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Chapter

Valorization of Native Nuts from Brazil and Their Coproducts

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Abstract

The consumption of nuts as part of a healthy diet and active lifestyle has long been associated with chronic disease prevention. Nuts and their coproducts such as oil, cake, plant-based milk substitutes, flour, and shell are rich in lipids, proteins, phenolics, and other bioactive compounds. Nut flour also presents interesting physical properties, such as water or oil holding capacity, foam properties, emulsifying activity, and emulsion stability. These biological and physical properties make these products commercially attractive as organic ingredients in several foods such as spreads, bakery products, and cereal bars. In this chapter, the nutritional and bioactive profiles, as well as the evidenced health-promoting effects of nuts originating from Brazil, will be discussed. The focus will be on commercial nuts such as cashews, pecan, and Brazil nuts, along with some underexplored and relatively unknown indigenous species, such as sapucaia, chichá, monguba, and pracaxi. The knowledge of these Brazilian native nuts and their coproducts is important for stimulating their consumption among the population and their large-scale commercialization.

Keywords: oilseeds, biodiversity, bioactive compounds, lipids

1. Introduction

The consumption of nuts as part of a healthy diet and active lifestyle has long been associated with chronic disease prevention such as cardiovascular diseases, type 2 diabetes, cognitive function impairment, inflammatory disorders, among others. A closer look into the composition of nuts may help understand their healthpromoting effects. They are rich in unsaturated acids such as oleic and linoleic, and have low concentrations of saturated fatty acids. In addition, the oil fraction presents significant amounts of tocopherols and phytosterols. The cake and shell, coproducts obtained from nuts, are rich in polyphenols. Besides the lipids and bioactive substances, nuts and their coproducts are also rich in other macronutrients (protein and fiber) and micronutrients (vitamins and minerals). The composition and concentration of bioactive compounds vary according to the type of nut and its coproducts [1].

Brazil has a great diversity of nut trees distributed in five of its six biomes Amazon, Cerrado, Atlantic Forest, Caatinga, Pampas, and Pantanal. **Figure 1** presents the Brazilian biomes where the nuts discussed in this chapter are found.

Brazil nuts and cashew are commercial nuts native to Brazil. The cashew tree (*Anacardium occidentale* L.), which is well adapted in tropical and subtropical regions, is present in Cerrado, a biome known for long periods of drought. The nut,



Figure 1. Distribution of different nut trees in Brazilian biomes.

which is obtained from the cashew fruit, is composed of shell, skin, and almond. The largest producer of cashew nuts in 2018 was Vietnam (863,060 tons), followed by India (745,000 tons), Côte d'Ivoire (711,000 tons), Philippines (222,541 tons) and Brazil (141,418 tons) [2]. The Brazilian state of Ceará led the production with 61.9% of the planted area of cashew trees, followed by Rio Grande do Norte (15.4%), and Piauí (15.2%) [2].

Brazil nut tree (*Bertholletia excelsa*) is present in the Amazon, where it grows in well-drained soil along the Amazon River without the use of pesticides and herbicides. Brazil is the largest producer of Brazil nuts in the world (36,923 tons), followed by Bolivia, Ivory Coast, and Peru (25,749; 19,356; and 6042 tons, respectively) [2].

On the other hand, the pecan nut (*Carya illinoinensis*) is native to northern Mexico and southern United States. It was introduced in Brazil in 1866, and it is cultivated in the biomes Atlantic Forest, and mainly in the Pampas in the southeast and south regions. The tree is large-sized and can grow up to 20-40 m, and its fruit is technically classified as a drupe, characterized by a single pit surrounded by husk [3, 4].

These commercial or named conventional nuts in Brazil are usually consumed in a variety of ways such as raw, roasted and salted, caramelized, and coated. In addition, they can be incorporated into other food products, such as cereal bars, chocolates, bakery goods and spreads, among other foods. They can also be used for the extraction of specialty oils and for obtaining plant-based milk [1, 5–7].

However, the availability of nuts in Brazil is not limited to cashew, pecan, and Brazil nuts. A large variety of nut trees is available, especially in the Amazon region. These relatively unknown indigenous nuts represent a vast potential for the introduction into the diet of Brazilians and other consumers around the world. Sapucaia, chichá, monguba, and pracaxi are some of the nuts, which are not commercialized on a large scale and are usually consumed in their natural form by the local population. Therefore, data on their production is not found in the literature. A few

reports showed that such nuts are also rich in macro and micronutrients, including phenolic compounds [8–10].

Sapucaia (*Lecythis Pisonis*) grows in the Atlantic Forest biome [9], while monguba (*Prachira aquatica*) and pracaxi (*Pentaclethra macroloba* (Wild.) Kuntze) can be found in the Amazon. The monguba tree is cultivated in different regions of the Amazon biome as an ornamental plant. Its fruits are oval-shaped, surrounded by a brown wooden peel where large-sized seeds are contained. The seeds are edible and can be consumed in a variety of ways, such as roasted, boiled, or fried [10]. The pracaxi tree produces a pod-shaped fruit containing edible seeds, from which phenolic-rich oils can be obtained [11]. Chichá (*Sterculia striata*), a nut tree originated from India and Malaysia, has thrived in the semi-arid conditions of the Cerrado, yielding nuts rich in phenolic compounds and lower lipid content [8].

This chapter presents the nutritional composition, phytochemical properties, and bioactive compounds of commercial (cashew, Brazil nuts, and pecan) and non-commercial (sapucaia, chichá, monguba, and pracaxi) nuts found in Brazil. The health benefits associated with their consumption, as well as novel products based on these nuts and their coproducts will be discussed with emphasis on their functional properties and nutritional profile.

2. Nutritional composition of native Brazilian nuts

Table 1 shows the macronutrient composition of conventional and nonconventional nuts native to Brazil. Brazil nuts present the highest lipid content and energy value. On the other hand, cashew nuts have higher protein content followed by chichá, which has the highest content of carbohydrates and the lower content of lipids. The sapucaia nut presents the highest fiber content among all nuts showed in **Table 1**.

Table 2 shows that the conventional and non-conventional nuts are rich in lipids considered beneficial to health, such as monounsaturated fatty acids (MUFAS) and polyunsaturated fatty acids (PUFAS). Pecan nut presents the highest content of the MUFA oleic acid (C18:1, ω 9) followed by the cashew and pracaxi. Besides the nutritional benefits, another advantage of oleic acid is related to its higher oxidative stability compared to PUFAS. On the other hand, Brazil nuts show a high PUFA

Component (g/100 g)	Co	onventional		Non-conventional				
	Brazil nuts [12, 13]	Cashew [14]	Pecan [15]	Chichá [8, 16]	Monguba [10, 17]	Pracaxi [11]	Sapucaia [18, 19]	
Ashes	3.3	2.8-4.1	1.8	3.0-3.2	2.3-2.7	1.9	2.9-3.5	
Moisture	3.1-3.2	2.7-8.4	3.3	8.2-11.4	5.3-8.3	4.0	4.1-4.2	
Protein	14.4-16.2	19.7-24.5	8.6	18.5-22.5	13.3-15.4	15.5	15.5-20.5	
Lipids	64.9-67.3	39.8-47.1	62.2	24.5-28.6	41.9-45.6	53.4	58.7-60.8	
Total fiber	7.5-8.0	2.5-4.2	10.9	4.6-5.8	4.7-6.1		16.5	
Carbohydrate	10.9-15.9	27.1-34.9	13.4	40.5-45.8	34.3-36.2	25.2	4.9-13.8	
Energy value (kcal/100 g)	659-715	499-707	633.9	456-530	557-677	644	616-665	
-: not presented.								

Table 1.

Composition of macronutrients of conventional and non-conventional nuts native from Brazil.

Fatty acids (%)	Cor		Non-conventional				
_	Brazil nuts [12, 13, 20]	Cashew [21, 22]	Pecan [4, 15]	Chichá [8]	Monguba [10]	Pracaxi [11, 23]	Sapucaia [18]
Miristic (C14:0)	0-0.1		_	_			0.1
Palmitic (C16:0)	14.9-16.7	10.3	5.4	26.5	60.9	1.4-1.5	12.9-15.2
Palmitoleic (C16:1 cis 9)	0-0.4	0.3	—	2.4	_	_	0.2-0.3
Margaric (C17:0)	_	0.1		-	_	_	0-0.1
Stearic (C18:0)	9.9-11.9	9.8	1.4	4.0	1.8	2.5-2.7	7.7-8.4
Oleic (C18:1 cis 9)	28.5-36.3	60.6	71.8	37.8	7.7	53.2-53.5	39.7-44.4
Linoleic (C18:2 cis 9,12)	36-37.5	17.0	20.2	11.2	6.6	12.1-12.2	32.2-40.0
Linolenic (C18:3cis 9,12,15)	0.1-0.2	0.2	0.8	0.3	_	0.1	0.3-0.4
Arachidic (C20:0)	0-0.2	0.7	_	0.7	_	_	_
Gondoic (C20:1 cis 11)	0-0.1	0.2	_	_	_	_	0.1
Behenic (C22:0)	_	0.1	_	0.3	_	16.4-16.5	_
Lignoceric (C24:0)	_	_	_	_	_	11.1-11.6	_
\sum Saturated	24.9-28.9	21.3	7.0	31.5	62.7	33.3-33.6	21.5-23.3
\sum Monounsaturated	28.5-36.8	61.1	71.8	40.4	14.2	54.1-54.3	40.1-45.7
∑Polyunsaturated	36.1-37.7	17.2	21.0	12.2		12.2-12.3	32.7-40.4
Tocopherol (µg/g)							
α-Tocopherol	72.5	78.4	1.7	16.6	ND	ND	11.2
β-Tocopherol	_	1329.8		1.1	ND	ND	ND
γ-Tocopherol	74.4	300.3	26.8	88.5	5.1	416.1	285.0
δ-Tocopherol	5.9	6.3		21.0	ND	7.8	2.8
Total	152.8	1714.8	28.7	127.0	5.1	423.9	299.0
Phytosterols (mg/100 g)					\ \		
Brassicasterol	1.5	101.4	76	ND			ND
β-Sitosterol	39.5	7.8		184.9	Л (-) ,		93.7
Campesterol	4.0			18.6			8.6
Stigmasterol	11.3	_	_	54.2		_	11.2
Sitostanol	39.5	8.6	_			_	
δ5-Avenasterol + δ7-stigmasterol	6.7	_	_	_	_	_	_
Total	47-148	117.8	0.2-0.3	257.7	_		113.5

Table 2.

Lipid composition of conventional and non-conventional nuts.

linoleic acid (C18:2, ω 6) content (36-37%), which is an essential fatty acid. It also presents a balanced fatty acid composition containing significant concentrations of MUFAs and saturated fatty acids (SFAs). The main fatty acids present in Brazil nuts

is oleic (C18:1, ω 9), linoleic (C18:2, ω 6), and palmitic (C16:0) acids. In addition, most of the nuts have a low concentration of saturated fatty acids. The exception is monguba, carrying 63% saturated fatty acid, with palmitic acid being the main fatty acid.

Between the nuts shown in **Table 2**, cashew has the highest tocopherol content (1714.80 μ g/g) followed by the pracaxi nuts (423 μ g/g). The main tocopherols identified in the cashew nut were β -tocopherol > γ -tocopherol > α -tocopherol > δ -tocopherol. The chichá nut presents the highest content of phytosterols (257.7 mg/100 g), followed by the cashew nut (117 mg/100 g). β -sitosterol and brassicasterol were the main phytosterols found in these nuts. The bioactive composition of Brazilian nuts is presented in item 3 of this chapter.

Table 3 shows that Brazil and sapucaia nuts are a source of selenium. Considering the level of Se detected in Brazil (36.1 μ g/g), and sapucaia (46.9 μ g/g) nuts, a daily intake of more than one or two nuts can exceed the recommended daily dose of selenium for adults (55 μ g/day) [18]. A selenium intake higher than 400 μ g/ day has been associated with toxic effects, including selenosis, which symptoms are hair loss, skin damage, and nervous system disorders [12]. Sapucaia nuts are also rich in magnesium (1572 μ g/g) and calcium (1168 μ g/g). Chichá is rich in potassium (8718 μ g/g) and presents the highest concentration of zinc (24.2 μ g/100 g). On the other hand, cashew is rich in potassium (K) and pecan in phosphorus (P).

Minerals play fundamental roles in several functions in the human body, acting as cofactors in enzymatic processes, structural elements, and participating in the regulation of acid-base balance, nerve impulse, and muscle activity [24]. The consumption of nuts as part of a balanced diet can contribute to a proper consumption of minerals, which play an important role in maintaining good health.

Mineral (µg/g) —	Conventional			Non-conventional				
	Brazil nuts [25]	Cashew [26]	Pecan [27]	Chichá [8, 16]	Monguba [10, 17]	Pracaxi [28]	Sapucaia [18, 19]	
Al	_	_	_	6.2	_	_	1.7	
Ca	7432.8 ± 10.2	35.8 ± 0.7	70.0	149.1	558.9	8.9 ± 0.2	1168.0	
Cd	_	_	_	0.4	_	_	0.3	
Cr	1.3 ± 0.2			0.4	_		0.5	
Cu	59.4 ± 0.5	9.5 ± 0.2	_	7.5	7.5	_	16.9	
Fe	74.3 ± 0.5	26.1 ± 0.5	2.5	218.2	4.4	1.7 ± 0.1		
К	$\Box \Box \Box \Box \Box$	1443.3 ± 26.2	4.1	8718.0		$\Lambda \Box $	7 –	
Mg	9678.5 ± 68.5	612.7 ± 13.2	121.0	1327.0	875.3	5.6 ± 0.2	1572.0	
Mn	3.4 ± 0.4	7.6 ± 0.2	4.5	32.1	2.0	_	41.4	
Na	_	148.5 ± 2.6	_		11.4		0.5	
Ni	_	0.6 ± 0.5	_	0.4	_	_	_	
Р	_	_	277.0	_	_	18.1		
Pb	_	_	_	0.5	_	_	0.5	
Se	36.1 ± 0.4	0.2 ± 0.7	_	_	_	_	46.9	
Sn	_		_	16.6	_	_	11.1	
Zn	110.3 ± 1.3	28.9 ± 1.2	4.5	24.2	9.9	_	20.9	
-: not presen	ted.							

Table 3.Mineral composition of conventional and non-conventional nuts.

On the other hand, an excessive consumption of Brazil and sapucaia nuts is not recommended due to the high levels of selenium.

3. Bioactive composition of Brazilian nuts

Tocopherols and tocotrienols are a group of eight compounds widely spread in nature. They are monophenols chemically characterized by a chromanol ring, in which a hydroxyl group is attached. The configuration of the side hydrocarbon chain determines whether the compound is either tocopherol or tocotrienol (saturated side chain or three double bonds, respectively). Both tocopherols and tocotrienols have four homologs each (α , β , γ , and δ), which are defined by the methylation pattern on the chromanol ring. These compounds can act as antioxidants by the donation of a hydrogen atom from the hydroxyl group to free radicals, stabilizing them and reducing oxidative stress. α -Tocopherol presents the highest *in vivo* antioxidant capacity and 100% of vitamin E activity. The activity of α -tocopherol is related to the transfer protein (α -TTP) in the liver, involved in the absorption of tocopherols [29].

Nuts, seeds, and vegetable oils are good sources for tocopherols, and α -tocopherol is the most abundant one in photosynthetic tissues. On the other hand, seeds accumulate about 10–20 times more γ -tocopherol. Tocopherols can be found in considerable amounts in Brazil nuts, where they are concentrated in the oil fraction due to their lipophilic character, as reported by Costa et al. [20]. The authors reported a total tocopherol content of 152.80 µg/g for Brazil nuts, composed of α -tocopherol (72.55 µg/g), γ -tocopherol (74.35 µg/g), and δ -tocopherol (5.90 µg/g). This profile may change according to the region where the nuts are grown. Funasaki et al. [30] reported the tocopherol composition of Brazil nuts from seven different Amazon rainforest areas. α -Tocopherol content ranged from 37.92 µg/g (Manicoré 2-AM) to 74.48 µg/g (Manicoré 1-AM) and γ -tocopherol levels varied between 106.88 µg/g (Manicoré 2-AM) and 171.80 µg/g (Xapuri – AC). The differences in the tocopherol content can be related to climate variations and post-harvest handling.

As natural antioxidants, tocopherols play a role in the protection of nuts against oxidation. Zajdenwerg et al. [31] showed a correlation between the decrease in tocopherol concentration and the appearance of secondary oxidation products in Brazil nuts after a period of storage of 16 days at 80°C γ -tocopherol was depleted by 50%, and α -tocopherol was completely consumed, while aldehydes started to build up from hydroperoxide breakdown. The authors suggested that α -tocopherol acted as a primary antioxidant, which would explain why this homolog was depleted first. α -Tocopherol is less polar than γ -tocopherol due to the presence of three methyl groups on its chromanol ring, which gives it higher antioxidant efficiency in nonpolar systems [31].

Cashew nuts, on the other hand, present a lower concentration of tocopherols when compared with Brazil nuts. Ryan et al. [32] reported α -tocopherol and γ -tocopherol contents of 3.6 mg/g and 57.2 mg/g, respectively, for cashew oil. Meanwhile, Brazil nut oil was composed of 82.9 mg/g of α -tocopherol and 116.2 mg/g of γ -tocopherol. However, according to the same study, cashew oil is richer in other bioactive compounds than Brazil nut oil, namely some types of phytosterols, such as β -sitosterol (1768 mg/g against 1325 mg/g from Brazil nut) and campesterol (105.3 mg/g against 26.9 mg/g for Brazil nut). Nevertheless, stigmasterol is more concentrated in Brazil nuts oil (577.5 mg/g) than cashew oil (116.7 mg/g). The consumption of phytosterols has been associated with a decrease in LDL-cholesterol levels. The reason behind this bioactivity relies on the higher hydrophobicity of phytosterols compared with cholesterol, which would give them

an advantage in being transported by micelles and later exerted once humans do not absorb them. This would prevent cholesterol from accumulating in the enterocytes and further reaching the bloodstream [32]. Pecan nut is rich in γ -tocopherol, with 23.8-38.1 mg/100 g [4].

The bioactive composition of cashew, Brazil and pecan nuts goes beyond the presence of tocopherols and phytosterols in their oil fraction. Both are also rich sources of polyphenols, an extensive class of secondary plant metabolites with antioxidant properties. Polyphenols primarily act by donating a hydrogen atom to free radicals in order to interrupt oxidation reaction chains. As a minor antioxidant mechanism, phenolics also can chelate transition metals, preventing these prooxidant agents from initiating the reaction chain that originates from the oxidative process. Based on structural differences, this large group can be further divided into subgroups, with the main ones being flavonoids, hydroxycinnamic and hydroxybenzoic acids, hydrolysable tannins, and proanthocyanidins. In nuts, phenolics can be present as free soluble compounds, esterified to fatty acids (soluble esters), or insoluble-bound to macromolecules (e.g., cellulose, structural protein, pectin) [1].

John et al. [1] reported the phenolic composition and antioxidant activity of Brazil nut. Soluble phenolics (free plus esterified) were found to be the predominant state present in the whole nut (519.11 mg/100 g), as well as the kernel (406.83 mg/100 g) and the brown skin (1236.07 mg/100 g). However, a significant amount (352.48 mg/100 g) of insoluble-bound phenolics were detected in the brown skin of Brazil nuts. Gallocatechin, protocatechuic acid, catechin, and vanillic acid were the main phenolics identified in the bound fraction. Insoluble-bound polyphenols are related to beneficial effects on gut health, once they are associated with a decrease in the colonic pH, preventing the growth of harmful microorganisms [33]. The study of John et al. [1] also demonstrated that the brown skin extract of Brazil nuts showed the highest *in vitro* antioxidant activity, measured by DPPH, hydroxyl radical scavenging activity, reducing power and ORAC assay. The brown skin showed the highest amount of soluble and insoluble-bound polyphenols and this coproduct of Brazil nuts can be considered an economical source of natural antioxidants.

Yang et al. [34] compared the phenolic content and antiproliferative activities of Brazil nuts and cashew. Cashew showed a higher concentration of both soluble (86.7 mg/100 g) and insoluble-bound (229.7 mg/100 g) phenolics when compared to Brazil nuts (46.2 mg/100 g of soluble and 123.1 mg/100 g of insoluble-bound). Brazil nuts did not display antiproliferative activity against HepG2 (human liver cancer cells) at the doses tested in the study (from 1 to 200 mg/mL). On the other hand, cashew displayed the effect at high doses (100-200 mg/mL). In addition, neither of them showed inhibition for human colon cancer cells (Caco-2) proliferation.

The roasting, which is a common process in nut preparation, has shown evidence to impact the phenolic composition of cashew and Brazil nuts in different ways. Özcan et al. [35] reported that the total phenolic content of Brazil nuts significantly decreased from 68.97 mg/100 (raw nut) to 66.47 mg/100 g when ovenroasted (130°C for 20 min). The microwave-roasted (720 W for 5 min) showed the highest impact on the phenolic compounds, decreasing from 68.97 mg/100 to 25.88 mg/100 g. The DPPH radical scavenging capacity of the phenolic extracts also declined from 81.77% in the raw nut to 40.66% in the oven-roasted nut and 34.60% in the microwave-roasted nut. On the other hand, Chandrasekara and Shahidi [21] demonstrated that oven-roasting cashew at 130°C for 33 min increased the total phenolic content (both soluble and insoluble-bound) of the whole nut, as well as the kernel and the testa. At the same time, the levels of proanthocyanidins decreased, except for soluble phenolic extract from the kernel. In particular, the concentrations of the flavonoids (+)-catechin, (-)-epicatechin, and epigallocatechin were

enhanced after the roasting process, which also positively affected the antioxidant capacity of such extracts. According to the authors, these findings could be owed to the release of phenolics because of temperature, making them readily soluble in the extraction solvent. Although relatively high, the temperature was applied for a short period, which prevented an extensive degradation of polyphenols.

Pecan nutshell, a coproduct, have demonstrated great potential due to its rich phenolic composition and high antioxidant capacity. According to Hilbig et al. [36], extracts from this coproduct obtained under optimum conditions yielded total phenolic contents of 426.15-581.9 mg GAE/g, resulting in antioxidant activities of 2574.32-2573 µmol TEAC/g and 1268.03-1287.08 µmol TEAC/g measured by ABTS and DPPH assays, respectively. The extracts showed a variety of 29 different phenolic compounds, with gallic acid as the predominant one.

Demoliner et al. [9, 18] investigated the nutritional and phytochemical composition of sapucaia nut. The oil extracted from the nuts presented a considerable amount of total tocopherols (21.8-29.9 mg/100 g), with γ -tocopherol identified as the primary homolog (19.2-28.5 mg/100 g). α - and δ -Tocopherols were also identified in smaller quantities. Mounting evidence has shown that γ -Tocopherol excels in scavenging reactive oxygen species, which play an essential role in the development of chronic diseases [37–39]. Sapucaia nut oil also showed a significant concentration of phytosterols, namely β -sitosterol (92.8-193.9 mg/100 g), stigmasterol (9.92-13.2 mg/100 g), and campesterol (8.42-9.63 mg/100 g) [9].

Demoliner et al. [9] extracted the phenolic compounds from sapucaia nut and shell and used LC-ESI-MS/MS to identify and quantify the individual polyphenols present. The nut extracts were composed of 14 compounds, mainly phenolic acids, and flavonoids, with myricetin, vanillic, ferulic, and ellagic acid showing the highest amounts. Interestingly, shell extracts demonstrated to carry a greater variety of phenolics, with 22 compounds identified, with high levels of phenolic acids (gallic, protocatechuic, vanillic, ferulic, and ellagic) and flavonoids (epigallocatechin, catechin, epicatechin, taxifolin, myricetin, and vanillin). Shell extracts were also superior to the nut extracts in terms of *in vitro* antioxidant activity, measured by DPPH, FRAP, and ABTS. These outcomes highlight the potential for using nuts coproducts as sources of natural antioxidants.

Similar to sapucaia, the coproducts of chichá, namely the pellicle (26.26 mg GAE/g) and the shell (21.42 mg GAE/g), have been reported to be richer in total phenolic compounds than the nut (16.85 mg GAE/g). The extracts presented a wide variety of phenolic acids, such as ellagic, ferulic, salicylic, protocatechuic, and rosmarinic acid [8].

It has been reported that monguba oil is source of γ -tocopherol (513.5 mg/kg). In addition, ten phenolic compounds have been identified, mainly phenolic acids and flavonoids. The majority of phenolics (74.58%) were in the esterified form, followed by the glycosylated (13.02%), free (8.22%), and insoluble bound (4.18%) forms. Caffeic acid Monguba was the main phenolic compound found in this raw material (57.5%) [10].

Teixeira et al. [11] reported total phenolic contents ranging from 31.92 to 54.05 mg GAE/kg for pracaxi oil extracted by supercritical CO₂ extraction. The highest phenolic content and in vitro antioxidant activity of the extracts was obtained using 200 bar at 40-60°C. The oils obtained under low pressure demonstrated high antioxidant capacity measure by the CUPRAC method, indicating a significant content of both hydrophilic (phenolics) and lipophilic (carotenoids and tocopherols) antioxidants. The presence of natural antioxidants may also have positively affected the stability oxidative index (OSI of 11.38 h at 110°C and 10.83 at 120°C), which suggests a prolonged shelf life for the oil [11].

4. Bioavailability and health-promoting benefits

The nutritional profile and bioactive compounds present in Brazilian nuts are certainly a positive characteristic of these raw materials. However, the presence of these nutrients and minor compounds do not guarantee their conversion into health-promoting benefits. They need to be efficiently released from the food matrix and be absorbed in sufficient amounts to be converted into biologically active metabolites for having and positive impact on human health. In addition, the potentially toxic compounds should be assessed to ensure its safety. That is especially true when considering expanding the commercialization of relatively unknown nuts, like the ones we have been presenting throughout this chapter.

Moreda-Piñeiro et al. [40] assessed the *in vitro* bioavailability of essential and toxic metals in several nuts and seeds, including Brazil nuts and cashew. Essential metals (Ba, Ca, Cd, Co, Cu, K, Li, Mg, Mn, Mo, P, Pb, Se, Sr., Tl, and Zn) consistently presented moderate bioavailability (dialyzability of 2.1-40.7%) among the samples. The exception was iron, which presented a low dialyzability (0.70-3.7%). On the other hand, toxic metals (Al, Ba, Cd, and Hg) demonstrated poor bioavailability (dialyzability ratios between 0.35-16.8%). The results suggest that the consumption of these nuts can be considered as safe and beneficial because of the high bioavailability of the essential metals. The authors also found a positive correlation between carbohydrate content and dialyzability ratio, meaning that the higher the carbohydrate concentration, the greater the bioavailability. On the other hand, nuts with high-fat content were found to present lower mineral bioavailability.

Nascimento et al. [41] reported the *in vitro* bioavailability of Cu and Fe in cashew nuts using simulated gastric and intestinal fluids as well as dialysis procedures. The results showed that 83% of Cu and 78% of Fe were recovered during the experiment, indicating a high level of bioavailability for these minerals in cashew nuts. These two minerals are essential for a variety of physiological and metabolic processes. Cu deficiency can lead to high blood pressure and infertility, while Fe deficiency can cause anemia.

Using an *in vitro* dialyzability approach, Herbello-Hermelo et al. [42] evaluated the bioavailability of the polyphenol fraction of selected nuts and seeds. Brazil nuts and cashew were among the samples with the highest recovery of phenolics in the digested extracts (81 and 89%, respectively). The authors also showed that polyphenol bioavailability was dependent on Cu content. This can be explained by the strong binding ability between Cu⁺ and phenolics, with the latter being reported to reduce Cu²⁺ to Cu⁺, even though the mechanism by which this happens is not entirely understood yet.

Brazil nuts are one of the main sources of Se in nature, which are constituents of selenoproteins (e.g., glutathione peroxidases – GSH-Px), enzymes that are part of the endogenous antioxidant defenses system. A high blood concentration of such enzymes is associated with a lower risk of cardiovascular diseases. Stockler-Pinto et al. [43] conducted a human trial on the supplementation of Brazil nuts to patients on hemodialysis, which produces a large amount of reactive oxygen species. The administration of one nut per day for three months increased the subjects' GSH-Px activity. Before the supplementation, 11% of the patients presented GSH-Px levels below the normal range. After the supplementation, all subjects showed results within the normal range.

Inflammation processes are essential biological responses when the organism needs to fight intrusive agents. However, inflammatory disorders are extremely damaging and can lead to conditions such as cancer, type 1 diabetes, and rheumatoid arthritis, among others [44]. Colpo et al. [45] monitored the activity of inflammation markers upon the intake of different portions of Brazil nuts (from 0 to 50 g) by healthy individuals. The trial revealed that the consumption of 20 or 50 g of Brazil nuts was responsible for a decrease in serum levels of inflammation markers (IL-1, IL-6, TNF- α , and INF- γ).

Nanoemulsions prepared from cashew nut shell liquid showed cytotoxicity against human breast cancer cell line MCF-7. The cells treated with the nanoemulsion presented reduced viability, primarily through apoptosis or necrosis [46]. Cashew nut has also demonstrated a positive impact on cholesterol levels and systolic blood pressure. In a trial conducted with 300 type 2 diabetic adult patients, the administration of 30 g of cashew nuts daily for 12 weeks could reduce the subjects' blood pressure while the concentration of plasma HDL cholesterol increased.

Müller et al. [47] reported a potential biological effect of pecan nutshell extracts *in vivo* and *in vitro* studies. The phenolic-rich extracts from pecan nutshell demonstrated protection against liver damage induced by ethanol in rats by increasing the levels of endogenous antioxidant defenses, such as glutathione (by 33%), super-oxide dismutase (by 47%) and catalase (by 47-73%). Hilbig et al. [48] showed that aqueous extracts from pecan nutshell were able to reduce the viability of MCF-7 breast cancer cells. The effect was attributed to the high abundance of phenolic compounds in the extract, such as gallic, ellagic, and chlorogenic acid, as well as catechin, epigallocatechin, among others.

5. Nut-based products

Nuts are usually consumed as a snack, in their natural form, as well as toasted, salted, or caramelized. The Brazil nuts, cashew and pecan and are used as ingredients in several industrialized food products such as bakery goods, sweets, chocolates and ice creams, among others. The underexplored nuts, such as chichá, monguba, pracaxi, and sapucaia, although not reaching the same level of commercialization, have shown to be potentially suitable for these types of application.

5.1 Nut oil

Nut oils are usually obtained by pressing, and since they are not refined, they are classified as extra virgin. The main steps involved in the processing of an extra virgin nut oil are harvesting, pre-drying, peeling, drying, oil extraction, and centrifugation. Because of the appreciable sensorial attributes and elevated price compared with other vegetable oils, the nut oils are considered gourmet oils. The price will differ according to the nut type, its availability, and the processing used.

Brazil nut, pecan and cashew nut oils are usually found in specialized stores of natural products, in pharmacies (for use as cosmetics) and are available for online purchase, where their price ranges from 8 US \$ to 17 US \$. The pracaxi oil can be found for commercialization, mainly as a cosmetic, due to its emollient properties. On the other hand, chichá, sapucaia and monguba oils have not been commercially produced yet. However, studies show that these oils are rich in monounsaturated fatty acids and possess high oxidative stability, thus showing great potential for commercialization [8, 18]. Monguba oil, which is rich in palmitic acid, has a great potential for food applications as a substitute for cocoa butter [10].

5.2 Cereal bars

Cereal bars are consumed mainly as a diet substitute for sugar-dense snacks, as well as an energy and protein source for athletes. In the formulation of cereal bars, it is important to take into account the cereal choice (oats, wheat, rice, barley, maize). In addition, the selection of the appropriate carbohydrate to maintain a balance between taste and shelf life, the nutrient profile, the dietary fiber, and the processing stability [49] are also important. Cereal bars made with nuts are widely accepted by consumers. Besides their nutritional and sensory quality, they remain stable during product storage. Currently, we can easily find cereal bars containing Brazil nuts and cashew as ingredients.

5.3 Nut flour

Nuts can be ground into flour for use in bakery goods. Cake, the residue left after nut oil extraction, can be used as raw material to produce defatted nut flour. This is considered a sustainable process since it adds value to a coproduct, reducing waste generation [50]. Nut flour is rich in dietary fiber, protein, vitamins, minerals, and bioactive compounds. The application of partially defatted nut flour has been reported to improved consumer acceptance of gluten-free bakery products [50]. The combination of rich nutritional composition with appreciable physical properties makes these flours suitable for bakery products, such as cookies, bread, cakes, sweets, among others.

Physical properties, such as water or oil retention capacity, foam properties, emulsifying activity, and emulsion stability, are very important for the incorporation of flour into bakery products. Sanchez et al. [51] reported that pistachio and cashew nut flours with thermal trapping in autoclave showed interesting emulsifying and water rectifying properties for application in bakery products. In another study, Teixeira et al. [19] reported functional properties of defatted sapucaia flour. The parameters of emulsion formation and stability indicated that it could be applied as an ingredient in emulsified products such as cakes, creams, sauces and sausages, among others.

5.4 Nut-based milk alternative

Plant-based milk alternatives are beverages obtained from crushing a specific feedstock homogenized in water. The resulting particle size distribution should be between 5 and 20 μ m to mimic cow's milk in appearance and consistency. Sethi et al. [5] reported that the vegetable-based milks can be divided in five categories according to the raw material used: cereals (oats, rice, corn, spelled), vegetables (soy, peanuts, lupines, cowpea), nuts (almonds, coconut, hazelnuts, pistachios, walnuts), oilseeds (sesame, flax, hemp, sunflower), and pseudo-cereals (quinoa, teff, amaranth).

The improved diagnosis of conditions related to cow's milk consumption, such as milk protein allergy and lactose intolerance, increased the demand for nondairy milk alternatives. Besides, vegans also prefer these beverages, and it is being considered a continuously growing niche [5]. Nuts, such as walnuts, chestnuts, and almonds, are used to produce plant-based milk alternatives, mainly due to their functionality and better sensory characteristics [5]. The allergenic potential and high cost are some of the limiting factors presented by the nut-based milks.

The addition of Brazil nuts extract in a soybean-based drink positively influenced the sensory characteristics of the product [52]. On the other hand, prebiotic drinks based on cashew nuts and fruit juice have proved to be a viable alternative for the development of functional products [53]. Bruno et al. [6] reported that cashew nut-based milk alternative was a good matrix for the development of probiotics. They showed that *Bifidobacterium animalis*, *Lactobacillus acidophilus* and *L. plantarum* remained viable during 30 days at 4°C. The probiotic drink based on

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cashew nuts also achieved a good sensory acceptance, without significant changes in whiteness and microbiological quality.

Plant-based milk of sapucaia nut cake using block freeze concentration, which was done in five consecutive stages, allowed the concentration of the phenolic compounds (gallic, vanillic, ferulic, sinapic and salicylic acids, catechin, taxifolin and sinapaldehyde) and minerals in all the five fractions [54]. Studies with different raw materials and formulations, especially non-conventional nuts, are still scarce. The knowledge about such products should contribute to encouraging their consumption.

6. Nuts shell and cake

Industrial nut processing results in a large amount of shells, a coproduct that can represent approximately 40-50% of the original total mass. The reuse of these coproducts, which are usually discarded, should be encouraged for reducing waste disposal, preserving the environment and adding value to the raw materials.

Some nutshells, such as pecan, are sold in pieces to make tea [4]. The ethnopharmacological use of nutshell tea includes the prevention and treatment of various diseases, such as type 2 diabetes, obesity, hypertension, hypercholesterolemia, cancer and, inflammatory diseases [24]. The therapeutic effects of the tea made with pecan nutshell have been associated with the presence of several phenolic compounds, such as phenolic acids, flavonoids, and proanthocyanidins. The antioxidant, antimicrobial, and antitumor activity of pecan peel extract have been reported [4, 50]. Other nutshells may have health benefits due to their bioactive composition.

Cashew nut is covered with a thin antioxidant-rich layer of reddish-brown color, known as testa. This fraction is an excellent source of hydrolysable tannins and polymeric proanthocyanidins. It comprises of phenolic acids like syringic acid, gallic acid, and *p*-coumaric acid as the major components. The concentration of catechin and epicatechin were found as 5.70 and 4.46 g/kg of dry matter, respectively [55].

The process of mechanical oil extraction generates a partially defatted byproduct known as cake. The agro-industrial use of the defatted nut cake has great nutritional value, based on its high lipid and protein contents and the functional aspect present in this material, adding value to food products. The nuts cake can be used in bakery (as presented in item 5.3), but also in sweets. In the study by Lima et al. [56], the cashew nut cake was used to replace peanuts in the production of a sweet known as *paçoca*, made by mixing ground peanuts with other ingredients, such as corn flour, sugar, honey, and oil. The product showed physicochemical and microbiological stability, as well as good sensory acceptance. In addition, the nut cake presents bioactive compounds. For instance, Maciel et al. [57] demonstrated that pecan nut cake is rich in phenolic compounds with antioxidant activity.

7. Future perspectives

Commercial and non-commercial Brazilian nuts are nutritionally rich in macronutrients and bioactive compounds, with considerable amounts of natural antioxidants. Such substances are related to a myriad of health benefits since they are able to reduce oxidative stress. A significant number of studies have investigated the bioavailability of these bioactive compounds of Brazil nuts and cashew with promising results. The effect of the nuts on health using human trials had positive outcomes.

However, relatively unknown Brazilian nuts, such as sapucaia, chichá, pracaxi, and monguba remain an underexplored topic. Information about their bioavailability aspects and their impact on human health is still necessary. Therefore, more studies should be done in order to stimulate large-scale commercialization.

Finally, nuts are incredibly versatile with great economic potential. The incorporation of the coproducts, which are rich in nutrients and bioactive compounds, is an opportunity to enrich food formulation with these cost-effective ingredients, diminishing the waste generated by nut processing.

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