



Contribution of melanoidins from heat-processed foods to the phenolic compound intake and antioxidant capacity of the Brazilian diet

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Abstract In the present study we aimed at studying, determined and estimated the daily intake the contents of melanoidins and of their phenolic-bound compounds, and the antioxidant capacity of thermally processed foods regularly consumed in the Brazilian diet. Among twenty-three heat-processed Brazilian food samples, melanoidins contents ranged from 1.6 (dulce de leche) to 21.4 g/100 g (soluble coffee). Considering melanosaccharides, roasted maté showed the highest content of bound phenolics (6415.1 µg/100 mg), whereas whole grain breakfast cereals (229.3 µg/100 mg) stood out among melanoproteins. The antioxidant capacity of melanoidins was strongly correlated with their bound phenolic compounds ($r > 0.8522$, $p < 0.0001$). We estimated that up to 10.7 g of melanoidins are daily consumed by the Brazilian population, with beer the major contributor (44%), followed by cereal products (36%) and coffee (17%). Brazilians ingest up to 26.0 mg of bound phenolics a day, mainly from

coffee (75%) and beer (13%) melanoidins. Therefore, the estimated intake of phenolic compounds by Brazilians is underestimated by up to 7%. Moreover, melanoidins contribute to up to 21% of the Brazilian dietary antioxidant capacity.

Keywords Melanosaccharides · Melanoproteins · Maillard reaction · Bioactive compounds

Introduction

The Maillard reaction is one of the predominant reactions that occurs during thermal processing (cooking, baking, and roasting) of foods. This non-enzymatic browning reaction encompasses a network of several reactions between reducing sugars and compounds with a free amino group, forming a variety of compounds which can be classified as early, intermediate, or last stage products (Echavarría et al. 2012). Melanoidins are the major compounds of this latter class, generically defined as high molecular-weight nitrogenous and brown-colored molecules that contribute to food texture, color and flavor (Echavarría et al. 2012). Melanoidins may be divided into two classes, melanosaccharides (skeletons composed mainly of polysaccharides) and melanoproteins (skeletons composed mainly of proteins), depending on the food matrix composition in which they are formed.

Melanosaccharides derive from the reaction of amino acids and polysaccharides, they are usually negatively charged and thus quite water soluble (Pastoriza and Rufián-Henares 2014). That is the case of coffee, beer and cocoa melanoidins. On the other hand, melanoproteins derive from the crosslinking of proteins and sugars in protein-rich foods, such as bread products and breakfast cereals, and

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consist of a network of extremely high molecular weight molecules, largely insoluble (Helou et al. 2016; Lindenmeier et al. 2002). Due to their high content in frequently consumed foods, dietary ingestion of melanoidins is quite high, up to 12.2 g/day (Fogliano and Morales 2011; Pastoriza and Rufián-Henares 2014), mainly due to coffee and bread consumption.

To date, the chemical structure of melanoidins has not been completely established. Some authors have reported that phenolic compounds play an important role in melanoidins formation, and consequently a certain amount of these phenolic compounds remain linked to their structure. The incorporation of phenolic compounds into melanoidins has already been described for bread (Alves and Perrone 2015) and coffee (Moreira et al. 2017; Perrone et al. 2012). Contents of bound phenolic compounds in these melanoidins ranged from 1.5 mg/100 g in bread (Alves and Perrone 2015) to 370 mg/100 g in coffee (Perrone et al. 2012). Phenolic compounds are usually associated with some of the physiological activities ascribed to melanoidins, such as antioxidant, antimicrobial, and prebiotic (Borrelli and Fogliano 2005; Delgado-Andrade et al. 2005; Rufián-Henares and De La Cueva 2009; Tagliacruzchi and Verzelloni 2014).

Considering that phenolic compounds are linked to melanoidins and their high dietary ingestion, one can assume that these macromolecules may significantly contribute to the dietary intake of phenolic compounds as well as to the dietary antioxidant capacity. This would be especially interesting in a scenario of low dietary intake of phenolic compounds, such as that observed in Western populations that do not usually consume enough plant-based foods. To investigate this hypothesis, we determined the contents of melanoidins and of their phenolic-bound compounds, and the antioxidant capacity of twenty-three thermally processed foods regularly consumed in the Brazilian diet. Then, based on food consumption data, we estimated the daily intake of melanoidins in the Brazilian population and their contribution to the intake of phenolic compounds and to the dietary antioxidant capacity.

Materials and methods

Standards and chemicals

2,2'-Azino-bis(2-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), 2,4,6-tris(2-pyridyl)-S-triazine (TPTZ), potassium persulfate, (\pm)-6-hydroxy-2,5,7,8-tetramethyl-chroman-2-carboxylic acid (Trolox®) and protease from *Streptomyces griseus* type XIV (pronase E) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). Sodium carbonate was purchased from

Spectrum Chemical Manufacturing Corp. (Gardena, CA). Iron (II) sulfate was purchased from Merck KGaA (Darmstadt, Germany). Phenolic compounds standards were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). All solvents were HPLC grade from Tedia (Fairfield, OH). HPLC grade water (Milli-Q system, Millipore, Bedford, MA) was used throughout the experiments.

Samples

Samples were selected among heat-processed foods regularly consumed in the Brazilian diet, and divided into two groups, according to the solubility of their melanoidins: melanosaccharides (water soluble) from coffee, decaffeinated coffee, soluble coffee, decaffeinated soluble coffee (all samples of medium roast), roasted maté (*Ilex paraguariensis*), black beer (stout-type), blond beer (American lager-type) and soluble cocoa powder; melanoproteins (water insoluble) from Aussie bread, Brazilian cheese bread, brioche, corn bread, French bread, white bread, whole wheat bread, cream cracker, cornstarch biscuits, malted milk biscuits, wafer, dulce de leche, pound cake, corn flakes breakfast cereal and whole grain breakfast cereal.

Three different brands of each food were analyzed separately. Each of these analytical samples was composed of three different lots, which were acquired in supermarkets in Rio de Janeiro, Brazil.

Melanosaccharides contents

Samples containing melanosaccharides were prepared according to the characteristics of each sample (Supplementary Table 1). Samples were subjected to ultrafiltration and subsequent diafiltration, as described by Delgado-Andrade et al. (2005). Aliquots of 10–50 mL were passed through Amicon® centrifugal filters with a 3 kDa membrane cut-off (Millipore, Cork, Ireland) to isolate melanosaccharides samples. The retentates were repeatedly washed with water until the filtrates were colorless, followed by freeze drying (Labconco, Kansas City, MO). Melanosaccharides contents were expressed as g per 100 g or 100 mL (in the case of beer samples).

Melanoproteins contents

Samples containing melanoproteins were prepared according to the characteristics of each sample (Supplementary Table 1). Extraction of melanoproteins followed the procedure described by Borrelli and Fogliano (2005). After centrifugation at 3000g for 10 min at 25 °C (Microspin, Eppendorf AG, Hamburg, Germany), the

supernatant containing the hydrolyzed products was subjected to ultrafiltration and subsequent diafiltration, as described above for melanosaccharides. Melanoproteins contents were expressed as g per 100 g.

Analysis of bound phenolic compounds in melanoidins

Alkaline hydrolysis of both melanosaccharides and melanoproteins followed the methodology described by Perrone et al. (2012).

Phenolic compounds were analyzed by HPLC-DAD. The LC system (Shimadzu, Kyoto, Japan) comprised a LC-10ADvp quaternary pump, a CTO-10ASvp column oven, an 8125 manual injector (Rheodyne) with a 20 μ L loop and an SPD-M10Avp diode array detector (DAD). Chromatographic separations were achieved using a Kromasil® C18 column (5 μ m, 250 mm \times 4.6 mm) coupled to a Kromasil® C-18 pre-column (5 μ m, 10 mm \times 3 mm) maintained at a constant temperature of 40 °C. The LC mobile system consisted of a gradient of water with 0.3% formic acid (eluent A), methanol (eluent B) and acetonitrile (eluent C, kept at 1% during the whole run), with a constant flow rate of 1.0 mL/min. Prior to injection, the column was equilibrated with 81% A. After injection of sample, this proportion was decreased to 79% A in 1 min, 56% in 18 min and 14% in 23 min and kept constant until the end of the 30 min run. Between injections, 10 min intervals were used to re-equilibrate the column with 81% A. Phenolic compounds were monitored by DAD between 190 and 370 nm and identified by comparison of their retention times and UV spectra with those of commercial standards. Quantification was performed by external standardization. Data were acquired by LCMS solution software (Shimadzu Corp., version 2.00, 2000). Results were expressed as μ g of compound per 100 g.

Antioxidant capacity

The antioxidant capacity of melanoidins solutions in water (1–2 mg/mL) was determined by Ferric Reducing Antioxidant Power (FRAP) and Trolox Equivalent Antioxidant Capacity (TEAC) assays, as described by Alves and Perrone (2015), using calibration curves prepared with FeSO₄ and Trolox, respectively. Results were expressed as μ mol of equivalents per g. Each sample was analyzed in triplicate.

Consumption databases

To estimate the daily dietary intake of melanoidins, we obtained consumption data from: (1) analysis of personal food consumption in Brazil 2008–2009 (Brazilian

Household Budget Survey—POF_{con}, IBGE 2011); (2) per capita household food acquisition in Brazil 2008–2009 (POF_{acq}, IBGE 2011); (3) associations of food industry sectors. In this latter case, data were obtained from the Brazilian Manufacturers Association of Biscuits, Pasta and Industrialized Breads & Cakes (ABIMAPI), Brazilian Manufacturers Association of Chocolate, Cocoa, Peanuts, Candies and Derivatives (ABICAB), Brazilian Coffee Industry Association (ABIC) and National Union of Beer Industry (SINDICERV). Then, to estimate the contribution of melanoidins to the dietary intake of phenolic compounds and to the dietary antioxidant capacity in the Brazilian diet, we used data regarding the dietary intake of phenolic compounds (Corrêa et al. 2015; Miranda et al. 2016) and the dietary antioxidant capacity (Koehnlein et al. 2014).

Statistical analysis

Data were expressed as mean \pm standard deviation. Analysis of variance (two-way ANOVA) followed by Tukey's multiple comparison test was used for investigating the differences between samples and brands regarding melanoidins contents, incorporated phenolic compounds contents and antioxidant capacity of melanoidins. Statistical analyses were performed using GraphPad Prism software for Windows (version 6.01, GraphPad Software, San Diego, CA). Differences were considered significant when $p < 0.05$. Pearson's correlation coefficients between incorporated phenolic compounds and antioxidant capacity were calculated using Statistica software (version 7.0, StatSoft Inc., Tulsa, OK).

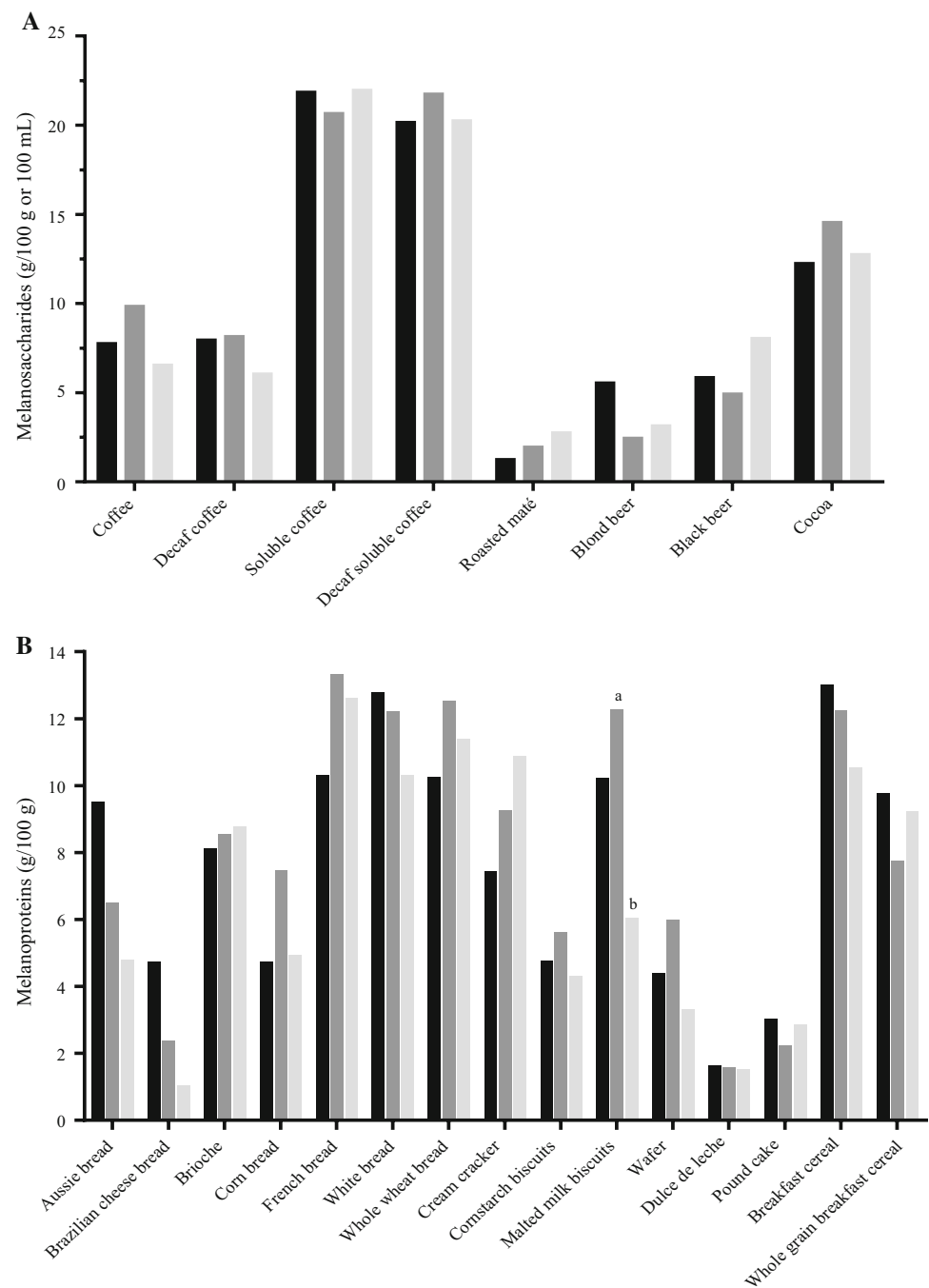
Results and discussion

Melanoidins contents in foods

Melanoidins contents ranged from 1.6 ± 0.1 g/100 g (dulce de leche) to 21.4 ± 0.7 g/100 g (soluble coffee), with an average content of 8.5 g/100 g (Fig. 1). The brand had no significant effect on melanoidins contents (two-way ANOVA, $p > 0.1$), while the food itself had a significant effect ($p < 0.0001$). In general, the contents of melanosaccharides (10.3 g/100 g, on average) (Fig. 1a) were higher than that of melanoproteins (7.7 g/100 g, on average) (Fig. 1b), probably due to the very high content of melanosaccharides in both soluble and decaffeinated soluble coffees.

In coffee, melanosaccharides are mainly formed during the roasting of the green bean, but other processes that involve heating, such as bean drying and decaffeination, may also contribute to their formation. The contents of melanosaccharides in soluble coffees (21.0 ± 0.8 g/100 g)

Fig. 1 Melanoidins content in selected heat-processed foods samples regularly consumed in the Brazilian diet, divided into two groups, according to their solubility: melanosaccharides (g/100 mL) (a) and melanoproteins (g/100 g) (b). Bars represent brands #1 (black square), #2 (dark gray square) and #3 (light gray square). Different letters indicate significant difference between brands at the same sample (two-way ANOVA followed by Tukey's multiple comparison test, $p < 0.05$)



was 2.7-fold higher in comparison to ground coffees (7.7 ± 1.3 g/100 g) (Fig. 1a), as observed in other studies (Fogliano and Morales 2011; Vignoli et al. 2011). This result might be explained by differences in the production process of these types of coffee. Although both processes entail roasting and grinding, the extraction process for the production of soluble coffee occurs at temperatures of up to 175 °C and under pressure, resulting in a higher efficiency in terms of solubilization of coffee solids than percolation (Vignoli et al. 2011), which is used to prepare home

brewed coffee. Moreover, soluble and ground coffees are usually produced with blends of different proportions of *Coffea canephora* and *C. arabica* beans; the proportion of *C. canephora* beans, which have a higher content of soluble solids (and possibly melanosaccharides), is higher in soluble coffee than in ground coffee.

Similarly to coffee, roasted maté melanosaccharides are formed mainly due to roasting of green mate leaves, but other processes such as blanching and drying of green leaves may also form these macromolecules. In this study,

the content of melanosaccharides in roasted maté was 1.9 ± 0.8 g/100 g (Fig. 1a). To the best of our knowledge, there is no data available in the literature regarding melanoidins contents in roasted mate.

Beer melanosaccharides derive mainly from malted cereals, although they may also be formed during mashing and wort boiling (Rivero et al. 2005). The contents of melanosaccharides in black beer (4.2 ± 0.6 g/100 mL) were twice that of blond beer (2.0 ± 1.3 g/100 mL) (Fig. 1a), probably because malt roasting is an additional step in which melanosaccharides are formed. Our results were lower than data reported by Pastoriza and Rufián-Henares (2014) (8.7 and 15.0 g/100 mL in Pilsen and black beers, respectively), which employed ultrafiltration with 5 kDa cut-off to isolate melanoidins, a process similar to that used in this study. On the other hand, our results were much higher than those reported by Rivero et al. (2005) (0.06 and 0.15 g/100 mL in blond and dark beers, respectively) and Zhao et al. (2013) (from 0.16 to 1.48 g/100 mL in lager beers), probably due to the isolation procedures employed by these authors, namely gel permeation and dialysis, which are known to afford lower yields, but of higher purity.

During chocolate production, melanosaccharides are formed due to roasting of cocoa beans, contributing to the mild aroma and intense brown color of cocoa (Taş and Gökmen 2016). In this study, the content of melanosaccharides in cocoa was 13.1 ± 1.2 g/100 g (Fig. 1a), in accordance with Quiroz-Reyes and Fogliano (2018), which reported contents from 6.2 g/100 g to 17.2 g/100 in cocoas from different varieties and roasting degrees.

In some bakery products, such as bread and cake, melanoproteins are found mostly in their crust baking, probably because dough surface reaches higher temperatures during baking and loses water more rapidly, providing optimum conditions for the formation of these macromolecules (Thorvaldsson and Skjöldebrand 1998). On the other hand, in products such as biscuits, breakfast cereals and dulce de leche, melanoproteins are homogeneously found throughout the product, due to a more homogeneous distribution of heat and water.

Melanoproteins contents in breads ranged from 2.7 ± 1.9 g/100 g (Brazilian cheese bread) to 12.1 ± 1.6 g/100 g (French bread) (Fig. 1b). In breads produced exclusively with wheat flour (white bread roll, white bread, whole wheat bread and brioche), melanoproteins contents (10.9 g/100 g, on average) were lower than data from other studies performed in Europe (Fogliano and Morales 2011) (14 and 18 g/100 g in baguette and sliced bread, respectively). European breads usually have a harder and thicker crust than Brazilian breads, which may explain this difference. The contents of melanoidins in Brazilian breads produced exclusively with wheat flour were twice

that of breads that contained other types of flour, such as corn (corn bread), tapioca (Brazilian cheese bread) and rye (Aussie bread) (5.1 g/100 g, on average). This difference may possibly be explained by higher protein content of wheat flour in comparison to corn, tapioca and rye flours (USDA 2018). To the best of our knowledge, this is the first study that investigated various types of breads, including those produced not exclusively with wheat flour.

Among biscuits, melanoproteins contents ranged from 4.6 ± 1.4 g/100 g (wafer) to 9.2 ± 1.7 g/100 g (cream cracker) (Fig. 1b), lower than data reported by Fogliano and Morales (2011) (12.0 g/100 g) and Pastoriza and Rufián-Henares (2014) (20.0 g/100 g). Similarly, to that observed for breads, melanoproteins contents in cornstarch biscuits (4.9 ± 0.7 g/100 g) were lower than that of cream cracker biscuits, probably due to the lower protein content in the former.

Breakfast cereals showed high contents of melanoproteins (10.4 g/100 g, on average) in this study, although even higher contents were reported by Pastoriza and Rufián-Henares (2014) (25.5 g/100 g). On the other hand, pound cake (2.7 ± 0.4 g/100 g) and dulce de leche (1.6 ± 0.1 g/100 g) showed the lowest contents of melanoproteins (Fig. 1b), possibly because both samples have a higher water activity than the other samples containing melanoproteins. It is well known that browning reaches maximum rates at intermediate water activities (0.5–0.8) and then decreases at higher water activities due to reactants dilution, as well as equilibrium shift towards the reactants in the dehydration steps of the Maillard reaction (Echavarría et al. 2012).

Bound phenolic compounds in melanoidins

Nine phenolic compounds were identified in melanosaccharides from different samples (Table 1), whereas only four of them were bound to melanoproteins (Table 2). All samples, except Brazilian cheese and Aussie breads, pound cake and dulce de leche, showed phenolic compounds bound to melanoidins structures. On average, melanosaccharides showed 24-fold higher bound phenolic compounds contents (1447.4 μ g/100 mg) in comparison to melanoproteins (59.0 μ g/100 mg). This huge difference is mainly due to the very high contents of bound phenolic compounds in coffee and maté, but also because flours are the only phenolic-containing ingredient in the formulation of bakery products. In general, caffeic acid was the major phenolic compound incorporated in melanosaccharides (1310.5 μ g/100 mg, on average), whereas in melanoproteins ferulic acid was the most abundant (48.6 μ g/100 mg, on average), representing 90% and 82% of total bound phenolic compounds, respectively.

Table 1 Contents ($\mu\text{g}/100\text{ mg}$) of phenolic compounds bound to melanosaccharides structures of Brazilian heat-processed foods¹

Sample #brand ²	5-CQA ³	3,4-Dihydroxy-phenylacetic acid	4-Hydroxy-phenylacetic acid	Caffeic acid	Ferulic acid	Gallic acid	<i>p</i> -Coumaric acid	Quercetin	Rutin	Total
Cocoa #1	nd ⁴	12.1 ^a	nd	nd	nd	106.5 ^a	nd	nd	nd	118.6 ^a
Cocoa #2	nd	9.3 ^b	nd	nd	nd	82.8 ^b	nd	nd	nd	92.2 ^a
Cocoa #3	nd	15.5 ^c	nd	nd	nd	116.4 ^c	nd	nd	nd	131.9 ^a
Coffee #1	nd	nd	nd	879.8 ^a	188.7 ^a	nd	15.9 ^a	nd	nd	1084.3 ^a
Coffee #2	nd	nd	nd	990.8 ^b	290.4 ^b	nd	17.3 ^a	nd	nd	1397.3 ^b
Coffee #3	nd	nd	98.8	580.7 ^c	84.3 ^c	nd	17.4 ^a	nd	nd	682.3 ^c
Decaf coffee #1	nd	nd	66.5	1159.5 ^a	331.7 ^a	nd	24.0 ^a	nd	nd	1581.7 ^a
Decaf coffee #2	nd	nd	nd	695.0 ^b	94.7 ^b	nd	14.4 ^a	nd	nd	804.1 ^b
Decaf coffee #3	nd	nd	nd	1008.6 ^a	184.5 ^c	nd	15.9 ^a	nd	nd	1209.0 ^c
Soluble coffee #1	nd	nd	7.4 ^a	1217.2 ^a	323.1 ^a	nd	15.2 ^a	nd	nd	1562.8 ^a
Soluble coffee #2	nd	nd	9.9 ^b	1234.7 ^b	314.5 ^b	nd	15.9 ^a	nd	nd	1575.0 ^a
Soluble coffee #3	nd	nd	10.0 ^c	656.0 ^c	209.5 ^c	nd	10.6 ^a	nd	nd	886.1 ^b
Decaf soluble coffee #1	nd	nd	nd	1412.1 ^a	464.5 ^a	nd	26.1 ^a	nd	nd	1902.6 ^a
Decaf soluble coffee #2	nd	nd	nd	837.5 ^b	238.7 ^b	nd	12.6 ^b	nd	nd	1088.8 ^b
Decaf soluble coffee #3	nd	nd	nd	598.5 ^c	178.3 ^c	nd	9.9 ^b	nd	nd	786.7 ^c
Black beer #1	nd	nd	nd	nd	77.6 ^a	nd	nd	nd	nd	77.6 ^a
Black beer #2	nd	nd	nd	9.5 ^a	128.7 ^b	nd	nd	nd	nd	138.3 ^b
Black beer #3	nd	nd	nd	11.0 ^b	151.6 ^c	nd	nd	nd	nd	162.6 ^b
Blond beer #1	nd	nd	nd	5.8 ^a	60.8 ^a	nd	nd	nd	nd	66.6 ^{ab}
Blond beer #2	nd	nd	nd	4.8 ^a	40.6 ^b	nd	nd	nd	nd	45.4 ^a
Blond beer #3	nd	nd	nd	7.7 ^a	90.2 ^c	nd	nd	nd	nd	97.8 ^b
Roasted maté #1	22.6 ^a	422.9 ^a	nd	5496.2 ^a	218.8 ^a	279.0 ^a	152.0 ^a	161.0 ^a	982.9 ^a	7735.6 ^a
Roasted maté #2	50.7 ^b	121.5 ^b	nd	5069.9 ^b	261.3 ^b	39.2 ^b	88.1 ^b	113.2 ^b	676.8 ^b	6420.7 ^b
Roasted maté #3	nd	78.0 ^c	nd	4334.4 ^c	365.2 ^c	31.4 ^c	19.2 ^c	41.0 ^c	219.7 ^c	5088.9 ^c

¹Results expressed as mean of two replicates; analysis CV lower than 10% for all samples. In column, different superscript letters within the same sample indicate significant difference among brands (ANOVA followed by Tukey's multiple comparison post hoc test, $p < 0.05$)

²Each brand was obtained by pooling three different production lots

³5-Caffeoylquinic acid

⁴Not detected

In melanosaccharides (Table 1), caffeic and ferulic acids were identified in all samples, except for cocoa. In coffee samples, caffeic acid was the most abundant bound phenolic compound, representing 77% of total, followed by ferulic acid (20%). The contents of bound phenolic compounds in coffee melanosaccharides (1213.4 $\mu\text{g}/100\text{ mg}$, on average) were higher than those reported by Perrone et al. (2012) (from 67.6 to 370.3 $\mu\text{g}/100\text{ mg}$), which employed dialysis to isolate coffee melanoidins. In contrast, much higher contents of bound phenolic compounds were reported by Moreira et al. (2017) when alkaline fusion of melanoidins was employed (up to 8700 $\mu\text{g}/100\text{ mg}$). The same authors reported the release of lower contents of phenolic compounds from melanoidins upon saponification (up to 580 $\mu\text{g}/100\text{ mg}$), the same procedure employed in this work, which is in line with our data. Among coffee samples, brand generally influenced the contents of bound

phenolic compounds ($p < 0.05$), with differences of up to 142% (brands #1 and #3 of decaffeinated soluble coffee). This result may be probably related to differences in degrees of roasting and blends, which consequently influence chlorogenic acids contents in beans (Perrone et al. 2012). On average, soluble coffee presented 15% higher contents of bound phenolic compounds than ground coffee, 1300.3 and 1126.5 $\mu\text{g}/100\text{ mg}$, respectively ($p < 0.05$) (Table 1). This difference may be due to the higher proportion of *C. canephora* beans, richer in chlorogenic acids (Perrone et al. 2012), in soluble coffee in comparison to ground coffee.

The hydroxycinnamic acid derivatives observed in coffee melanosaccharides originate from the hydrolysis of covalently-linked chlorogenic acids, which have already been described in coffee melanoidins (Perrone et al. 2012). According to Moreira et al. (2017), coffee roasting

Table 2 Content of phenolic compounds bound to melanoproteins structures of Brazilian food ($\mu\text{g}/100\text{ mg}$)

Sample #brand ¹	Ferulic acid	Gallic acid	Naringerin	Rosmarinic acid	Total
Brioche #1	13.2 ^a	45.5 ^a	nd	nd	58.7 ^a
Brioche #2	12.5 ^a	36.6 ^b	nd	nd	49.0 ^a
Brioche #3	12.1 ^a	42.7 ^{ab}	nd	nd	54.8 ^a
Corn bread #1	26.9 ^a	nd	nd	nd	26.9 ^a
Corn bread #2	10.9 ^b	nd	nd	nd	10.9 ^a
Corn bread #3	48.0 ^c	nd	nd	nd	48.0 ^a
French bread #1	14.6 ^a	nd	nd	nd	14.6 ^a
French bread #2	9.4 ^a	nd	nd	nd	9.4 ^a
French bread #3	6.3 ^a	nd	nd	nd	6.3 ^a
White bread #1	25.9 ^a	nd	nd	nd	25.9 ^a
White bread #2	38.5 ^b	nd	nd	nd	38.5 ^a
White bread #3	60.1 ^c	nd	nd	nd	60.1 ^b
Whole wheat bread #1	110.5 ^a	nd	nd	nd	110.5 ^a
Whole wheat bread #2	113.6 ^{ab}	nd	nd	nd	113.6 ^a
Whole wheat bread #3	120.5 ^b	nd	nd	nd	120.5 ^a
Cream cracker #1	9.6 ^a	11.6	nd	nd	21.2 ^a
Cream cracker #2	26.5 ^b	nd	nd	14.7 ^a	41.1 ^a
Cream cracker #3	15.3 ^a	nd	nd	7.0 ^b	22.3 ^a
Cornstarch biscuits #1	74.4 ^a	20.7 ^a	nd	nd	95.1 ^a
Cornstarch biscuits #2	39.5 ^b	nd ²	19.6	nd	59.1 ^{ab}
Cornstarch biscuits #3	6.6 ^c	28.9 ^b	nd	nd	35.5 ^b
Malted milk biscuits #1	7.8 ^a	20.2 ^a	nd	nd	28.0 ^a
Malted milk biscuits #2	46.1 ^b	nd	nd	nd	46.1 ^a
Malted milk biscuits #3	9.8 ^a	12.6 ^b	nd	nd	22.4 ^a
Wafer #1	7.2 ^a	nd	nd	nd	7.2 ^a
Wafer #2	16.3 ^b	nd	nd	nd	16.3 ^a
Wafer #3	17.6 ^b	nd	15.6	nd	33.2 ^a
Breakfast cereal #1	19.7 ^a	nd	nd	nd	19.7 ^a
Breakfast cereal #2	30.6 ^b	nd	nd	nd	30.6 ^a
Breakfast cereal #3	34.1 ^b	nd	nd	nd	34.1 ^a
Whole grain breakfast cereal #1	253.2 ^a	14.9	nd	18.6	286.7 ^a
Whole grain breakfast cereal #2	278.0 ^b	nd	33.4	nd	311.5 ^a
Whole grain breakfast cereal #3	89.7 ^c	nd	nd	nd	89.7 ^b

¹Results expressed as mean of two replicates; analysis CV lower than 10% for all samples. In column, different superscript letters within the same sample indicate significant difference among brands (ANOVA followed by Tukey's multiple comparison post hoc test, $p < 0.05$)

²Each brand was obtained by pooling three different production lots

³Not detected

promotes depolymerization and debranching of polysaccharides and the formation of new polymers through non-enzymatic transglycosylation reactions, which can also occur between carbohydrates and aglycones of phenolic compounds, leading to their incorporation.

Among all samples, roasted maté showed the highest content of bound phenolic compounds (6415.1 $\mu\text{g}/100\text{ mg}$, on average), as well as the highest variety of compounds (quercetin, rutin and 5-caffeoylquinic, 3,4-dihydroxyphenylacetic, caffeic, ferulic, gallic and *p*-coumaric acids) (Table 1). With the exception of 3,4-

dihydroxyphenylacetic acid, the occurrence of these phenolic compounds in maté melanosaccharides may be explained by their presence (rutin, quercetin and gallic acid) (Heck and De Mejia 2007; Murakami et al. 2011) or of their precursors (caffeoyl, feruloyl and *p*-coumaroylquinic acids) (Marques and Farah 2009) in *Ilex paraguariensis*. Caffeic acid was the most abundant bound phenolic compound (77%) in maté melanosaccharides, followed by rutin (10%). Similarly to coffee, brand influenced the contents of bound phenolic compounds in maté ($p < 0.05$), with differences of up to 52% (brands #1 and

#3), which may occur due to variations in different steps of maté production, especially harvesting, drying, cutting and roasting of leaves, which may affect phenolic compounds profile.

In beer melanosaccharides, ferulic and caffeic acids were the only bound phenolic compounds (Table 1). To the best of our knowledge, this is the first study to report the contents of phenolic compounds in beer melanosaccharides. These hydroxycinnamic acid derivatives have already been described in beers and originate from malted barley, which contributes with at least 70% of beer phenolic compounds (Gerhäuser and Becker 2009). Quercetin, a hop-derived phenolic compound, was not observed in beer melanosaccharides, and other compounds that originate from this ingredient, such as catechins, proanthocyanidins and flavonones (Gerhäuser and Becker 2009), were not investigated in this study. On average, total bound phenolic compounds content was 80% higher in black beer (126.2 µg/100 mg) in comparison to blond beer (69.9 µg/100 mg), possibly because black beer production includes an additional heating step (malt roasting), which may increase the incorporation of phenolic compounds in melanosaccharides. Once again, brand influenced the contents of bound phenolic compounds in beer melanosaccharides, with differences of up to 115% (brands #1 and #3 of black beer), which may be explained by variations in formulation and/or brewing process among the analyzed brands.

Cocoa melanosaccharides showed a low content of bound phenolic compounds (114.2 µg/100 mg, on average), from which 89% was gallic acid and the remainder was 3,4-dihydroxyphenylacetic acid (Table 1). Very recently, Oracz et al. (2018) reported the release of 14 phenolic compounds upon alkaline hydrolysis of cocoa melanosaccharides, with contents ranging from 251 to 579 µg/100 mg, comprised of up to 75% of catechins, a class of compounds not investigated in our study.

In melanoproteins, ferulic acid was identified in all samples (Table 2). Samples containing whole cereals showed a 5.1-fold higher bound phenolic compounds content (172.1 µg/100 mg, on average) than those produced with refined cereals (33.9 µg/100 mg, on average) ($p < 0.0001$). This result may be explained by the localization of phenolic compounds in cereals, preferably in the bran, which is removed upon milling to produce refined flours (Abozed et al. 2014). In particular, whole grain breakfast cereal samples showed the highest amounts of bound phenolic compounds (229.3 µg/100 mg, on average) among all melanoproteins samples (Table 2), probably because these products contain brans as their main ingredients. Analogously, whole wheat bread samples showed the second highest bound phenolic compounds contents (114.9 µg/100 mg, on average), as they are produced

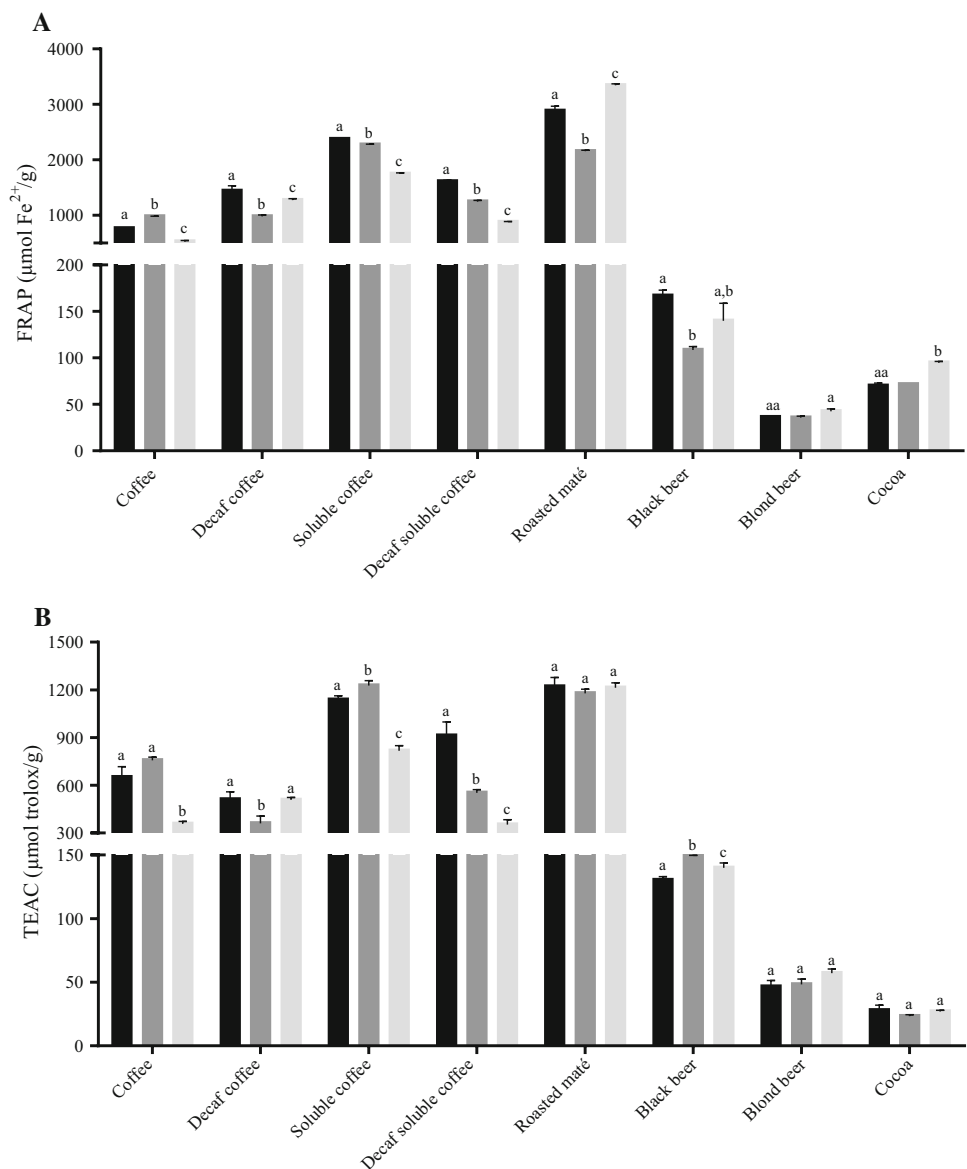
mainly with whole wheat flour and contain lower contents of other phenolic-rich ingredients (i.e. wheat fiber, wheat gluten, wheat bran, oat bran and soy flour).

Among biscuits, samples containing malted ingredients (malted milk and cornstarch biscuits) had a tendency ($p = 0.071$) to show a 2.0-fold higher bound phenolic compounds content (47.7 µg/100 mg, on average) than those non-malted (cream cracker and wafer biscuits) (23.6 µg/100 mg, on average) (Table 2). During malting of cereals, the availability of phenolic compounds to undergo the Maillard reaction may increase. This could be explained by the action of endogenous enzymes synthesized during the germination process, which would release insoluble phenolic compounds from the cellular matrix (Maillard et al. 1996), or through de novo synthesis. Moreover, the heating step of the malting process may also change plant cell wall structures, as well as increase the incorporation of phenolic compounds into high molecular weight molecules.

Antioxidant capacity of melanoidins

One of the most important characteristics assigned to melanoidins is their antioxidant property. FRAP values ranged from 38.2 µmol Fe²⁺/g (blond beer) to 2793.6 µmol Fe²⁺/g (roasted maté), with an average of 424.4 µmol Fe²⁺/g. TEAC values ranged from 25.6 µmol Trolox/g (Brazilian cheese bread) to 1204.2 µmol Trolox/g (roasted maté), with an average of 218.6 µmol Trolox/g. Independently of the assay, melanosaccharides (Fig. 2) showed higher antioxidant capacity in comparison to melanoproteins (Fig. 3), with differences of up to 11.8-fold when FRAP assay was employed. This result is explained by the higher content of bound phenolic compounds in melanosaccharides in comparison to melanoproteins, as previously discussed. In fact, both FRAP and TEAC values showed strong positive correlations with bound phenolic compounds contents ($r = 0.8769$ and $r = 0.8522$, respectively; $p < 0.0001$). The role of bound phenolic compounds to the antioxidant capacity of melanoidins have already been described by many authors (Alves and Perrone 2015; Delgado-Andrade et al. 2005; Rufián-Henares and Morales 2007). Nevertheless, non-phenolic compounds present in melanoidins structure, such as pyrrolinone reductones (Lindenmeier et al. 2002), may also contribute to their antioxidant capacity. These other non-phenolic compounds are probably those responsible for the antioxidant capacity of melanoidins isolated from Aussie and Brazilian cheese breads, dulce de leche and pound cake, since no bound phenolic compounds were observed in their melanoidins. In fact, these samples were among those with the lowest FRAP and TEAC values, corroborating this hypothesis.

Fig. 2 Antioxidant capacity measured by FRAP (a) and TEAC (b) assays of melanossacharides of Brazilian heat-processed foods. Bars represent mean \pm standard deviation ($n = 3$) of brands #1 (black square), #2 (dark gray square) and #3 (light gray square). Different letters indicate significant difference between brands at the same sample (two-way ANOVA followed by Tukey's multiple comparison test, $p < 0.05$)

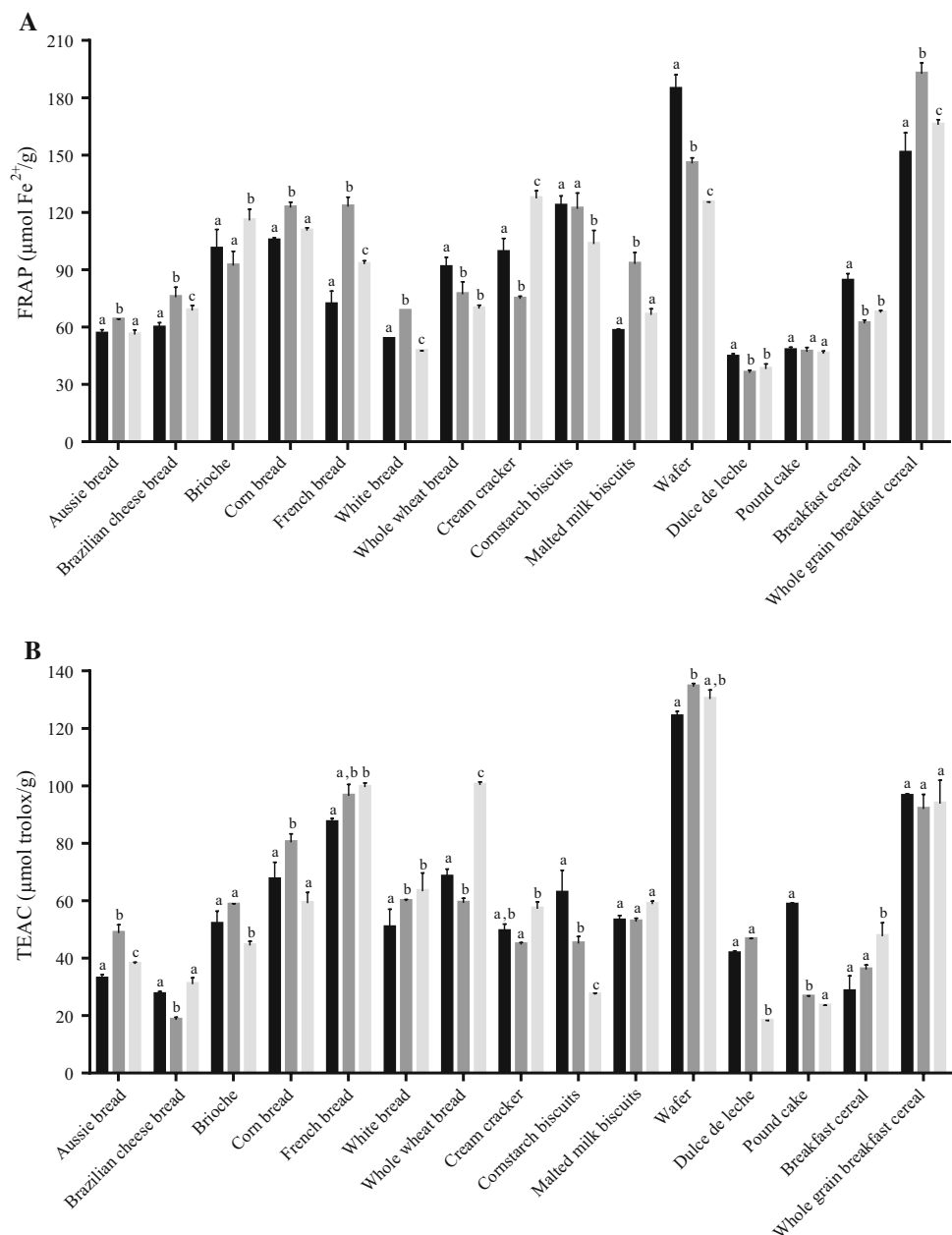


In general, the antioxidant capacity measured by FRAP and TEAC assays showed a strong positive correlation ($r = 0.9693$, $p < 0.0001$). This correlation was much stronger for melanosaccharides ($r = 0.9527$, $p < 0.0001$) than for melanoproteins ($r = 0.3994$, $p = 0.007$). Moreover, the correlation between antioxidant activity and bound phenolic compounds was consistently stronger for melanosaccharides ($r > 0.7976$, $p < 0.0001$) than melanoproteins ($r = 0.5311$, $p < 0.0001$). In fact, no correlation was observed between TEAC values and bound phenolic compounds in melanoproteins. Together, these results suggest that even though both assays are suitable for measuring the antioxidant capacity of food melanoidins, FRAP assay seems to be more appropriate to assess the contribution of bound phenolic compounds to the antioxidant capacity of melanoidins.

Contribution of melanoidins from heat-processed foods to the dietary intake of phenolic compounds and to the dietary antioxidant capacity

Consumption data of heat-processed foods in Brazil were obtained from three different databases. From the Brazilian Household Budget Survey 2008–2009 (POF), published by the Brazilian Institute of Geography and Statistics (IBGE 2011), we considered both the food consumption (POF_{con}) and the food acquisition (POF_{acq}) databases. We also obtained coffee, beer, chocolate and bakery products consumption data from industries' associations. Considering these data and the contents of melanoidins determined in this study, we estimated the minimum (3.6 g/day) and maximum (10.7 g/day) dietary daily intake of melanoidins in the Brazilian population (Table 3). The dietary intake of

Fig. 3 Antioxidant capacity measured by FRAP (a) and TEAC (b) assays of melanoproteins of Brazilian heat-processed foods. Bars represent mean \pm standard deviation ($n = 3$) of brands #1 (black square), #2 (dark gray square) and #3 (light gray square). Different letters indicate significant difference between brands at the same sample (two-way ANOVA followed by Tukey's multiple comparison test, $p < 0.05$)



melanoidins may be associated with health benefits, since studies show that these macromolecules have several biological activities, such as antimicrobial against food pathogenic bacteria (Rufián-Henares and De La Cueva 2009), prebiotic (Borrelli and Fogliano 2005) and anticarcinogenic (Stauder et al. 2010). The estimated maximum value is very similar to that published by Fogliano and Morales (2011) (10 g/day) in Western diets and lower than that reported by Pastoriza and Rufián-Henares (2014) (12.2 g/day) in the Spanish diet. In that study, the major contributors to melanoidins dietary intake in Spain were cereal products (64%), beer (27%) and coffee (7%). In Brazil, on the other hand, data from our study shows that

the contribution of beer is more prominent (44%), followed by cereal products (36%) and coffee (17%). This difference may be attributed to the high level of beer consumption reported by the Brazilian National Union of Beer Industry (128.8 mL/day), as well as to the lower contents of melanoproteins in Brazilian cereal products in comparison to those in Spain, as previously discussed.

Combining the daily intake of melanoidins with the contents of melanoidin-bound phenolics (Tables 1, 2), we estimated the Brazilian daily intake of phenolic compounds from melanoidins of heat-processed foods (Table 3), which ranged from 9.4 to 26.0 mg/day. To the best of our knowledge, this is the first study that estimated the dietary

Table 3 Minimum and maximum melanoidins intake and their consequent phenolic compounds intake and dietary antioxidant capacity in the Brazilian population

Food	Consumption (g or mL/day)			Melanoidins intake (mg/day)	Phenolics intake from melanoidins (mg/day)	Dietary antioxidant capacity from melanoidins	
	POF _{con} ¹	POF _{acq} ²	Industry ³			FRAP (μmol Fe ²⁺ /day)	TEAC (μmol Trolox/day)
Coffee	21.51	6.6	13.4	528.6–1,722.2	5.6–18.2	400.0–1,306.0	310.6–1,014.0
Soluble coffee	–	0.4	–	85.7	1.2	182.7	91.0
Roasted maté ⁴	2.7	1.3	–	25.7–36.5	1.6–2.3	102.1	44.0
Blond Beer	31.1	15.4	128.8	563.6–4,713.7	0.4–3.3	21.5–180.1	28.6–238.9
Cocoa ⁵	1.1	1.1	1.7	139.3–224.6	0.2–0.3	11.0–17.7	3.6–5.9
Sweet biscuits ⁶	8.6	6.4	6.0	382.0–543.6	0.1–0.2	43.4–61.7	29.3–41.6
Salty biscuits ⁶	6.8	5.5	2.6	234.1–624.9	0.1–0.2	23.5–62.8	10.2–27.4
French bread	53.0	34.3	–	1430.7–2,208.8	0.1–0.2	137.2–211.8	135.1–208.6
Corn bread	–	0.3	–	3.1	< 0.001	0.4	0.2
Brazilian cheese bread	–	0.5	–	4.0	ND ⁷	0.3	0.1
Brioche	–	2.4	–	48.3	< 0.1	5.0	2.5
White bread	–	2.3	5.9	60.6–152.5	0.0–0.1	3.4–8.6	3.5–8.8
Whole wheat bread	0.9	0.5	–	14.1–24.3	< 0.1	1.1–1.9	1.1–1.8
Pound cake	13.9	2.4	0.4	3.3–104.5	ND	0.2–4.9	0.1–3.8
Dulce de leche	–	0.4	–	6.8	ND	0.3	0.2
Breakfast cereal	0.8	1.7	–	95.4–200.3	0.0–0.1	6.8–14.3	3.6–7.5
Total				3624.3–10,703.8	9.4–26.0	836.7–2,160.4	619.7–1,696.4

¹Analysis of personal food consumption in Brazil 2008–2009 (Brazilian Household Budget Survey—POF_{con}, IBGE)

²Per capita household food acquisition in Brazil 2008–2009 (POF_{acq}, IBGE)

³Data obtained from the Brazilian Coffee Industry Association (ABIC), the National Union of Beer Industry (SINDICERV), the Brazilian Manufacturers Association of Chocolate, Cocoa, Peanuts, Candies and Derivatives (ABICAB) and the Brazilian Manufacturers Association of Biscuits, Pasta and Industrialized Breads & Cakes (ABIMAPI)

⁴For POF_{con} and POF_{acq}, “tea” and “maté tea” ingestion data were considered, respectively

⁵Ingestion data were estimated considering that chocolate (available in POF_{con} and ABICAB), chocolate powder (available in POF_{con}) and cocoa powder (available in POF_{acq}) had 25%, 25% and 50% of cocoa, respectively

⁶Ingestion data were estimated considering all types of sweet and salty biscuits available in each database

⁷Not detected

intake of phenolic compounds from melanoidins. Beverages accounted for up to 96% of melanoidin-bound phenolics intake, being coffee the major contributor (75%), followed by beer (13%). The relevance of coffee to this estimative is related to its high consumption combined with its high melanoidins and melanoidin-bound phenolics contents. In spite of its very high consumption and high melanoidins contents, beer's relevance is much lower since its melanoidins showed low contents of bound phenolics.

To put these data in perspective, we calculated the contribution of melanoidin-bound phenolic compounds to the dietary intake of phenolic compounds. Data from different studies were considered and they varied in terms of the assessment methodology for phenolic compounds contents in foods (open databases, i.e. USDA and Phenol-Explorer, versus HPLC analysis performed as part of the

same study), as well as in terms of the population studied (different European countries and Brazil) (Corrêa et al. 2015; Miranda et al. 2016; Navarro González et al. 2017; Witkowska et al. 2015). Considering the highest daily intake of phenolic compounds (1365.1 mg/day), which was reported for the Spanish population (Navarro González et al. 2017), the contribution of melanoidin-bound phenolic compounds would range from 0.7 to 1.9%, which is not very meaningful. On the other hand, if we consider the lowest daily intake of phenolic compounds (377.5 mg/day), reported for the population of São Paulo (Miranda et al. 2016), the largest Brazilian city, their relevance is much higher, ranging from 2.5 to 6.9%. This difference reflects the diet profile of these populations and therefore of the different food groups responsible for phenolic compounds intake. While beverages (including

coffee), legumes, fruits and cereals contributed almost equally (20–26%) to the dietary phenolic compounds intake in the Spanish population, coffee alone accounted for 70% in São Paulo, Brazil. If we exclude coffee phenolic compounds from this dietary intake, the relevance of melanoidin-bound phenolic compounds would be even higher, of up to 24%. Despite their estimated relevance, one should remember that in order to exert their many biological activities, these phenolic compounds would have to be released from melanoidins prior to their absorption.

Combining the daily intake of melanoidins with their antioxidant capacity (Figs. 2, 3), we estimated the Brazilian dietary antioxidant capacity from melanoidins of heat-processed foods (Table 3), which ranged from 0.84 to 2.16 mmol Fe²⁺/day and 0.62 to 1.70 mmol Trolox/day, when FRAP and TEAC assays were used, respectively. Coffee and bread were the major contributors to the dietary antioxidant capacity in the Brazilian population. Pastoriza and Rufián-Henares (2014) reported a dietary antioxidant capacity from melanoidins of 0.72 mmol Trolox/day for the Spanish population, which agrees with our results. On the other hand, they found that coffee, but not bread, significantly contributed to this value.

Once again, these data were compared to estimated values of dietary antioxidant capacity from different countries (Dilis and Trichopoulou 2010; Koehnlein et al. 2014; Saura-Calixto and Goñi 2006). If we consider the highest dietary antioxidant capacity values (10.30 mmol Fe²⁺/day and 9.38 mmol Trolox/day), which was reported for the Brazilian population (Koehnlein et al. 2014), the contribution of melanoidins would range from 7 to 21%. Considering the lowest dietary antioxidant capacity values (4.36 mmol Fe²⁺/day and 3.55 mmol Trolox/day), reported for the Greek (Dilis and Trichopoulou 2010) and Spanish populations (Saura-Calixto and Goñi 2006), respectively, their relevance reached from 14 to 50%. These values agree with the 20.2% estimated contribution of melanoidins to the Spanish dietary antioxidant capacity (Pastoriza and Rufián-Henares 2014) and highlight the relevance of these macromolecules to the many potential biological effects associated with antioxidant capacity.

Conclusion

In this study, we investigated various heat-processed foods consumed as part of the Brazilian diet. Their melanoidins contents were determined, as well as the contents of bound phenolic compounds and the antioxidant capacity of these macromolecules. We estimated that up to 10.7 g of melanoidins are consumed daily by this population, being beer the major contributor, followed by cereal products and coffee. Brazilians ingest up to 26.0 mg/day of phenolic

compounds bound in melanoidins, mainly from beverages, such as coffee and beer. Therefore, the estimated intake of phenolic compounds by the Brazilian population is underestimated by up to 7%. Moreover, melanoidins contribute to up to 21% of the Brazilian dietary antioxidant capacity. The findings of this study highlight the need to take melanoidins into account when considering the biological activities and potential health benefits associated with phenolic compounds.

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