$, $p \leq 0.01$ and $p \leq 0.001$, respectively, ns – not significant.

Table 3

Retention time (Rt; min), negatively charged molecular ions ($[M-H]^-$), MS^2 results, calibration curves, determination coefficient (R^2), linear range (µg/L), LOD (µg/L) and LOQ (µg/L) of the phenolic compounds standards.

	Rt	$[M-H]^-$	MS^2	Calibration curve	R^2	Lin
Procyanidin B1	3.5	577	451, 407, 289	y=0.0020x-0.3368	0.9986	5
(+)-Catechin	5.0	289	245	y=0.0004x-0.0138	0.9998	20
Procyanidin B2	5.7	577	451, 407, 289	y=0.0019x+0.7566	0.9993	10
(-)-Epigallocatechingallate	7.5	457	331	y=0.0025x-0.3022	1.000	2
(-)-Epicatechin	8.9	289	245	y=0.0004x+0.0976	0.9999	20
(-)-Epicatechingallate (IS1)	12.6	441	331	y=0.0011x-0.1250	0.9989	2
Quercetin-3-*O* -glucoside	27.8	463	301	y=0.0046x-0.3125	0.9989	5
Quercetin-3-O-rutinoside	29.1	609	301	y=0.0070x-0.1631	0.9988	2
Myricetin	31.0	317	179, 151, 192	y=0.0002x-0.0179	0.9999	2
Quercetin-3-*O* -rhamnoside	31.4	447	301	y=0.0008x-0.6638	0.9999	10
Quercetin	35.2	301	179, 151, 273	y=0.0007x-0.4405	0.9999	10
Luteolin	37.0	285	241, 217, 199	y=0.0012x-0.3052	1.000	5
Apigenin (IS 2)	40.9	269	225, 201	y=0.0005x-0.0301	0.9999	2

IS=internal standard

Table 4.

Volatile compounds, reported as mean GC peak areas ($\times 10^6$), found in raw and roasted licuri seeds and results of ANOVA analysis (p). For each compound the odour descriptors from Acree and Arn (2012) are also reported.

Compound	LRI	ID[§]	Odour	**Raw licuri seed**	**Roasted licuri seed**	***p***
Acids						
Acetic acid	1438	R	Sour	113.1	115.8	ns
Propionic acid	1525	R	Pungent, rancid, soy	-[#]	1.24	-
Isobutyric acid	1560	R	Rancid, butter, cheese	-	1.68	-
Butyric acid	1620	R	Rancid, cheese, sweat	5.9	0.7	***
Isovaleric acid	1665	R	Sweat, acid, rancid	5.6	6.5	ns
Hexanoic acid	1842	R	Sweat	166.7	12.7	***
Octanoic acid	2058	R	Sweat, cheese	383.8	64.4	***

Decanoic acid	2268	R	Rancid, fat	18.1	2.62	ns
∑ *Acids*				693.4	205.7	***
Alcohols						
Ethanol	930	R	Sweet	4.5	10.1	**
Isobutanol	1097	R	Wine, solvent, bitter	6.9	20.3	***
2-Pentanol	1123	R	Green	2.6	1.0	***
1-Butanol	1145	R	Medicine, fruit	2.6	2.7	ns
3-Methyl-1-butanol	1202	R	Whiskey, malt, burnt	17.8	62.8	***
1-Pentanol	1250	R	Balsamic	2.4	2.6	ns
2-Heptanol	1320	R	Mushroom, citrus	30.4	25.2	ns
1-Hexanol	1351	R	Resin, flower, green	4.7	4.6	ns
2-Butanol	1367	T	-	-	2.7	-
2-Buthoxy-ethanol	1387	T	-	1.3	-	-
2-Nonanol	1519	R	Cucumber	5.3	2.3	***
1-Octanol	1555	R	Chemical, metal, burnt	-	1.7	-
2-Furanmethanol	1199	R	Burnt	-	13.5	-
2-Phenylethyl alcohol	1907	R	Honey, spice, rose, lilac	1.8	2.3	***
∑ *Alcohols*				80.3	151.9	***
Aldehydes						
Acetaldehyde	-	R	Pungent, ether	-	1.6	-
2-Methyl-propanal	820	R	Pungent	-	21.5	-
2-Methylbutanal	910	R	Cocoa, almond	-	34.4	-
3-Methylbutanal	911	R	Malt	0.9	59.7	*
Hexanal	1071	R	Grass, tallow, fat	-	1.7	-
Nonanal	1383	R	Fat, citrus, green	2.0	4.2	**
Benzaldehyde	1504	R	Almond, burnt sugar	-	3.3	-
Furfural	1445	R	Bread, almond, sweet	-	3.9	-
∑ *Aldehydes*				2.9	130.3	***
Ketones						
Acetone	810	R	-	2.1	-	-
2-Butanone	895	R	-	-	2.3	-
2-Pentanone	965	R	Ether, fruit	-	2.1	-
Diacetyl	965	R	Butter	-	1.8	-
2-Heptanone	1171	R	Soap	9.7	36.6	**
Acetoin	1270	R	Butter, cream	2.4	22.6	***
1-Hydroxy-2-propanone	1280	T	-	-	12.7	-
3-Hydroxy-2-pentanone	1151	MS	-	-	3.2	-
2-Nonanone	1379	R	Hot milk, soap, green	-	11.0	-
2-Undecanone	1540	MS	Orange, fresh, green	6.5	11.7	***
2-Tridecanone	1809	R		-	2.7	-
∑ *Ketones*				20.6	106.7	***
Esters						
Ethyl acetate	880	R	Pineapple	3.6	5.0	**
Isoamyl acetate	1117	R	Banana	1.5	0.8	*
Ethyl hexanoate	1226	R	Apple peel, fruit	1.6	0.7	***

Methyl octanoate	1380	MS	Orange	8.8	-	-
Ethyl octanoate	1336	R	Fruit, fat	8.7	1.8	***
∑ *Esters*				24.1	8.4	***
Lactones						
γ-Butyrolactone	1638	R	Caramel, sweet	3.5	4.0	ns
δ-Decalattone	2156	R	Coconut	19.3	34.8	**
δ-Undecalattone	2270	MS	Peach	1.3	1.6	ns
∑ *Lactones*				24.1	40.4	**
***N*-heterocyclic compounds**						
Methyl pyrazine	1300	R	Popcorn	-	8.1	-
2,6-Dimethyl-pyrazine	1344	R	Roasted nut, cocoa, roast beef	-	4.6	-
2-Ethylpyrazine	1340	R	Peanut butter, wood	-	1.7	-
2-Ethyl-6-methylpyrazine	1407	MS	Sweat, roasted-sweet	-	1.0	-
Trimethyl-pyrazine	1420	MS	Roast, potato, must	-	3.7	-
3-Ethyl-2,5-dimethyl-pyrazine	1430	MS	Potato, roast	-	2.1	-
Pyrrole	1525	T		-	0.9	-
∑ *N-heterocyclic compounds*				-	22.1	-
Monoterpenes						
δ-3-Carene	1136	R	Lemon, resin	8.0	2.4	**
β-Myrcene	1166	R	Balsamic, must, spice	0.9	-	-
Limonene	1181	R	Lemon, orange	11.9	0.5	**
Σ Monoterpenes				20.9	2.9	**

Data were expressed as means (n=9) ± standard deviations

*, **, *** Significantly different at $p \leq 0.05$, $p \leq 0.01$ and $p \leq 0.001$, respectively; ns – not significant.
LRI: Linear retention index on DB-Wax column.

[#]-: not detected; [§]: Reliability of identification: R, identified by comparison of mass spectrum and LRI with authentic reference substance; MS, tentatively identified by mass spectrum and comparison of LRI with homologues; T, tentatively identified by mass spectrum only.

Figure captions

Figure 1. Licuri fruits

Figure 2. Typical licuri-based products available on Brazilian markets.

Figure 1.

Figure 2.