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# Effect of Almond and Pistachio Juices Processing By-Products on Physicochemical, Sensorial and Textural Properties of Cookies

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**Abstract**

The aims of the present work were to study the composition of almond and pistachio juices processing by-products and their use in cookies formulation. These by-products have relatively high carbohydrate, protein, fat, calcium and magnesium contents. There were slight difference ($p>0.05$) in essential amino acid contents between almond by-products and pistachio by-products and also both juices processing by-products showed contains polyunsaturated fatty acids (22.43% in almond juices by-products processing (ABP) and 20.83% in pistachio juices by-products processing (PBP). The incorporation of ABP and PBP in the formulation of cookies did not affect physical and textural parameters. This study suggested that almond and pistachio juices processing by-products may be alternative additives in food, pharmaceuticals and cosmetic preparations.

**Keywords:** Almond; Pistachio; By-products; Nutritional quality; Cookies formulation

## Introduction

Nowadays, there is great political and social pressure to reduce the pollution arising from industrial activities. Almost all developed and undeveloped countries are trying to adapt to this reality by modifying their production processes and often contain undesirable contaminants so that their residues can be recycled. During the last ten years there has been an increased consciousness of environmental protection. Agro-industrial by-products present potential air and water pollution problems. High-moisture wastes are also difficult to burn [1]. Indeed, Agro-industries are major contributors to the worldwide industrial pollution problem. With the tremendous pace of technology development, substantial research is devoted to cope with wastes of ever increasing complexity generated by agro-industries [1,2]. Therefore, agro-industries more than any other industrial sector in this field, require a dynamic and comprehensive approach for appropriate waste management.

Juice processing generates large amounts of wastes, which create burdensome disposal problems and environmental concerns. The utilization of these by-products, which has a wide range of nutritional values, may be economically worthy [3]. This biowaste contains, however, several biomass materials that can be exploited to produce useful marketable products. It contains large amounts of biomolecules with high added-value that can be used for the formulation and development of various pharmaceutical, medicinal, and nutritional products. In fact, agro-waste has traditionally been transformed into flour which is used as fertiliser or animal feed [3]. The low value-added flour, from agro-industrial by-products, led scientists to search for new alternatives to add value to these by-products.

The aims of this work were to characterize the almond and pistachio juices processing by-products and to evaluate their physicochemical and textural effects on characteristics of cookies.

## Materials and Methods

### Reagents

All chemicals and reagents used were of analytical grade. Water was obtained from a Culligan system; the resistivity was approximately 18 MΩ. Commercial ingredients were used for preparation of cookies.

### Materials

The pistachio (*Pistacia vera*) and bitter almond (*Prunus amygdalus var amara*) by-products were obtained in fresh condition from a juices processing plant located in Sfax, Tunisia. The samples were packed in polyethylene bags, placed in ice with a sample/ice ratio of approximately 1:1 (w/w) and transported to the research laboratory within 30 min.

### Almond and pistachio juices extraction

Almond and pistachio fruits were supplied from a local market in Tunisia. Fruits were washed with water and grinding. Almond and pistachio fruits powder were soaked in water for 1 or 2 hours and finally filtered with a 50-mesh sieve. The juice samples were then transferred into 200 ml hermetically capped glass bottles. The residue (almond and pistachio juices processing by-products) was stored in sealed plastic bags at -20°C.

### Determination of chemical composition

The moisture and ash content were determined according to the AOAC standard methods 930.15 and 942.05, respectively [4]. Total nitrogen content was determined by using the kjeldahl method [5]. Crude protein was estimated by multiplying total nitrogen content by the factor of 5.18 for bitter almond (F.A.O) and 6.25 for pistachio [6]. Crude fat was determined gravimetrically after soxhlet extraction of dried samples with hexane [5]. The total sugars were determined by the

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phenolesulphuric acid method [7]. All measurements were performed in triplicate.

## Determination of mineral contents

Analyses of calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) contents in freeze-dried samples were carried out using the inductively coupled plasma optical emission spectrophotometer (ICP-oes) (Model 4300 dv, Perkin elmer, Shelton, Ct, USA) according to the method of AOAC [4]. Sample (1 g) was mixed well with 1 ml of 70% nitric acid. The mixture was heated on the hot plate until digestion was completed. The digested sample was transferred to a volumetric flask and the volume was made up to 10 ml with deionized water. The solution was then subjected to analysis. The solution was then subjected to analysis. The concentration of minerals was calculated and expressed as mg/kg sample.

## Determination of dietary fibers

Insoluble and soluble dietary fibres were determined according to the AOAC enzymatic-gravimetric method of Prosky et al. [8]. Briefly, the defatted samples were gelatinized with heat stable alpha amylase (100°C, pH 6) for 15 min and then enzymatically digested with protease (60°C, pH 7.5) for 30 min, followed by incubation with amyloglucosidase (60°C, pH 4.5) for 30 min, to remove protein and starch. Then, the samples were filtered, washed (with water, 95% ethanol and acetone), dried and weighted to determine insoluble fibre. Four volumes of 95% ethanol (preheated to 60°C) were added to the filtrate and to the water washings. Then, the precipitates were filtered and washed with 78% ethanol, 95% ethanol and acetone. After that, the residues (soluble fibre) were dried and weighted. The obtained values were corrected for ash and protein. Total dietary fibre was determined by summing insoluble dietary fibre and soluble dietary fibre.

## Determination of starch contents

After removing sugars with ethanol (80%), starch was isolated by extraction with perchloric acid reagent (52%) twice, from a sugar-free residue according to the method described by McCready et al. [9]. Starch in the extract was determined using the anthrone reagent and colorimetric measurement at 630 nm.

## Total phenolic content

Total phenolic contents were determined according to Escarpa and González [10]. 5 g of samples were extracted for 1 h with 10 ml of methanol at room temperature and in darkness. The mixture was centrifuged at 4186 g for 15 min. The pellet was extracted for 30 min with 10 ml of methanol and then with 5 ml for 30 min. The extracts were adjusted to a final volume of 25 ml using methanol. The total concentration of phenol in the extract was determined according to the Foline-Ciocalteu method [11]. Results were expressed as milligrams of gallic acid equivalents (GAE).

## Amino acid analysis

Samples were dissolved (1 mg/ml) in ultrapure water and the boiled with 6 N HCl containing 0.1% phenol and norleucine (Sigma–Aldrich, Inc., St. Louis, MO, USA) as internal standard. HCl was removed under vacuum after 24 h of hydrolysis 110°C. Dried samples were reconstituted in application buffer and injected in application buffer and injected onto a Biochrom 20 amino acid analyser (Pharmacia, Barcelona, Spain).

## Fatty acids analysis

Samples were dissolved in 0.5 ml of hexane. Then, 0.2 ml of potassium hydroxide in methanol (2N) was added for the fatty acid methylation process. The mixture was vortexed then centrifuged and the upper phase containing fatty acid methyl esters were analyzed by Gas Chromatography (GC). GC analyses were performed on a Shimadzu, GC 17 A chromatograph, equipped with a flame ionization detector and a capillary column (50 m × 0.32 mm × 0.5 mm, PERICHROM Sarl, France). The oven temperature was programmed as follows: the initial temperature (100°C) was raised to 150°C at a rate of 30°C/min and held at this temperature for 5 min. The temperature was then increased to 190°C (at 10°C/min) and maintained for 14 min before being increased (at 5°C/min) to 255°C and held for 10 min. The injector and detector temperatures were 255 and 70°C, respectively. Nitrogen was the carrier gas with a flow rate of 1.13 ml/min. The identification of fatty acids was achieved by comparing retention times with those of authentic standards analysed under the same conditions. Peak areas were measured with an HP computing integrator. Results which are means of triplicates were expressed as w/w percentage of total fatty acids by Sagdiç et al.

## Preparation of cookies

**Formulation:** All ingredients used in the cookies' formulation were commercially available (Table 1). All cookies were prepared according to AACC International Method 10-53.01 [12]. After baking at 200°C for 11 min, cookies were removed from the oven and kept on the baking sheet for 5 min. Cookies were then removed from the baking sheet and placed on a wire cooling rack for 25 min. Once the cookies reached room temperature, they were used in subsequent experimental analysis.

**Textural analysis:** For one-cycle compression, a Texture Analyzer (LLOYD instruments, Fareham, UK) was used. All experiments were conducted in a controlled temperature room at 25°C. A cylinder probe (diameter 19 mm) compressed samples, placed in a plastic food container at fixed quantity. The crosshead was allowed to descend at the rate of 40 mm/min to a total compression at 20 mm in all experiments. The instrument automatically recorded the forceetime curve. All operations were automatically controlled by the texture "Nexygen Lot" software connected to the instrument Firmness (g) is the peak force of the compression of the product and was measured by the Nexygen MT machine software [13]. Three replicates were conducted at each sample. Volume and propagation rate of cookies were determined according to the AOAC standard methods [12]. Weight loss was determined by weight difference before and after cooking.

**Sensory analysis:** The products were evaluated by an untrained panel consisting of thirty panellists (11 males and 19 females) from the students and the staff members of the National School of Engineer

| Ingredient | Weight (g) | | | | |
|---|---|---|---|---|---|
| | Control | Cookie A | Cookie B | Cookie C | Cookie D |
| Flour | 150 | 100 | 75 | 100 | 75 |
| Sugar | 85 | 85 | 85 | 85 | 85 |
| Shortening | 85 | 85 | 85 | 85 | 85 |
| Sodium bicarbonate | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 |
| Salt | 1 | 1 | 1 | 1 | 1 |
| Water | 15 | 15 | 15 | 15 | 15 |

Cookie A + B: Substitution of flour by almond by-products.
Cookie C + D: Substitution of flour by pistachio by-products.

**Table 1:** Cookies baking formulation.

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(Sfax, Tunisia). Their ages ranged from 22 to 50 years. The cookies were evaluated based on a six-point hedonic scale, where one represented "disliked extremely" and seven represented "liked extremely". Each consumer was given 7 samples labelled with random 3-digit codes simultaneously and asked to evaluate the cookies for appearance, taste, color, odour and texture. The mean value of these sensory proprieties was evaluated as overall acceptability

**Microbiological analysis:** Specimen of each sample were suspended in sterile 0.1% (w/v) peptone-water solution and homogenized at 350 rpm for 2 min at room temperature. Total floral bacteria were determined after 48 h of incubation at 30°C using a Plate Count Agar (PCA) medium. Fecal coliforms were determined on a desoxycholate citrate agar lactose (DCL) medium after 48 h of incubation at 44°C. Staphylococci were determined on a Baird–Parker agar medium after 48 h of incubation at 37°C. Moulds were determined after cooking as reported by Guiraud and Galzy (1980). All measurements were performed in triplicates.

### Statistical analysis

All experiments were carried out in triplicate, and average values with standard deviation errors are reported. Mean separation and significance were analyzed using the SPSS software package (SPSS, Chicago, IL). Correlation and regression analysis was carried out using EXCEL program.

## Results and Discussion

### Proximate composition

The composition of almond juices processing by-products (ABP) and pistachio juices processing by-products (PBP) is shown in Table 2. There were not significant differences ($p<0.05$) in moisture and fat contents between almond by-products (25.92 and 45.56%, respectively) and pistachio by-products (26.41 and 43.87%, respectively). Fat represent the major component for both juices processing by-products, similar results were previously reported by Prosky et al. [8] for Tunisian almond (45.56%) and by Ghrab et al. for Tunisian pistachio (50%). The PBP showed higher protein content (19.68 ± 3.51%) when compared ($p<0.05$) to the ABP (12.81 ± 2.1%) that indicates their possible use in different food formulations for improving functional properties. As expected, the contents in total sugars the PBP (21.59 ± 2.35%) was significantly lower ($p<0.05$) than that of the ABP (32.01 ± 0.76%).

### Mineral contents

The ash content in ABP and PBP (Table 2) was comparable to the other by-products (washed orange bagasse, washed peach bagasse, oat bran, rice bran and wheat bran) which have relatively low ash content (between 2.6% and 8%) [14-17]. Human, as well as animal, studies originally showed that optimal intakes of elements such as sodium, potassium, magnesium, calcium, manganese and iodine could reduce individual risk factors, including those related to cardiovascular disease [18,19]. Both juices processing by-products were rich in mineral elements. Macroelements (Ca and Mg) play a crucial rule for enzymes and proteins physiological activities. Magnesium is the most abundant element presented in ABP and PBP. The potassium concentration was similar to that in pistachio juice processing by-products (26 mg/100g) and in almond juices processing by-products (29 mg/100g). These results may be useful for the evaluation of dietary information.

| Compositions | ABP | PBP |
|---|---|---|
| **Moisture (%)** | 25.92 ± 0.37[a] | 26.415 ± 0.25[a] |
| **Protein (%)** | 12.81 ± 2.10[a] | 22.68 ± 3.51[b] |
| **Fat (%)** | 45.56 ± 0.72[a] | 43.87 ± 0.30[a] |
| **Ash (%)** | 3.12 ± 0.035[a] | 3.11 ± 0.21[a] |
| **Magnesium (mg/100 g)** | 1366.96 2.51[a] | 1071.87 1.95[b] |
| **Calcium (mg/100 g)** | 717.92 ± 1.88[a] | 516.20 ± 1.46[b] |
| **Sodium (mg/100 g)** | 452.08 ± 1.2[a] | 362.91 ± 0.97[b] |
| **Potassium (mg/100 g)** | 29.75 ± 0.33[a] | 26.53 ± 1.03[a] |
| **Total Sugars (%)** | 32.01 ± 0.76[a] | 21.59 ± 2.35[b] |

Values expressed are means of three independent determinations. [a,b]Different superscripts in the same row indicate the significant differences ($p<0.05$).

**Table 2:** Proximate composition of almond and pistachio juices processing by-products. Physico-chemical composition was calculated basis on the dry mater.

| Compositions | ABP | PBP |
|---|---|---|
| **Starch (%)** | 0.38 ± 0.04[a] | 2.32 ± 0.05[b] |
| **Total fibers (%)** | 26.3 ± 0.21[a] | 21.49 ± 0.10[a] |
| **Insoluble fibers (%)** | 23.83 ± 1.57[a] | 17.80 ± 0.92[a] |
| **Soluble fibers (%)** | 2.45 ± 0.14[a] | 3.68 ± 0.28[a] |
| **Total phenolic (mg of gallic acid/100 g)** | 54.30 ± 2.66[a] | 480.48 ± 9.95[b] |

Values expressed are means of three independent determinations.
[a,b]Different superscripts in the same row indicate the significant differences ($p<0.05$).

**Table 3:** Proportion of starch, dietary fibers and phenolic compounds in almond and pistachio juices processing by-products.

### Starch and dietary fibers contents

Dietary fibers and starch contents were also determined (Table 3). The starch content of the pistachio juices processing by-products (2.32%) was significantly ($p<0.05$) higher than that of almond juices processing by-products (0.38%). Starch properties and interactions with other constituents, particularly water and lipids, are of interest to the food industry and for human nutrition [20]. There are no significant differences ($p<0.05$) in dietary fibers contents between ABP (26.3 ± 0.21%) and PBP (21.49 ± 1.1%), with a predominance of insoluble fibers. Epidemiologic support that dietary fiber intake preventing obesity is strong and that fiber intake is inversely associated with body weight and body fat [21]. Furthermore, almond and pistachio juices processing by-products can be exploited into dietetic foods.

### Total phenolic content

As shown in Table 3, the PBP showed higher total phenolic content (480.48 mg of gallic acid/100 g) when compared ($p<0.05$) to the ABP (54.30 mg of gallic acid/100 g). The pistachio juices processing by-products may be an alternative additive in food, pharmaceuticals and cosmetic preparations instead of many toxic synthetic antioxidants.

### Amino acid composition

The amino acid compositions of almond and pistachio juices processing by-products expressed as residues per 1000 total amino acid residues were shown in Table 4. Significant differences ($p<0.05$) were observed for the amino acid proportions between almond and pistachio juices processing by-products.

Glutamic acid is the most dominant amino acid in ABP and PBP (116 and 202 residues, respectively). Alanine and leucine concentrations were significantly ($p<0.05$) higher in ABP than in PBP. Nevertheless, pistachio juices processing by-products contained higher levels of serine, glutamic acid, cysteine and arginine. There were slight difference in essential amino acid contents between almond by-products and pistachio by-products. Therefore, ABP and PBP show a high nutritional value, based on these amino acid profiles, and could be a good dietary protein supplements to poorly balanced dietary proteins. Furthermore, amino acid composition analyses of almond and pistachio juices by-products processing help to study their antioxidant effect and mechanism. As presented in Table 4, The hydrophobic

| Amino acids | Number of residues/1000 | |
|---|---|---|
| | ABP | PBP |
| Asp | 106[a] | 103[a] |
| Thr | 54[a] | 33[b] |
| Ser | 58[a] | 72[b] |
| Glu | 116[a] | 202[b] |
| Gly | 91[a] | 88[a] |
| Ala | 119[a] | 66[b] |
| Cys | 4[a] | 15[b] |
| Val | 61[a] | 55[a] |
| Met | 19[a] | 12[a] |
| Ile | 43[a] | 36[b] |
| Leu | 91[a] | 74[b] |
| Tyr | 25[a] | 22[a] |
| Phe | 42[a] | 43[a] |
| His | 21[a] | 20[a] |
| Lys | 52[a] | 35[b] |
| Arg | 53[a] | 77[b] |
| Pro | 45[a] | 47[a] |
| TEAA | 387[a] | 310[a] |
| THAA | 455[a] | 354[b] |
| Essential/non-essential ratio | 0.63 | 0.45 |

TEAA = total essential amino acids
THAA = total hydrophobic amino acids
[a,b]Different superscripts in the same row indicate the significant differences ($p$<0.05).

**Table 4:** Amino acid composition of almond and pistachio juices processing by-products.

amino acids content of the almond by-products (455 residues per 1000 residues) was significantly ($p$<0.05) higher than that of pistachio juices processing by-products (354 residues per 1000 residues). Amino acids in ABP and PBP are possibly involved in antioxidative activity. Several amino acids, such as Tyr, Met, His, Lys, and Trp, may significantly contribute to the antioxidant activity [22].

Comparison of the amino acid content and almond juices processing by-products to the reference values recommended by the FAO/WHO/UNU33 showed that ABP would meet the range of amino acids requirements for children and adults. The ratios of essential to non-essential amino acids in ABP and PBP were 0.63 and 0.45, respectively.

## Fatty acid composition

The fatty acid compositions of almond and pistachio juices processing by-products lipids were determined (Table 5).

Two fatty acids are highly represented in the lipidic composition of almond and pistachio juices by-products processing: oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids. These fatty acids account for 91% and 90% of the total fatty acids of ABP and PBP lipids, respectively. Similar results were previously reported by [23-25]. Oleic acid has a fundamental role in cardiovascular disease prevention and is indispensable for the healthy growth of human skin [26]. Monounsaturated fatty acids (MUFA) were the major fatty acids, representing 69.56% and 70.70% of the total fatty acids in the ABP and in PBP, respectively. It has been recognized that a diet rich in MUFA may be an alternative choice to a low-fat diet, which may lower blood cholesterol levels, modulate immune function, decrease susceptibility of LDL oxidation and improve the fluidity of HDL [2,27,28]. Both juices processing by-products showed contains polyunsaturated fatty acids (PUFA) (22.43% in ABP and 20.83% in PBP). PUFA are described as having various health benefits (Ruxton et al.). The American Heart Association (AHA) has currently endorsed the use of n-3 PUFA at a dose of approximately 1 g/day of combined eicosapentaenoic acid (DHA) and docosahexaenoic acid (EPA), either in the form of fatty fish or fish oil supplements (in capsules or liquid form) for patients with documented coronary heart disease [29].

## Incorporation of juices processing by-products in the formulation of cookies

Almond and pistachio juices by-products processing were used in the formulation of cookies as the substituent of the wheat flour at levels of 33% (Cookie A) and 50% (Cookie B) almond by-products and 33% (Cookie C) and 50% (Cookie D) pistachio by-products.

**Textural analysis:** Textural analyses of different cookies were shown in Table 6. Volume, weight loss and propagation rate of cookies decrease with the increase in the rate of substitutions. There were not significant differences ($p$>0.05) between control, ABP and PBP. Hardness for control cookies was found to be 63.59 ± 3.35 while for cookies D it was 77.13 ± 5.14. Cookies A and B were found to be harder than control and cookies C and D, the difference made by the structural strength provided by physic-chemical composition of almond and pistachio by-products processing. Based in the statistic test, the level of substitution exerted a main effect on peak force; the addition of all by-products resulted in cookies with force peak that were significantly ($p$<0.05) different from that of the wheat control. Cookies with almond by-products have a peak force higher ($p$<0.05) than that for the wheat control and cookies with pistachio by-products. No significant differences ($p$>0.05) in peak force were found between degrees of substitution that are less than 50%.

**Sensory analysis:** The sensory analysis scores (Data not shown) indicated that no significant differences were observed in odour between cookies. However, significant differences ($p$<0.05) were observed in taste, appearance, and texture. In fact, the consumer rather appreciates the texture of cookies C and D, the taste of the control without by-products and the appearance of cookies A and B.

**Microbiological quality:** All the cookies samples were free of aerobes, mould, coliforms and staphylococcus. These results could be related to the richness in polyphenolic compounds of the almond and

| Fatty acid (%) | ABP | PBP |
|---|---|---|
| SFA | 8.015[a] | 8.474[a] |
| MUFA | 69.561[a] | 70.695[a] |
| PUFA | 22.425[a] | 20.831[b] |
| UFA | 91.986[a] | 91.526[a] |
| UFA/SFA | 11.48[a] | 10.80[a] |
| PUFA/MUFA | 0.32[a] | 0.29[a] |
| $C_{14:0}$ | 0.015[a] | 0.025[b] |
| $C_{16:0}$ | 6.192[a] | 6.713[a] |
| $C_{16:1}$ | 0.828[a] | 1.149[b] |
| $C_{17:0}$ | 0.025[a] | 0.024[a] |
| $C_{17:1}$ | 0.028[a] | 0.040[a] |
| $C_{18:0}$ | 1.755[a] | 1.650[a] |
| $C_{18:1}$ | 68.705[a] | 69.367[a] |
| $C_{18:2}$ | 22.384[a] | 20.747[b] |
| $C_{18:3}$ | 0.041[a] | 0.084[b] |
| $C_{20:0}$ | 0.028[a] | 0.062[b] |
| $C_{20:1}$ | - | 0.139 |

Values expressed are means of three independent determinations.
[a,b]Different superscripts in the same row indicate the significant differences ($p$<0.05).

**Table 5.** Fatty acid composition of almond and pistachio juices processing by-products (% of total fatty acids).

| | Control | Cookie A | Cookie B | Cookie C | Cookie D |
|---|---|---|---|---|---|
| **Volume** | 33.96 ± 0.59$^{a,A}$ | 29.72 ± 0.84$^{b}$ | 27.27 ± 0.52$^{b}$ | 29.60 ± 0.22$^{B}$ | 27.12 ± 0.39$^{C}$ |
| **Propagation rate** | 1.67 ± 0.09$^{a,A}$ | 0.34 ± 0.09$^{b}$ | 0.24 ± 0.09$^{b}$ | 0.39 ± 0.05$^{B}$ | 0.18 ± 0.08$^{C}$ |
| **Weight loss (g)** | 2.16 ± 0.05$^{a,A}$ | 2.14 ± 0.06$^{b}$ | 2.11 ± 0.05$^{b}$ | 2.13 ± 0.10$^{B}$ | 1.82 ± 0.04$^{C}$ |
| **Peak force (N)** | 63.59 ± 3.35$^{a,A}$ | 105.24 ± 2.4$^{b}$ | 116.64 ± 2$^{b}$ | 67.00 ± 4.59$^{B}$ | 77.13 ± 5.14$^{C}$ |

Values expressed are means of three independent determinations.
$^{A,B,C,a,b}$ Different letters indicates significant differences among samples.

**Table 6:** Physical and textural properties of different cookies.

pistachio juices processing by-products. The phenolic compounds are well-known for their antimicrobial activity [30]. Also Microbiological quality of cookies could be related to the heat treatment during the cooking.

## Conclusion

The aims of this work were to characterize the almond and pistachio juices processing by-products and to evaluate their nutritional quality. Results revealed that almond and pistachio juices processing by-products have relatively high carbohydrate, fat, calcium magnesium and essential amino acid, contents. Indeed, both juices processing by-products showed high nutritional value, based on their amino acid contents. Monounsaturated fatty acids were the major fatty acids of both by-products. ABP and PBP can be incorporated into formulations of cookies. Therefore, they represent a potential source of oil and protein for the human diet.

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