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Characterization of apple, pineapple, and melon by-products and their application in cookie formulations as an alternative to enhance the antioxidant capacity

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Abstract

This work aimed at determining the physicochemical properties of pineapple, apple, and melon by-products, as well as evaluating their influence on the antioxidant capacity and phenolic compounds of cookies. Proximate composition, pH, color, water activity, particle size, total phenolic content, antioxidant capacity, identification, and quantification of phenolic acids and flavonoids were performed. The low pH (4.19 ± 0.01–5.48 ± 0.00) and water activity (0.17 ± 0.00–0.19 ± 0.00) indicated that these by-products are not easily susceptible to deterioration. The by-products presented light color and yellow tones, which are desirable for their application in cookies. The apple by-product presented the highest total phenolic content (5.92 ± 1.78 mg GAE/g) and antioxidant capacity. Vanillic acid, gallic acid, sinapic acid, salicylic acid, *p*-coumaric acid, catechin, epicatechin, and rutin were quantified in both the by-products and cookies. Therefore, fruit by-products are considered a good alternative for use in cookies to improve their antioxidant capacity and phenolic compounds.

Practical applications

The use of fruit by-products in the formulation of cookies can contribute to increase antioxidant capacity of these foodstuffs, since the non-conventional parts of fruits, such as apple endocarp, pineapple central axis, and melon peels present significant contents of phenolic acids and flavonoids. In addition to contributing to the functionality of cookies, this approach suggests an alternative for the use of fruit by-products, thus avoiding food waste.

1 | INTRODUCTION

It is estimated that after industrial processing, around 50% of the total weight of fruits become residues, which entail environmental problems and operational costs. These by-products, however, usually present high nutritional value and considerable contents of bioactive compounds, which are important for a good intestinal functioning, weight control, reduction in the blood cholesterol levels, and a better control of the glycemia and insulin responses (Gómez & Martinez, 2017). Even with so many attributes, there are still scarce viable alternatives for the major part of plant by-products, which are usually employed as fertilizers or for animal feeding.

Fruits like apple, pineapple and melon are popularly consumed both *in natura* and processed (e.g., juices, pulps, jellies, and craft candies). After processing, peels, bagasse, membranes, and seeds are the main by-products obtained. These materials usually

present significant amounts of fibers, vitamins, and polyphenols (De Camargo, Vidal, Canniatti-Brazaca, & Shahidi, 2014; Sato et al., 2010; Selani et al., 2016).

Phenolic compounds are derived from the plant secondary metabolism, and act mainly as a response to ecological and physiological pressures. They are related to plant pigmentation and can play an antipathogenic role. In addition to being related to the antioxidant capacity, these compounds attribute sensory qualities to the foods (e.g., color, aromas, bitterness, and astringency) (Mallek-Ayadi, Bahloul, & Kechaou, 2017). Several phenolic compounds are described in literature, and for fruits, phenolic acids, and flavonoids are predominant.

Given their high acceptance and versatility, baked products, and cookies are often employed as vehicle of bioactive compounds and nutrients. Studies demonstrated that formulations enhanced with plant by-products can contribute to the rise in the content of phenolic compounds and the antioxidant capacity (Aksoylu, Çagindi, & Kose, 2015; Bhol, Lanka, & Bosco, 2016).

In a previous study (Toledo, Nunes, Silva, Spoto, & Canniatti-Brazaca, 2017), it was observed that cookies prepared with pineapple central axis presented satisfactory results from the sensory and technological properties, whereas cookies made with melon by-products showed more unsatisfactory results than the control treatment. It is known that besides these aspects, investigating the presence of bioactive compounds, such as phenolic acids and flavonoids in these cookies may be relevant to determine the effects of the use of by-products on the antioxidant capacity of this foodstuff. Moreover, as far as we know, no literature was found focusing on the use of pineapple central axis, apple endocarp, and melon peels as potential sources of antioxidant compounds in cookies formulations.

Therefore, the present work aimed at characterizing pineapple, apple, and melon by-products, as well as evaluating their influence on the antioxidant capacity and the phenolic acids and flavonoids of cookies prepared with 15% of these by-products. It is expected that this new approach will stimulate the use of non-conventional parts of foods, thus avoiding waste, besides to adding value to the by-products, and functionality to cookies formulations.

2 | MATERIALS AND METHODS

2.1 | By-products

Pineapple (Perola) central axis, melon (Yellow honeydew) peels, and apple (Gala) endocarp were obtained from a minimally processed food industry (Engenheiro Coelho, SP, Brazil). In the factory, the fruits have undergone a sanitation process with the application of chlorine dioxide (1 ml/L). The by-products were collected from three different batches in November, 2015. The by-products were kept frozen and transported to the Human Nutrition Laboratory of ESALQ/USP, then stored in a freezer (−18°C) for a maximum of 30 days. The material was dehydrated in an E-C Modulyo freeze-dryer (Apparatus Inc., New York, USA) for 96 hr at −40°C under pressure of 0.998 mbar. Subsequently, the by-products were ground in a cutting mill (Marconi, Piracicaba, Brazil), sieved at 35 mesh (Abronzinox, 0.425 mm) and stored wrapped in aluminum foil and inside plastic bags properly closed at −18°C.

2.2 | Characterization of the fruit by-products

2.2.1 | Proximate composition

Moisture (gravimetric), ash (gravimetric), proteins (Kjedahl, N × 6.25), and lipids (Soxhlet) were performed as described by Association of Official Analytical Chemists (2005). Fibers (soluble and insoluble) were determined according to Asp, Johansson, and Hallmer (1983). Available carbohydrates were obtained by difference. All analyses were performed in triplicate.

2.2.2 | Physicochemical analysis

The pH was measured using a potentiometer (Quimis, Q799-D2, São Paulo, Brazil) in 10% (w/v) aqueous solution of the sample. Water activity was verified using an Aqualab appliance (Series 4TE, Decagon devices Inc., Pullman, USA) at 25°C. Color parameters such as lightness (L), hue angle (h), and chroma (C) were read in a colorimeter (Minolta CR-400, Konica Minolta, Osaka, Japan) with a standard illuminant C. For the granulometry of by-products, sieves from 20 to 60 mesh were submitted to the action of a vibrator for 15 min (Coelho & Wosiacki, 2010). All analyses were performed in triplicate.

2.3 | Cookies preparation

For the preparation of the cookies (common house-hold raisin cookies), formulations developed by Toledo et al. (2017) were adopted. Four different treatments were prepared, which comprised of control treatment and cookies containing 15% of different fruit by-products (pineapple central axis, apple endocarp, and melon peels). The procedure occurred in triplicate (three independent batches for each by-product). The ingredients used in cookies preparation included wheat flour (type 1, 10% of protein, Dona Benta, J. Macêdo S.A.—Londrina, PR, Brazil), refined sugar (União, Raízen Paraguaçu Ltda—Tarumã, SP, Brazil), baking powder (Royal, Mondelez Brasil Ltda—Curitiba, PR, Brazil), eggs (GRC, Granja Morishita—Tupã, SP, Brazil), salted butter (Scala, Scalon & Cerchi Ltda—Sacramento, MG, Brazil), and pieces of semisweet chocolate bar with 40% of cocoa (Nestlé, Chocolates Garoto S.A.—Caçapava, SP, Brazil), which were obtained from the local market in Piracicaba, SP, Brazil. A previous study (Toledo et al., 2017) showed that biscuits containing 15% of by-products presented better physicochemical, technological, and sensory properties, and therefore, this was the concentration of fruit by-products used in the preparation of cookies of the present study.

Initially, 105 g of refined sugar and 75 g of butter were mixed in a beater mixer (Philips Walita, RI7915, China) for 10 s. Then, 50 g of egg was added and the dough was mixed for another 5 s. A total of 200 g of flour was used to prepare the dough. For the

control cookies, only wheat flour was used, whereas for the treatments containing fruit by-products, 170 g of wheat flour and 30 g of each fruit by-product (pineapple central axis, apple endocarp, and melon peels) were used. After flour addition, 10 g of baking powder and 25 g of semisweet chocolate were integrated into the cookie dough and the mixture was beaten for 10 s. The dough was open and cut using circular molds. The cookies were baked in an electric oven (Perfecta, Ponta Grossa, Brazil) at 180°C for 10 min. Lastly, they were cooled at room temperature and stored in glass containers.

2.4 | Total phenolics and antioxidant capacity

2.4.1 | Extraction

The extracts (for by-products and for cookies) were prepared as described by Bloor (2001). Samples (1 g) were extracted in triplicate, with 10 ml of solvent (ethanol:water, 80:20 v/v). The solution was subjected to an ultrasonic bath (Ultra Cleaner, Unique, Indaiatuba, Brazil) (25°C, 20 min). The material was centrifuged (4,000 rpm, 15 min), and the supernatant was used for the analyses of total phenolics, antioxidant capacity, and determination of phenolic acids and flavonoids.

2.4.2 | Total phenolic content

The total phenolic content was determined according to Singleton, Orthofer, and Lamuela (1999) using the Folin-Ciocalteau method and the absorbance was measured at 765 nm using a UV–vis spectrophotometer (Shimadzu, model UV-1800). The analyses were conducted in triplicate and the results were expressed as milligram of gallic acid equivalent per gram of sample (GAE/g).

2.4.3 | Antioxidant capacity

The antioxidant capacity was evaluated by DPPH assays, according to Brand-Williams, Cuvelier, and Berset (1995), and by ABTS assays, following the methodology described by Re et al. (1999). In both methods, the analyses were conducted in triplicate and Trolox was used as reference standard. The results were expressed as micromoles of Trolox equivalent per gram of sample (μmol TE/g).

2.4.4 | Identification and quantification of the phenolic acids and flavonoids

The quantitative and qualitative determination of the phenolic acids and flavonoids was performed according to He et al. (2011) with adaptations. Aliquots of 20 μl of the extracts were injected into a Shimadzu HPLC (model 20A, Kyoto, Japan), equipped with a pumping system model LC-20AT, automatic sample injector model SIL-20AHT, column oven model CTO-20A, communicator model CBM-20A and UV detector (280 and 370 nm) model SPD-20A. A C18 column (Waters Spherisorb ODS2; 4.6 × 250 mm, 5 μm) was employed for the separation at 40°C maintained by the column oven. The mobile phases used were A (1% formic acid in aqueous solution) and B (100% methanol), which were eluted in a linear gradient: solvent A from 100% to 40% in 45 min and from 40% to 0% in 5 min, returning to 100% in 10 min and lastly maintained at 100% for 5 more minutes, with a flow of 0.7 ml/min.

The identification of the compounds was confirmed by the comparison of their retention times and UV/visible spectrum with those of the authentic materials. For quantification, the calibration curves were made from authentic standards (Sigma-Aldrich, St Louis, MO, USA). A stock solution (1 mg/ml) of each standard was prepared and diluted. To prepare the stock solution, 10 mg of each phenolic acid and flavonoid were dissolved in 10 ml of ultrapure water and then serially diluted: 1, 2.5, 5, 10, 25, 50, 100, and 150 μg/ml of vanillic acid; 2.5, 5, 10, 25, 50, 100, and 200 μg/ml of gallic acid; 1 2.5, 5, 10, 25, 50, 100, 200, and 300 μg/ml of synapic acid; 1, 2.5, 5, 10, 25, and 50 μg/ml of salicylic acid; 1, 2.5, 5, 10, 25 and 50 μg/ml of p-coumaric acid; 1, 2.5, 5, 10, 25, 50 μg/ml of catechin; 1, 2.5, 5, 10, 25, 50, and 100 μg/ml of epicatechin; and 2.5, 5, 10, 25, and 50 μg/ml of rutin. The content of phenolic acids and flavonoids was expressed in micrograms per gram of dry matter (μg/g), and the analyses were carried out in triplicate. The linearity, limits of detection (LOD) and quantification (LOQ) were performed as validation parameters.

2.5 | Statistical analysis

A randomized block design was used, with three blocks, since each block corresponded to an independent cookie preparation. The data were subjected to analysis of variance (ANOVA) for the *F* test and the comparison of means by Tukey's test ($p < 0.05$). The analyses were performed by the software Statistical Analysis System (SAS) version 9.2 (2005).

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the fruit by-products

3.1.1 | Proximate composition

Carbohydrates were the major macronutrients identified in the composition of the pineapple central axis and apple endocarp (Table 1). The values found for pineapple and apple by-products were superior to those observed in studies that used the same lyophilized by-products, which registered 43.46% (pineapple peel and bagasse) and 39.35% (apple bagasse) of carbohydrates (Sato et al., 2010; Selani et al., 2014). This variation can be explained by the differences in the composition of the analyzed material: in the present study, pineapple by-product was composed only by the central axis and apple by-product by the endocarp. Regarding melon by-products, values between 20% and 45% were reported for melon peels (Gondim, Moura, Dantas, Medeiros, & Santos,

TABLE 1 Proximate composition of the pineapple (PIB), apple (APB), and melon (MLB) by-products

	PIB	APB	MLB
	(g/100 g of fresh weight basis)		
Moisture	6.48 ± 0.03[a]	4.69 ± 0.14[b]	4.42 ± 0.23[b]
Ash	1.11 ± 0.10[c]	2.95 ± 0.10[b]	10.64 ± 0.50[a]
Lipid	0.54 ± 0.02[c]	1.33 ± 0.14[b]	1.76 ± 0.05[a]
Protein	3.23 ± 0.13[a]	2.91 ± 0.13[b]	3.11 ± 0.16[ab]
Carbohydrate	74.01	68.62	33.77
Total dietary fiber	14.63 ± 0.30[a]	19.50 ± 0.31[b]	46.30 ± 2.49[c]
Insoluble dietary fiber	13.55 ± 0.31[b]	15.73 ± 0.21[b]	43.53 ± 2.64[a]
Soluble dietary fiber	1.08 ± 0.08[c]	3.77 ± 0.27[a]	2.77 ± 0.21[b]

Note: Results are expressed as the mean value ± standard deviation (n = 3).
[a,b,c]Different letters in the same row indicate significant difference (p < 0.05).

2005; Storck, Nunes, Oliveira, & Basso, 2013), which are consistent with the present study.

By-products showed large amounts of fibers with the highest contents registered for melon by-product (46.30% ± 2.49%), which was already expected since peels usually present more significant amounts of fiber (Morais et al., 2017). In general, the insoluble fibers were prominent in relation to the soluble fibers. Insoluble fibers are essential to the regulation of the intestinal movements and aids in the prevention of constipation (Almaraz et al., 2015). Regarding the content of soluble fibers, apple endocarp was prominent compared to the other by-products, possibly because of the high pectin content found in apple bagasse, which is one of the main raw materials for the commercial extraction of this polysaccharide (Willats, Knox, & Mikkelsen, 2006). The soluble fibers present an important physiological function, since they positively affect the metabolism of available carbohydrates and lipids, promoting the reduction in the absorption of these nutrients in the human intestine. The proper consumption of fibers is related to the reduction in the risk of chronic diseases, such as obesity, cardiovascular diseases, and chronic diseases of the kidneys and diabetes (Fujii et al., 2013).

For pineapple by-product, the contents of total fibers found in the fruit central axis (14.63% ± 0.30%) were lower than those reported in the peels (Leonel, Leonel, & Sampaio, 2014). Conversely, the fiber contents in melon peels were similar to that reported by Storck et al. (2013). In relation to apple by-product, in a study using the fruit bagasse, Coelho and Wosiacki (2010) reported a higher amount (43.02%) of fibers in comparison to the present study. This fact may be related to the presence of peels in apple bagasse, which contributes to the superior contents of fibers (Morais et al., 2017).

Concerning the moisture, pineapple central axis presented the highest value (6.48% ± 0.03%). In general, higher values were observed in the literature (except for pineapple), with moisture varying between 3.77% and 11.85% for pineapple by-products (bagasse and peels) (Leonel et al., 2014; Selani et al., 2014), 7.10%–13.72% for apple bagasse (Coelho & Wosiacki, 2010; Sato et al., 2010), and 6.77%–10.2% for melon peels (Gondim et al., 2005; Storck et al., 2013). It is known that moisture values may vary depending on the drying method, time of exposure to the drying process, and storage conditions, since after dehydration processes, the products become highly hygroscopic, potentially absorbing significant amounts of water.

For the ash, there was a significant difference (p < 0.05) among all treatments. The melon peels presented ash content 10 times superior to the pineapple central axis, representing the highest and the lowest ash contents, respectively. Compared to the literature, values of 11.66% were detected for the ash of melon by-products (Storck et al., 2013), between 2.24% and 4.70% (Gondim et al., 2005; Selani et al., 2014) for pineapple and values from 1.46% to 2% were observed for apple (Coelho & Wosiacki, 2010; Sato et al., 2010). Factors such as cultivar, soil, climate conditions, and fertilization might influence in the minerals available in the foods and, consequently, in their ash content (Davis, Epp, & Riordan, 2004).

Proteins and lipids were the least representative macronutrients in the by-products. Values superior to those found for proteins in the present study were reported for pineapple by-products (4.71%–6.63%) (Gondim et al., 2005; Selani et al., 2014) and for melon by-products (2.03%–9.56%) (Storck et al., 2013), whereas for apple, values from 2.42% to 3.35% were registered (Coelho & Wosiacki, 2010; Sato et al., 2010), which are coherent with this research. On the contrary, for lipids, the results found endorsed the literature, with contents of 0.61% observed for pineapple bagasse (Selani et al., 2014); 1.06%–2.14% for apple bagasse (Sato et al., 2010) and 0.25% for melon peels (Storck et al., 2013). The low lipid contents were expected, since the by-products analyzed did not present seeds in their composition, which usually are the main source of fatty acids in plant-derived products (Morais et al., 2017).

3.1.2 | Physicochemical analysis

Comparing the different by-products, a significant difference (p < 0.05) was observed among the pH values (Table 2), with pineapple and melon by-products exhibiting the lowest and the highest values, respectively. Other studies that have used the edible parts of the fruits reported pH values for pineapple between 4.07 and 4.38 (Pereira et al., 2009); for apple, 3.70 to 3.88 (Fontes, Sarmento, Spoto, & Dias, 2008) and for melon, values between 5.01 and 6.95 (Aroucha et al., 2007). Such variations in pH are considered acceptable, since this parameter is associated with the process of fruit ripening and might present alterations according to the point of harvest (Pereira et al., 2009).

With respect to the water activity, melon peels obtained the lowest value (0.17 ± 0.00), significantly differing (p < 0.05) from the other by-products. The results found are consistent with the study

TABLE 2 pH, water activity (a_w), color parameters (*L*, *C*, *h*) of the fruit by-products

	PIB	APB	MLB
pH	4.19 ± 0.01[c]	4.37 ± 0.06[b]	5.48 ± 0.00[a]
a_w	0.19 ± 0.00[a]	0.19 ± 0.00[a]	0.17 ± 0.00[b]
L	90.47 ± 0.60[a]	77.35 ± 0.78[c]	88.44 ± 0.48[b]
C	18.90 ± 0.44[b]	27.00 ± 0.52[a]	18.72 ± 0.80[b]
H	97.85 ± 0.31[a]	86.97 ± 0.68[c]	94.57 ± 1.03[b]

Note: Results are expressed as the mean value ± standard deviation ($n = 3$).
Abbreviations: APB, apple by-product; C, chroma; h, hue angle; L, lightness; MLB, melon by-product; PIB, pineapple by-product.
[a,b,c]Different letters in the same row indicate significant difference ($p < 0.05$).

TABLE 3 Size distribution of the particles of pineapple (PIB), apple (APB), and melon (MLB) freeze-dried by-products

	% Oversize particles		
Size (μm)	PIB	APB	MLB
841	8.86 ± 0.43[a]	5.08 ± 0.04[b]	3.94 ± 0.18[c]
500	12.50 ± 0.24[c]	18.61 ± 0.70[b]	21.29 ± 0.34[a]
350	3.81 ± 0.08[c]	5.03 ± 0.22[b]	7.40 ± 0.51[a]
300	6.67 ± 0.36[c]	8.33 ± 0.09[b]	10.10 ± 0.26[a]
250	3.69 ± 0.13[b]	9.95 ± 0.47[a]	4.06 ± 0.10[b]
<250	64.47 ± 0.81[a]	53.00 ± 0.66[b]	53.21 ± 0.49[b]

Note: Percentage of particles with diameter over the size (μm) described in the first column.
[a,b,c]Different letters in the same row indicate significant difference ($p < 0.05$).

of Selani et al. (2014), who found a value of 0.14 for pineapple bagasse, but inferior to those reported by Coelho and Wosiacki (2010) for apple bagasse (0.81).

Given the fact that plant by-products can be used as ingredients in formulations of new products, it is important to consider their color parameters, since this attribute is directly related to consumer's acceptance (Selani et al., 2016). All by-products evaluated presented elevated lightness values (L), with emphasis for pineapple central axis, indicating that this by-product is lighter than the others. This is an important and positive result, since the ingredients with dark colorations present limitations for application in foods. No significant differences ($p > 0.05$) were observed between pineapple and melon by-products for chroma (C). The apple by-product presented the highest C value and, consequently, was considered the treatment with the highest purity and color intensity. Considering the values of the hue angle, it was proven that the by-products presented tones closer to yellow, with a significant difference ($p < 0.05$) among all treatments.

One of the main applications suggested for the use of fruit by-products is the preparation of baked goods and cookies. For these products, the particle size composition of the flour is considered a quality attribute, since particle size interferes in water absorption capacity, in the time of mixing, and in sensory characteristics, such as texture, flavor, and visual aspect (Abera, Solomon, & Bultosa, 2017). The granulometric composition of the flours obtained from the fruit by-products (Table 3) was mostly smaller than 250 μm, which refers to a flour with fine and small particles. The flour obtained from pineapple central axis was considered the one with the lowest granulometry and most homogeneous composition. There was no significant difference ($p > 0.05$) of final yield (particles < 250 μm) between the flours of apple and melon by-products. Coelho and Wosiacki (2010) developed a flour from apple bagasse and reported granulometry smaller than 500 μm for around 60% of the product. Selani et al. (2016) found granulometry smaller than 211 μm for 42% of flour obtained from pineapple peels and bagasse. Particle size may vary according to the fruit by-products, methods used for their preparation and considering the application of the material.

3.2 | Total phenolic contents and antioxidant capacity of by-products and cookies

Among the by-products, the extract of apple endocarp presented the highest value for total phenolic contents, followed by melon and pineapple by-products (Table 4). It is worth emphasizing that apple endocarp demonstrated content of total phenolics even higher to other by-products cited in the literature, such as passion fruit peel and seed (3.86 mg GAE/g) and mango bagasse (4.67 mg GAE/g) (Selani et al., 2016). Besides differences between species and cultivars, the content of phenolic compounds might vary according to the part of the fruit used for extraction. Leaves and peels, being more exposed to environmental damages than fruit pulp, require more protection against pathogens, leading to the production of secondary metabolites, such as phenolic compounds, to be higher in these parts (Storck et al., 2013). Melon peels, for instance, presented total phenolics content of 4.58 mg GAE/g, which was consistent with the study of Mallek-Ayadi et al. (2017). Regarding pineapple by-product, the result found corroborate with data of Selani et al. (2016), who reported total phenolics of 3.78 mg GAE/g for pineapple peel and bagasse.

Cookies are traditionally prepared with ingredients such as wheat flour and chocolate, which contain polyphenols, mainly phenolic acids (cereals) and flavonoids (cocoa) (Giordano et al., 2017; Ramos, Martín, & Goya, 2017). Nevertheless, traditional cookies usually do not present functional properties or added nutritional value. In this sense, the incorporation of plant by-products in the development of baked goods has been proposed as a strategy to carry bioactive compounds. The use of fruit by-products in the formulation of cookies contributed to an increase of more than 100% in the phenolic compounds contents (from 7.80 ± 0.13 up to 16.91 ± 0.19 mg GAE/g), being the cookies made with apple by-product the most promising formulation. Aksoylu et al. (2015) also developed cookies, but with poppy and grape seeds and detected 8.44 and 17.90 mg GAE/g of total phenolics, respectively. Likewise, Bhol et al. (2016) employed pomegranate bagasse for the

TABLE 4 Total phenolic contents and antioxidant capacity (DPPH and ABTS) of the fruit by-products and cookies

	Total phenolic content (mg GAE/g)	DPPH (μmol TE/g)	ABTS (μmol TE/g)
PIB	2.82 ± 0.60[c]	7.14 ± 0.34[c]	7.24 ± 0.16[c]
APB	5.92 ± 1.78[a]	23.83 ± 0.38[a]	19.87 ± 0.44[a]
MLB	4.58 ± 1.31[b]	16.60 ± 0.23[b]	15.48 ± 0.12[b]
CCT	7.84 ± 0.05[c]	3.94 ± 0.70[c]	5.39 ± 0.33[c]
CPI	7.80 ± 0.13[c]	5.82 ± 0.11[b]	7.17 ± 0.33[b]
CAP	16.91 ± 0.19[a]	11.97 ± 0.25[a]	12.35 ± 0.83[a]
CML	11.26 ± 0.23[b]	11.98 ± 0.46[a]	12.84 ± 0.49[a]

Note: Results are expressed as the mean value ± standard deviation (n = 3).
Abbreviations: APB, apple by-product; CAP, cookies containing 15% of apple by-product; CCT, cookie control; CPI, cookies containing 15% of pineapple by-product; CML, cookies containing 15% of melon by-product; MLB, melon by-product; PIB, pineapple by-product.
[a,b,c]Different letters in the same column indicate significant difference ($p < 0.05$) among the same treatments (by-products or cookies).

development of breads and obtained a total of phenolics five times superior to the control.

Similarly to the content of total phenolics, there was also a significant difference ($p < 0.05$) among the antioxidant capacity of the by-products, especially apple endocarp. Mostly, the incorporation of fruit by-products in cookies increased their antioxidant capacity (Table 4). Despite being considered indirect methods, it was observed by the DPPH assays, that the values of antioxidant capacity varied between 7.14 ± 0.34 and 23.83 ± 0.38 μmol TE/g for the by-products and 3.94 ± 0.70 to 11.98 ± 0.46 μmol TE/g for the cookies, whereas with the ABTS assays, results varying from 7.24 ± 0.16 to 19.87 ± 0.44 μmol TE/g and between 5.39 ± 0.33 and 12.84 ± 0.49 μmol TE/g were observed for by-products and cookies, respectively. This variation was attributed to the distinct way of evaluation of the antioxidant capacity of each method, besides being distinguished in relation to the solubility of the compounds: the ABTS assay is based on the formation of a blue/green $ABTS^{+}$, which can identify both lipophilic and hydrophilic compounds, whereas DPPH assay uses a radical dissolved in organic solvent and, therefore, has a higher sensitivity for the hydrophobic compounds (Kim, Lee, Lee, & Lee, 2002).

For both methods, the antioxidant capacity of the by-products was superior to that of the cookies, which was expected since the fruit by-products usually present more complex profiles and more expressive amounts of phenolics than the products based on cereals (Giordano et al., 2017; Gómez & Martinez, 2017). In the case of baked goods and cookies, the baking step can assist in the release of conjugated phenolic acids, contributing to the increased content of total phenolic compounds and antioxidant capacity. Maillard reaction, caramelization, and oxidation of phenols may also contribute to the rise in total phenolic compounds in foods (Ragaee, Seetharaman, & Abdel-Aal, 2014).

3.3 | Phenolic acids and flavonoids

Considering the phenolic compounds identified, apple, and melon by-products presented seven and five phenolic compounds, respectively, among the eight compounds analyzed. The melon peels were prominent, especially for the presence of sinapic and salicylic acids (Table 5). Among the flavonoids, rutin was the compound of major relevance in this by-product. Other compounds, such as vanillic acid and catechin, were also identified, but in lower amounts. Rolim et al. (2018) demonstrated that there are differences among melon by-products, with higher occurrence of phenolics in the peels than in the seeds, with a prevalence of gallic acid, salicylic acid and catechin in the first, whereas in the seeds, higher concentrations of vanillic acid, salicylic acid, and catechin were observed.

Apple by-product, which represented higher values for total phenolic content and antioxidant capacity, also demonstrated high amounts of epicatechin and vanillic acid and, in lower concentrations, catechin, sinapic acid, rutin, and gallic acid (Table 5). Phenolic acids, such as salicylic, gallic, propylgalate, and sinapic are common in apple bagasse, whereas in the peels, there is predominance of flavonoids such as quercetin, catechin, epicatechin, and procyanidins, besides chlorogenic acid (Assumpção et al., 2018).

On the contrary, pineapple by-product presented the lowest significant amounts of phenolic compounds, with *p*-coumaric acid as the most relevant compound, followed by vanillic and salicylic acids. Regarding flavonoids, only catechin was identified. According to Bataglion, Da Silva, Eberlin, and Koolen (2015), in pineapple fruit there are phenolic acids such as *p*-coumaric, ferulic, sinapic, caffeic, syringic, and *p*-hydroxybenzoic, whereas among the flavonoids, kaempferol and quercetin are the most significant.

In general, the addition of fruit by-products in cookies significantly increased the concentrations of the phenolic compounds (Table 5). The control cookies presented a higher concentration of only sinapic acid when compared to cookies containing pineapple and apple by-products. Conversely, cookies made with melon peels demonstrated values of sinapic and salicylic acids 120% and 313% superior to the control, respectively, in addition of significant amounts of catechin, epicatechin, and rutin. It is worth mentioning that wheat flour, the main ingredient of the cookies, also

TABLE 5 Phenolic acids and flavonoids (μg/g) identified in fruit by-products and cookies

	By-products			Cookies				Validation parameters		
	PIB	APB	MLB	CCT	CPI	CAP	CML	LOD (μg)	LOQ (μg)	R^2
Vanillic acid	15.42 ± 0.46^{b}	928.21 ± 0.70^{a}	9.02 ± 0.27^{c}	2.18 ± 0.09^{c}	2.76 ± 0.11^{b}	74.49 ± 0.08^{a}	1.95 ± 0.02^{d}	0.09	0.29	0.999
Gallic acid	ND	9.22 ± 0.05^{a}	ND	118.30 ± 1.22^{c}	147.01 ± 7.56^{a}	129.30 ± 024^{b}	130.45 ± 7.35^{b}	0.10	0.30	0.998
p-coumaric acid	23.06 ± 0.42^{a}	ND	ND	ND	ND	ND	ND	0.01	0.03	0.996
Salicylic acid	13.53 ± 1.32^{b}	Tr	238.73 ± 1.23^{a}	3.20 ± 0.11^{b}	ND	ND	10.04 ± 0.78^{a}	0.07	0.22	0.999
Sinapic acid	Tr	50.14 ± 0.13^{b}	988.98 ± 4.17^{a}	220.06 ± 7.71^{b}	120.09 ± 5.52^{c}	97.86 ± 0.87^{d}	265.97 ± 7.69^{a}	0.21	0.65	0.995
Catechin	10.30 ± 0.03^{c}	91.69 ± 0.35^{a}	20.15 ± 0.73^{b}	12.63 ± 0.52^{c}	17.19 ± 3.92^{b}	26.60 ± 0.01^{a}	19.06 ± 1.82^{b}	0.01	0.02	0.998
Epicatechin	ND	1.051.49 ± 1.45^{a}	ND	6.51 ± 0.35^{d}	15.77 ± 1.82^{c}	34.05 ± 0.22^{a}	19.87 ± 1.40^{b}	0.22	0.67	0.992
Rutin	ND	24.28 ± 0.72^{b}	272.70 ± 1.41^{a}	ND	ND	1.68 ± 0.10^{b}	14.94 ± 1.18^{a}	0.23	0.69	0.994

Note: Results are expressed as the mean value ± standard deviation (n = 3).
Abbreviations: APB, apple by-product; CAP, cookies containing 15% of apple by-product; CCT, cookie control; CML, cookies containing 15% of melon by-product; CPI, cookies containing 15% of pineapple by-product; PIB, pineapple by-product; LOD, limit of detection; LOQ, limit of quantification; MLB, melon by-product; ND, not detected; Tr, traces.
^{a,b,c,d}Different letters in the same row indicate significant difference (p < 0.05) among the same treatments (by-products or cookies).

presents relevant amounts of phenolic compounds, with emphasis in the ferulic, sinapic, *p*-coumaric, syringic, and vanillic acids (Gotti et al., 2018).

For cookies containing apple endocarp, relevant concentrations of vanillic acid, catechin an epicatechin were obtained, whereas for cookies made with pineapple peels, there was prevalence of gallic acid, followed by sinapic acid, vanillic acid, epicatechin, and catechin. Hidalgo et al. (2018), studying formulations of biscuits prepared with only wheat flour and water, identified the predominance of ferulic acid, followed by *p*-coumaric, vanillic, and *p*-hydroxybenzoic acids. According to Ragaee et al. (2014), baking might also affect the proportion of phenolic compounds because of thermal degradation (e.g., vanillin and vanillic acid can be produced by the decomposition of ferulic acid). Furthermore, the heat treatment might favor the release of some phenolic acids, such as ferulic, syringic, vanillic, and *p*-coumaric or simple phenolics from wheat flour because of the degradation of conjugated compounds, such as tannins.

4 | CONCLUSION

Regarding fruit by-products, carbohydrates and fibers were the main components present. The low values for pH and water activity reported contribute to the low risk of by-product deterioration. Furthermore, all by-products presented light coloration and tones close to yellow, which is desirable for cookies. The partial replacement of wheat flour by fruit by-products was associated with a positive effect on the total phenolic content, antioxidant capacity, and the concentration of phenolic acids and flavonoids in cookies. The melon and apple by-products presented more significant amounts of phenolic compounds than pineapple by-product. Likewise, cookies containing apple and melon by-products presented the highest antioxidant capacity and demonstrated a complex profile of phenolic acids and flavonoids. Therefore, the use of fruit by-products can be indicated to enhance the quality of cookies with respect to the presence of phenolic compounds and antioxidant capacity.

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CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

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