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Bioactive compounds in pinhão and potential applications in dairy products: A review

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Abstract

The pinhão seed of *Araucaria angustifolia* is a rich source of bioactive compounds with potential for various applications in the food, pharmaceutical, and cosmetic industries. This study addresses a wide range of research on the pinhão, including its chemical composition, nutritional and functional properties, processing methods, and potential biological effects. Chemical analyses have revealed the presence of essential nutrients such as proteins, lipids, fibers, and bioactive compounds like flavonoids, galactomannans, and lignans, providing the pinhão with antioxidant, anti-inflammatory, and antinociceptive properties. Moreover, studies have shown the potential of pinhão as a source of edible oils and as an inhibitor of digestive enzymes, suggesting possible applications in diet and the treatment of metabolic disorders. Drying and extraction processes have been investigated to preserve its bioactive properties during industrial processing. The evaluation of the antimicrobial and anticancer activity of pinhão extracts has also been highlighted, revealing its potential as a therapeutic agent. In summary, this abstract synthesizes the importance of pinhão as a valuable source of bioactive compounds with potential benefits for human health and various industrial applications.

Keywords: bioactive compounds; pinhão; dairy products.

Practical Application: Pinhão flour, rich in fiber and protein, stands out for its gluten-free nature compared to wheat and corn flour. Its versatility extends to various food products, including *alfajores*, cakes, bread, and extruded foods. Utilizing the entire pinhão, including the husk, offers a sustainable solution, reducing environmental impact. With a 30% yield in processing and a shelf life of 120 days, pinhão flour ensures extended availability. By harnessing the seed's natural water activity and optimizing processing methods, we enhance its nutritional profile, offering a valuable ingredient for diverse food formulations.

1 INTRODUCTION

The pinhão, the seed of the *Araucaria angustifolia* tree, represents a valuable natural resource abundant in the southern regions of Brazil. This indigenous species has significantly influenced the local community's livelihoods, culture, and culinary traditions. However, beyond its cultural importance, recent scientific investigations have unveiled the immense potential of the pinhão as a source of bioactive compounds with diverse applications in various industries.

This introduction provides an overview of the extensive research on the pinhão, encompassing its chemical composition, nutritional attributes, functional properties, processing techniques, and potential biological effects. Detailed analyses have unveiled a rich nutritional profile, with the pinhão being a source of essential macronutrients such as proteins, lipids, and fibers, alongside an array of bioactive compounds, including flavonoids, galactomannans, and lignans.

These bioactive constituents endow the pinhão with remarkable antioxidant, anti-inflammatory, and antinociceptive properties, rendering it a promising candidate for various therapeutic and functional food applications. Moreover, investigations into the extraction of edible oils from the seed and its potential as a digestive enzyme inhibitor have shed light on its role in dietary interventions and metabolic disorder management.

Furthermore, efforts to optimize drying and extraction processes have aimed to preserve the bioactive integrity of the pinhão during industrial processing, ensuring maximal retention of its beneficial properties. Additionally, studies evaluating its antimicrobial and anticancer potential have underscored its significance as a source of novel therapeutic agents.

In summary, this introduction sets the stage for a comprehensive exploration of the multifaceted aspects of the pinhão, highlighting its relevance as a source of bioactive compounds with profound implications for human health and industrial innovation. Through a systematic review of existing literature, this article aims to elucidate the diverse applications and potential benefits of harnessing the bioactive potential of the pinhão.

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2 *ARAUCARIA ANGUSTIFOLIA*

Linked to the Araucariaceae family, the species *Araucaria angustifolia* was described by Bertoloni in 1820 as *Columbea angustifolia* Bert., later rewritten by Richard in 1922 as *A. brasiliana* Rich. and revised by Otto Kuntze as *A. angustifolia* (Bert.) Ktze (Soares & Mota, 2004). *A. angustifolia* is the only species of the genus naturally occurring in Brazil (Mattos, 2011) (Figure 1), commonly known by numerous names, such as pinheiro, pinheiro-araucária, pinheiro-do-Paraná, pinheiro-branco, pinheiro-brasileiro, pinheiro-nacional, pinheiro-das-missões, pinheiro-caiová, pinheiro-cajová, pinheiro-cajuvá, pinheiro-chorão, pinheiro-elegante, pinheiro-macaco, pinheiro-macho-fêmea, pinheiro-de-ponta-branca, pinheiro-preto, pinheiro-rajado, pinheiro-sãojosé, pinheiro-de-são-paulo, pinhão, pinho, pinho-brasileiro, pinho-do-Paraná, or simply, araucária (Carvalho, 1994; Lorenzi, 2000).

A. angustifolia is native to colder regions. It is located especially in the southern region of Brazil and is also found in high altitudes in the states of São Paulo, Minas Gerais, and Rio de Janeiro. The araucarias occur in the Mixed *Ombrophilous* Forest, which belongs to the Atlantic Forest biome (Wendling & Zanette, 2017).

Figure 1 illustrates an adult *A. angustifolia* with dense branching. Its original forest covered about 20 million hectares[2], with 40% of this total located in Paraná, 31% in Santa Catarina, 25% in Rio Grande do Sul, 3% in São Paulo, and 1% in Rio de Janeiro and in Minas Gerais (Guerra & Silveira, 2002). From the middle of the 19th century, araucaria wood began to be used in civil construction and furniture manufacturing. Its wood was widely used for about 100 years, reaching a peak in the 1970s. Due to the lack of replanting and the high rate of deforestation of the original forest, the exploitation of araucaria had to be drastically reduced, ending it if the economic cycle was the same (Wendling & Zanette, 2017).

However, predatory exploitation has introduced it to the endangered species list (Thomas, 2013) and under environmental protection (Danner et al., 2012). Therefore, it is of public importance to find sustainable alternatives to araucaria products to encourage the planting and preservation of the species (Helm et al., 2020).

Source: Embrapa Florestas (2018).
Figure 1. *Araucaria angustifolia* tree.

A. angustifolia belongs to the Kingdom: Plantae, Phylum: Gymnospermae, Class: Coniferopsida, Order: Coniferae, Family: Araucariaceae, Genus: *Araucaria*, Species: *angustifolia*; it is a tall perennial tree, reaching between 30 and 52 m in height, with a cylindrical trunk, almost always straight, simple, sometimes with small tillers (in numbers from 1 to 15), with a diameter between 1 and 2 m (Mattos, 2011).

According to Mattos (2011), the young plants of *A. angustifolia* have conical shapes, and their growth in height is proportionally faster than the growth of the branches; with the aging of the plant, the length of the branches in the pseudo-whorls decreases proportionally as the temperature increases. At this stage, the tree drastically reduces growth in height. Still, the branches continue to grow outward and upward so that the apical bud of the lower branches is at a higher level than the apical bud, configuring the crown as a cup (Mattos, 2011).

The leaves of *A. angustifolia* measure about 3–6 cm in length, are simple, with a very acute-pungent apex, and have a dark green color (Carvalho, 1994; Lorenzi, 2000). It is a dioecious plant; there are female and male trees with their respective inflorescences, sometimes monoecious due to trauma or disease, with unisexual flowers (Cunha et al., 2017).

Studies on the grafting and management of araucaria trees are led by the Brazilian Agricultural Research Corporation (EMBRAPA), making their production more viable. These studies aim to overcome the late flowering of araucaria, accelerating pinhão production in young trees. Grafting consists of grafting the bud of a mature araucária upon a young araucária, thus cloning high-quality matrices. Grafted araucaria begin to produce pinhão after 10 years, 2–5 years less than an araucaria that did not undergo the grafting process (Wendling & Zanette, 2017).

New specimens must be planted in suitable areas, and pinhão be valued as a non-timber forest product. Preserving araucarias positioned in dense forests does not guarantee the trees' safety. The araucarias must be planted at a distance of 10 m between one specimen and another, ensuring the best progress of the species. Planting from 100–120 trees per hectare is possible, manipulating the remaining soil with other annual crops, thus increasing product gains (Wendling & Zanette, 2017).

Few studies and research are identified as a reference to the people involved in the pinhão productive chain and the income generated by the seed harvest. However, it is known that the pinhão is a source of income and food for rural communities that live in areas with araucarias (Vieira da Silva et al., 2009).

Araucaria trees are rich in flavonoids, vitamins, and other bioactive compounds. Extracts of methanolic compounds of pinhão were presented as a source of minerals, phenolic compounds, and flavonoids, mainly rutin, catechin, and epicatechin. Additionally, studies emphasize that cooking the pinhão favors its bioactive compounds because they migrate from the husk to the seed when the latter is subjected to heat treatments (Cordenunsi et al., 2004).

Vegetable oils are a source of bioactive compounds, including polyunsaturated fatty acids, phytosterols, and tocopherols. These compounds have functional properties that reduce disease risks and promote health. Bioactive compounds have been widely applied in the pharmaceutical, food, and cosmetic industries, which shows the need for appropriate extraction methods to ensure product quality from raw vegetable materials (Ramos et al., 2022).

The flavonoids catechin, quercetin, epicatechin, apigenin, and rutin were identified as major compounds in extracts of araucaria bracts (Michelon et al., 2012; Souza et al., 2014).

3 PINHÃO

The term "pinhão" is given to the seeds of *A. angustifolia*, consisting of the following parts: bark or integument, which is brick red; almond, which is a yellowish white starchy mass; and the embryo, which is located at the center of the almond and normally has a white color (Mattos, 2011).

Pinhão is a regional product consumed in the southern states of Brazil. This food is the seed of the Paraná pine (*A. angustifolia* sin. *A. angustifolia*) and is normally eaten cooked or roasted. The pine grows naturally in southern Brazil and can also be found in Argentina and Paraguay. The annual harvest occurs at the beginning of winter, and as it is not completely consumed, it can be used for animal feed. Even so, there is a surplus of pinhão at the end of harvests (Daudt, 2013).

The araucaria seed (bark, endosperm, and embryo) averages 3–8 cm long and weighs approximately 8 g. The bark is the main by-product generated during its processing and consumption, comprising about 20% of its total weight. Because it is not commonly consumed, it is considered a residue normally discarded in the environment. Several studies have already evidenced the presence of bioactive compounds in this fraction, pointing to it as an important source of natural antioxidants for human health. They evaluated the profile of phenolic compounds in pinhão bark. They detected the presence of important flavonoids and flavones, especially quercetin, apigenin, and flavonols, mainly catechin and epicatechin (Ramos et al., 2022).

Pinhão is extracted by collecting mature pine cones that have fallen to the ground or cutting down pine cones from trees. In the first mode, the amount of pine cones collected per tree is usually small, so collectors must cover a large area to collect sufficient quantities. When practicing the collection, returning to the same trees several times during harvest is necessary, making the practice very laborious. Cutting down the pine cones from the trees is the most common method for pinhão extraction. Bamboo poles are usually used to help with the felling of the pine cones, or the workers climb the araucarias or nearby trees to reach the pine cones. It is a highly dangerous job, as this process is usually done without protective equipment (Santos et al., 2002).

Pinhão producers usually sell their harvest directly to markets and fairs, which work from intermediaries to the final consumer or directly to the final consumer, often to travelers who pass through the highways close to the pinhão harvest municipality. The pinhão marketing chain is characterized by a very low degree of post-harvest processing, with almost no point in adding value to the final product (Vieira da Silva et al., 2009). Frequently, the consumer buys the seed naturally or is already prepared in free fairs and specialized retail outlets. The seasonality of the product also restricts its sales mainly between March and June, reinforced by its low degree of industrialization (Santos et al., 2002).

According to the Brazilian Institute of Geography and Statistics (IBGE, 2022), in 2021, pinhão production in Brazil was 12,484 tons, with emphasis on Paraná and Santa Catarina (Table 1).

The particular composition of each pinhão kernel may result from variations in the developmental stage, temperature, and irrigation techniques or reflect genetic characteristics. The accumulation of nutrients occurs during seed dehydration in the final control phase, usually from April to May, when the protein content increases (Astarita et al., 2003). According to research carried out by EMBRAPA Florestas (2018), the amount of water in cooked pinhão reaches 55%, and carbohydrate is the second main component, with approximately 34% while cooked. Pinhão is also a good source of total fiber, at 5.5% on average. The approximate contents of proteins (3%) and lipids (1.4%) are low compared to other foods rich in starch, as shown in Table 2. The minerals are phosphorus, magnesium, calcium, zinc, iron, and copper.

3.1 The pinhão shell

The shell of cooked or raw pinhão is usually discarded in the environment. Approximately 10 tons of pinhão shells are estimated to be discarded periodically (Brasil et al., 2006). Since this shell takes a long time to break down and has a significant portion of pinhão, several people have been researching possible uses.

Table 1. Pinhão production in Brazil and the main producing states.

Federal units	2019	2020	2021
	Pinhão (t)	Pinhão (t)	Pinhão (t)
Brazil	9,374	10,605	12,485
Minas Gerais	2,139	3,546	3,464
São Paulo	5	5	5
Paraná	3,290	3,671	4,018
Santa Catarina	3,120	2,537	3,916
Rio Grande do Sul	819	846	1,081

Source: Adapted from IBGE (2022).

Table 2. Almond composition of raw pinhão and cooked pinhão.

Composition	Content	
	Raw pinhão	Cooked pinhão
Moisture (g/100 g)	46.90	55.21
Minerals (g/100 g)	2.06	0.94
Proteins (g/100 g)	3.85	3.62
Fibers (g/100 g)	4.78	5.53
Lipids (g/100 g)	1.53	1.46
Carbohydrates (g/100 g)	40.88	33.24
Total caloric value (kcal/100 g)	192.69	160.58

Source: Embrapa Florestas (2018).

Too many authors have studied pinhão as an alternative to promote the adsorption of potentially carcinogenic metallic ions and dyes from aqueous solutions in treating industrial effluents. The intense brown color of the pinhão shell is due to the presence of tannins that are mainly responsible for the adsorption of metallic ions, such as copper, for example (Lima et al., 2007).

In addition to this environmental protection alternative, it is important to mention the content of phenolic compounds in the pinhão shell. The phenolic compounds extracted from the raw and cooked bark were 77.56 and 31.63 mg of catechin equivalents/g dry weight, respectively (Koehnlein et al., 2012). Analyses of amylase inhibition resulted in delayed carbohydrate digestion and glucose absorption, attenuating hyperglycemic excursions. The observation that tannin-rich pinhão extract is an effective inhibitor of salivary and pancreatic a-amylases suggests that it could suppress postprandial hyperglycemia in diabetic patients. Furthermore, it has also been suggested that pinhão tannins could, at least in principle, be used to promote weight loss and combat obesity, perhaps even as a functional food. The possibility that the tannin-rich extract may be active on enzymes other than a-amylases, such as a-glucosidases, for example, cannot be excluded (Peralta et al., 2016).

4 INNOVATIVE TECHNOLOGIES IN PINHÃO

Pinhão flour is a good source of fiber and proteins, needing to be recognized when compared to wheat flour for being gluten-free and corn flour for representing an alternative for the formulation of expanded products. The use of flour mixtures for this purpose is not recent, and one of the main objectives is nutritional improvement, protein supplementation, and fiber incorporation (Capella et al., 2009).

Pinhão flour has already succeeded in Brazilian communities by adding alfajores, which is already a reality of its industrial application (Conforti & Lupano, 2008). In addition, this flour can also potentially be used in the production of gluten-free cake (Ikeda et al., 2018), gluten-free bread (Polet et al., 2019), and extruded foods (Zortéa-Guidolin et al., 2017).

The flour from the whole edible part of pinhão can be considered a new technological option for raw material use and a nutritional source for possible formulations of food products, including gluten-free bread (Polet et al., 2019). Whole pinhão flour is a nutritious food that should be commercialized and used as an ingredient in the food industry to formulate new products for special purposes, such as gluten-free, bakery, pasta, and cereal bars (Helm et al., 2020). Both the seed and the husk of the pinhão are prosperous raw materials, demonstrating their use in the development of new products. Also, it is assumed that 10 tons of pinhão bark are discarded annually in Brazil without any commercial value or form of use (Helm et al., 2020), increasing several problems. Therefore, the development of a whole pinhão flour (peel + almond) can be a possibility for the full use of the seed to restrict the environmental impacts that the incorrect disposal of the husks can cause, providing the circular use of the pinhão and adding nutritional value to the product (Capella et al., 2009; Daudt, 2013).

According to data from Barreto (2018), the performance of the flour preparation process is 30% better than that of the raw material. The shelf life of this pinhão flour is 120 days, representing a significant gain. The pinhão seed in nature exposes a high water activity; that is, the free water present in the seed, which microorganisms can use, makes the raw material susceptible to deterioration, which limits its consumption to the months of collection. When resigned to processing, after dehydration and appropriate filling, there is the possibility of offering this food for a longer time. Although white flour is more receptive, it is also possible, during the process of obtaining the flour, to use the film that covers the endosperm of the seed and, therefore, has the option of flour with a higher content of essential amino acids (leucine, phenylalanine + tyrosine, and valine) (EMBRAPA Florestas, 2018).

5 PINHÃO BIOACTIVE COMPOUNDS

5.1 Phenolic compounds

Polyphenols are compounds derived from phenylalanine and are characterized by having two or more phenol units in their structure (Granato, 2016). Phenolic compounds are mainly formed during the secondary metabolism of plants, whose function and variety are directly related to their defense. Phenolic compounds can be divided into flavonoids and non-flavonoids (Souza et al., 2014). The main phenolic compounds found in the seeds of pinhão, both raw and cooked, are catechin and quercetin (Koehnlein et al., 2012).

Recently, phenolics have gained greater interest from researchers because most of these compounds exhibit bioactive activity with functional mentions, capable of favoring health (Xu et al., 2017). Bioactive compounds, however, are classified as substances with functional or toxic claims; these substances can be present in different proportions in vegetables, seeds, and fruits, among others (Ho et al., 2010).

The most relevant group of common phenolic compounds in foods comes from flavonoids, tannins, and phenylpropanoids. Tannins can be hydrolyzable or non-hydrolyzable and are composed of glucose and gallic acid in different distributions (Nunes & Besten, 2016). Antioxidants are reported as agents capable of eliminating free radicals and reactive species to oxygen, which can be extremely important in inhibiting mechanisms of oxidative agents that cause degenerative diseases (Peralta et al., 2016).

The United States Department of Agriculture (USDA) publishes and regularly reviews an official database of flavonoid content in foods. The most recent data version (Bhagwat et al., 2014) contains information from 308 articles on flavonoid contents in 502 foods. A survey in this database indicates that flavanols are mainly found in cocoa and its derivatives, green tea, sugar-free chocolate powder, and carob seed flour, which are the main sources of this compound. Data published by the USDA also indicate that the most common flavanols in foods are, in this order: epicatechin, found in 116 indexed foods, catechin in 111 foods, epigallocatechin in 56 foods, and gallotecaquine in 20 foods (Bhagwat et al., 2014).

Among the phenolic compounds discovered in pinhão extracts are proanthocyanidins, resulting from catechins and epicatechins, the flavonol quercetin-3-glucoside, the flavanone eriodictyol hexoside, and two phenolic acids, these being derivatives of protocatechuic and ferulic acids (Freitas et al., 2018; Santos et al., 2018).

Studies alluding to the nutritional value of the seed reveal that, during cooking in water, some of the phenolic compounds in the skin move to the seed, which is one of the reasons the cooked seed identifies with its brown color. The seeds contain several polyphenols belonging to the flavonoid class, including catechin and epicatechin (subclass flavan-3-ol); rutin, quercetin (subclass of flavonol); and apigenin (subclass of flavone) (Branco et al., 2015). The main flavonoids that have been isolated belong to the class of bioflavonoids: amentoflavone, monomethyl amentoflavone, dio-methyl amentoflavone, ginkgetin, tri-O-methyl amentoflavone, and tetra-O-methyl amentoflavone, which differ according to the number and position of the methoxyl group in the amentoflavone molecule (Mota et al., 2014). The bioflavonoids reported in the pinhão seeds act as free radical sequestration agents and exhibit efficient protection against damage from oxidation. They are excellent options for antioxidants and photoprotection agents (Michelon et al., 2012). Phenolic compounds are secondary metabolites present in plants, relevant to human health, with benefits already confirmed in the fight against cardiovascular diseases and cancer and probably associated with their antioxidant properties (Helm et al., 2020; Peralta et al., 2016).

The general biosynthesis of flavonoids has as its central intermediate the p-coumaroyl-CoA thioester, which is elongated by the condensation of three malonyl-CoA units. The cyclization resulting in the A ring formation produces chalcone, which spontaneously tends to flavanone. However, it is known that chalcone cyclization can be catalyzed by an enzyme, chalcone isomerase, which leads to stereospecific closure of the ring, forming (2-S)-flavanone. The other types of flavonoids are formed by subsequent redox steps of p-coumaroyl-CoA thioester (Araújo et al., 2013).

Santos et al. (2018) distinguished 13 phenolic compounds in pinhão bark, 10 of which were proanthocyanidins (catechin and epicatechin derivatives), 2 phenolic acids (protocatechin acid and ferulic acid derivatives), 1 flavonol (quercetin-3-O-glucoside), and 1 flavone (eriodictyol-O-hexoside). The study was produced with the shell of pinhão that was previously cooked. The extraction was performed with a mixture of ethanol and water at different concentrations.

According to Thys and Cunha (2015), the higher content of total phenolic compounds in pinhão may be because, during the cooking process, the rupture of membranes present in the cell wall of the peel occurs, thus facilitating the migration of carotenoids to the endosperm, and consequently making it the most bioavailable. Partial hydrolysis of the tannins present in the pinhão shelling may also occur, producing simpler phenolics and migrating to the seed more easily (Koehnlein et al., 2012).

As cooking takes place, the colored compounds present in the inner and outer shells migrate not only to the water but also to the surface of the edible part of the seed (almond) (Cordenunsi et al., 2004). Compared to other commonly consumed foods, oilseeds, for example, which have a much higher lipid content, pinhão has a lower phenolic content. However, the phenolic content of pinhão is similar to that of many carbohydrate-rich foods, such as baked beans and potatoes (Han et al., 2007).

Sources of bioactive compounds, such as fruit extract, pulps, and juices, are usually studied as functional additives in fermented milk, becoming an important source for dairy research and a tendency to industries (Balthazar et al., 2019). Adding fruits' bioactive compounds in dairy formulations also enhances the viability and the development of probiotic cells, with a potential prebiotic property (Balthazar et al., 2019; Vicenssuto & Castro, 2020).

5.1.1 Flavonoids

Flavonoids are among the plants' most relevant phenolic compounds and are abundantly distributed. There is a vast diversity of flavonoids, and more than 2000 are of natural origin (Ho et al., 2010). Its fundamental structure contains 15 carbon atoms organized into three rings: benzene rings and pyran rings (Nunes & Besten, 2016).

The fundamental characteristic of the structure of phenolic compounds is at least one aromatic ring associated with at least one hydroxyl substituent that can lose electrons through the present hydrogen and oxidize. The presence of this radical is one of the main factors responsible for the antioxidant capacity of these compounds, having a relationship between the number and its position in the chemical structure (Faller & Fialho, 2008).

Groups of flavonoid compounds exhibit a range of substitution patterns such as hydroxylation, methoxylation, methylation, and glycosylation that provide diversity and complexity to them. Glycosylation, for example, can alter flavonoids' water solubility and stability (Yang et al., 2018). According to Ferreyra et al. (2012), referring to an abundant class of chemical substances of natural origin whose synthesis does not occur in humans, flavonoids have many pharmacological properties that allow their action in biological systems and thus favor human health. All classes of flavonoids can be isolated using different techniques, such as open column and high-performance liquid chromatography, being identified by mass spectrometry and nuclear magnetic resonance.

Flavonoids are widely distributed secondary metabolites in the plant kingdom and have several important roles such as pigments, bactericides, fungicides, and the like. Besides, they have other characteristic properties, such as anti-inflammatory, antibacterial, anticarcinogenic, and oestrogenic agents (Shen et al., 2022). Additionally, flavonoids can inhibit some enzymes, such as cyclooxygenase, lipoxygenase, and phospholipase A2 (Ferreyra et al., 2012), and are also able to chelate metals, which play an important role in metal-induced free radical reactions (Gulcin & Alwasel, 2022). Bioflavonoids are dimers of flavonoids linked by a C–O–C or C–C bond; their biological properties include anti-inflammatory and antiarthritic activity in animals (Ferreyra et al., 2012). Such capacities were associated with an ability to suppress reactive species and inhibit cyclooxygenases as well (Rosa et al., 2023).

According to Santos et al. (2018), flavonoids portray the highest proportion of phenolic compounds present in the hydroalcoholic extract (ethanol/water) of pinhão, equivalent to approximately 89–92% of the total constitution, among which the most abundant are catechin and epicatechin, flavonoids, and flavonol.

5.1.2 Catechin

Catechins belong to a group of polyphenols found in pinhão seeds, and it is a water-soluble compound, consequently responsible for the bitterness and astringency of pinhão. Because it oxidizes naturally, when it is present in the body and encounters a radical reaction quickly, it prevents healthy cell oxidation (Schmitz et al., 2005). Its composition includes epicatechins (EC), epicatechins gallate (ECG), epigallocatechin (EGC), and epigallocatechin gallate (EGCG), the latter being the most abundant and the one that deserves greater attention from a pharmacological point of view. Catechins are colorless and soluble in water, and there are no references to contraindications for their consumption (Schmitz et al., 2005).

Both raw and cooked pinhão contained significant amounts of catechin, specifically 17.5 mg/100 g of seed (edible part) and 21.1 mg/100 g of seed (edible part), respectively. The amounts of catechin in pinhão are comparable to those found in other catechin-rich foods such as raw apples (9.0 mg/100 g), apricots (11.0 mg/100 g), grapes (17.6 mg/100 g), and blackberries (18.7 mg/100 g) (Han et al., 2007).

This class of compounds is mainly found in the leaves of some teas, such as black and green, which come from the same plant, *Camellia sinensis*. Although *C. sinensis* is the main source of catechins, this subclass of phytochemicals is also found in grape juice, red wine, cocoa, apples, onions, beans, apricots, cherries, peaches, and pinhão nuts, as mentioned above. Its possible beneficial effects are reducing blood pressure, improving vascular function, inhibiting oxidized LDL-cholesterol uptake, reducing platelet reactivity, improving insulin sensitivity, and having anti-inflammatory effects (Strack & Souza, 2011).

It is an important metal chelator and inhibitor of lipoperoxidation, which is the introduction of molecular oxygen on the fatty acids of the cell membrane, leading to the destruction of its structure, loss of metabolic exchanges, and various toxic effects at the cellular level, among the most important cytotoxicity and, ultimately, cell death. This reaction has been associated with many cellular mechanisms that may occur in the onset of cancer, inflammation, and aging (Schmitz et al., 2005).

Heating at high temperatures can cause epimerization (a reaction where diastereoisomers that have the opposite absolute configuration in only one chiral center are produced) of the catechin, depending on the heating conditions, changing its composition qualitatively and quantitatively. The catechins present in green tea are epimerized by approximately 50% during heat treatment, thus losing half of their beneficial properties (Bazinet et al., 2010).

Catechin is called a condensed-type tannin when bound to two or more molecules. This molecule is a better antioxidant than its flavonoid because it is formed of three catechin structures; it can react with three radicals simultaneously, obtaining quinone as a product (Monteiro et al., 2005).

5.1.3 Epicatechin

Epicatechins have been the subject of extensive studies for their anticarcinogenic and antioxidant activities. Epicatechins refer to a group of epicatechin derivatives, including mainly (−)-epigallocatechin gallate (EGCG), (−)-epigallocatechin (EGC), (−)-epicatechin gallate (ECG), and (−)-epicatechin (EC). Green tea positively affects the blood lipid profile and decreases the risk for CHD. Anti-atherosclerosis activity of GTE was demonstrated in rabbits fed an atherogenic diet supplemented with GTE. Green or black tea was associated with increased plasma antioxidant capacity in human subjects, which effectively scavenged superoxide free radicals and hydroxyl radicals and prevented Cu-mediated LDL oxidation.

5.1.4 Quercetin

Quercetin is also one of the compounds of the subclass of flavonols, which are most widely distributed in nature. It is present in apples, onions, berries, and red wine. *In vitro* studies have demonstrated antioxidant, anti-inflammatory, antithrombotic, and vasodilatory action and reduced expression of adhesion molecules (Strack & Souza, 2011).

In pinhão, the quercetin content also increases after cooking, from 0.07 mg/100 g of seed to 0.7 mg/100 g of seed. The proanthocyanin content in the seed increased from 22.5 mg/100 g to 2035.0 mg/100 g after cooking. Also, as mentioned before, in catechin, cooking promotes the migration of phenolic compounds from the shell to the kernel (Koehnlein et al., 2012).

Growing evidence suggests that quercetin has therapeutic potential for preventing and treating diseases, including cardiovascular disease, cancer, and neurodegenerative disease. Quercetin has been shown to exert antioxidant, anti-inflammatory, and anticancer activities in several cellular and animal models and humans by modulating the signaling pathways and gene expression involved in these processes (Ay et al., 2021).

It was reported that quercetin has low aqueous solubility and bioavailability and is quickly metabolized in the body, which may reduce its efficacy as an application in preventing or treating diseases (Kumari et al., 2010). Quercetin has a high solubility in organic solvents such as ethanol, dimethyl sulfoxide (DMSO), and dimethyl formamide. Quercetin in human bodies is rapidly metabolized by liver enzymes and other organs or tissues (Wang et al., 2016).

5.1.5 Gallic acid

Gallic acid is a phenolic acid occurring naturally in various herbs, foods, and processed beverages. In the past few years, gallic acid has emerged as an immensely valuable molecule owing to its vast utility in various applications (Dhiman & Mukherjee, 2022). Gallic acid is a widespread plant metabolite with a trihydroxybenzoic acid structure, having several hydrogen atoms in its phenolic structure that readily delocalize free radicals. Its structure explains its strong antioxidant properties, indicating its ability to protect tissues and organs from oxidative stress. It was earlier reported that gallic acid is a common component of several foods and herbal drugs, especially Chinese medicines.

According to Koelhnein, both raw and cooked pinhão kernels were found to contain significant amounts of gallic acid (0.36 mg/100 g of seed), whereas, in cooked almonds, the content increased to 0.82 mg/100 g of seed (Koehnlein et al., 2012). Gallic acid is also substantially utilized to prepare various cosmetics, adhesives, printing inks, photography, lubricants, dyes, and the like. Gallic acid is extensively utilized to prepare food preservative propyl gallate. Furthermore, its application as a crop protection agent in agriculture makes it an extremely valuable molecule. Several attempts have been made to produce gallic acid through fermentation in the last two decades. Various methods, such as spectrophotometric estimation, chromatographic estimation, and a combination of more than two approaches, have been employed for the qualitative and quantitative analysis of gallic acid.

6 CHEMICAL STRUCTURE

Flavonoids are secondary metabolites biosynthesized from phenylalanine and acetic acid, with shikimic acid being the precursor of phenylalanine (Karam et al., 2013). The aromatic rings of flavonoids are composed of this joint biosynthetic pathway, where through condensation reactions aided by enzymes, three molecules of malonyl coenzyme A (CoA) from the acetate pathway are condensed together with a molecule of 4-hydroxycoumaryl-CoA, which is derived from the shikimate pathway. Units from the acetate pathway give rise to the A ring of the basic structure of the flavonoid. In contrast, the unit from the shikimate pathway gives rise to the B ring, and the three carbon atoms that interconnect the A and B rings formation of the A ring produce the chalcone that equilibrates with the corresponding flavanone (Krysa et al., 2022).

The other types of flavonoids are formed by subsequent oxidation–reduction steps of this common intermediate; their plant distribution depends mainly on the type of family, genus, and species. For example, the flavonoids found in leaves can present structural differences from those in flowers, branches, roots, and fruits. Thus, in the same plant, a single flavonoid can be found in different amounts depending on the plant organ (Machado et al., 2008). Natural extrinsic factors such as solar radiation, UV rays, periods of drought or rain, nutrients, and seasons also influence the metabolism and production of the most diverse flavonoids (Machado et al., 2008).

The basic structure of flavonoids is formed by a fundamental nucleus, with 15 carbon atoms (C15) arranged in three rings (C6–C3–C6), two of which are substituted phenolic rings (previously mentioned A and B rings) and one C ring (Dornas et al., 2007).

Variations in the C ring originate from the different classes of flavonoids. This ring can be of the pyranic type, as in the case of catechins and anthocyanidins, or of the pyrone type, as in flavanols, flavones, isoflavones, and flavanones, the last four having a carbonyl group in the C4 position of the C ring class of flavonoids are shown in Figure 2.

Catechins belong to the 3-flavanol family and consist of a phloroglucinol ring, a pyran ring, and a catechol ring (Figure 3).

Catechins neutralize oxygenated free radicals (R•) by donating hydrogen atoms from the hydroxyl groups, preferentially located on the catechol ring, due to their stereochemical accessibility and the ortho position of the two hydroxyl groups, which favor the electronic delocalization of the electron and confer great radical form stability (Albuquerque, 2009).

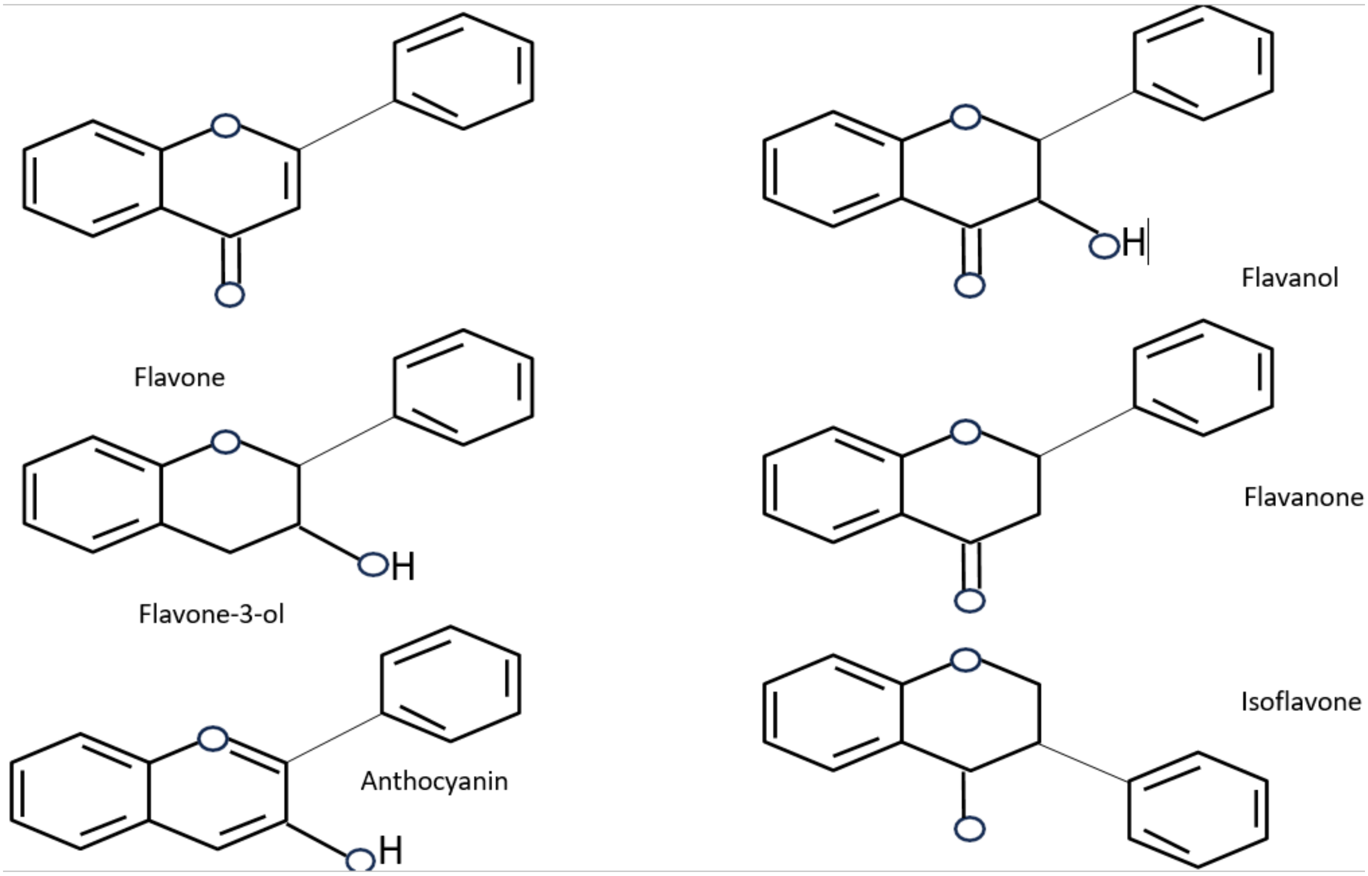
Epicatechin belongs to the group of phytochemicals known as flavonoids. They can be found in plant products like green tea, especially dark chocolate. Among its properties, it can be highlighted as a potent antioxidant, a precursor of nitric oxide (NO), which can increase follistatin and decrease myostatin. The importance of these isomers that we can find in food lies in the different biological effects they produce in our bodies. As can be seen from investigations, the (-)-epicatechin form has the greatest bioavailability (Jimenez et al., 2012).

Quercetin (3,5,7,3'-4'-pentahydroxyflavone) (Figure 4) is the main flavonoid present in the human diet, representing about 95% of the total flavonoids ingested, which may have benefits for health because quercetin is one of the flavonoids with the greatest ability to scavenge free radicals, having demonstrated excellent antioxidant potential *in vitro* (Huber & Rodriguez-Amaya, 2008).

Usually, quercetin is present in foods in a glycosylated form, covalently linked to a sugar molecule, as shown in Figure 4 (substances A, B, and C). The property that distinguishes one glycosidic form from the other is the type of glycosidic group present in the structure. For example, isoquercetin, also called quercetin-3-glucoside (shown in Figure 4 structure C), has a glucose molecule attached to position 3 (carbon 3 of ring C). In contrast, quercetin-3-rutinoside, also called rutin, has a rutinose group (disaccharide) attached to position 3 (Figure 4 structure A). On the other hand, quercetin-4'-glycoside has a glucose molecule attached to the 4' position of the B ring. Quercetin, in the aglycone form represented by structure D in Figure 4, does not have a glycosidic substituent in its structure. The presence of the glycosidic group promotes an increase in the solubility of the substances described in aqueous media. Thus, it can be concluded that the solubility of quercetin aglycone in water is lower than that of the others (Chen et al., 2010).

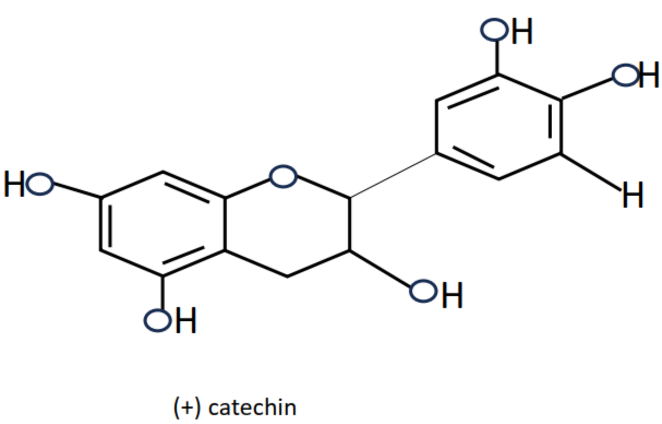
From the basic structure of flavonoids, it is possible to distinguish classes and components of each class through changes in substituents. Quercetin differs from other flavanols by adding hydroxyl substituents at positions 3, 5, 7, 3', and 4' and a carbonyl at position 4.

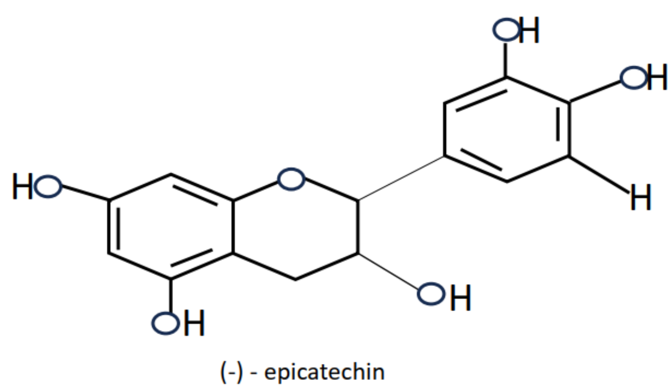
Gallic acid (3,4,5-trihydroxybenzoic acid; Figure 5) is an important polyhydroxyphenolic compound and a major hydrolysis product of tannin with valuable antioxidant, anticancer, and anti-inflammatory properties (Bai et al., 2021). It is commonly found in fruits and vegetables such as grapes, tea leaves, cherries, and longan seeds. It can also be extracted from liquid or solid



Source: Based on Krysa et al. (2022).

Figure 2. Structures of the main subclasses of flavonoids.





Source: Based on de Cunha et al. (2017).

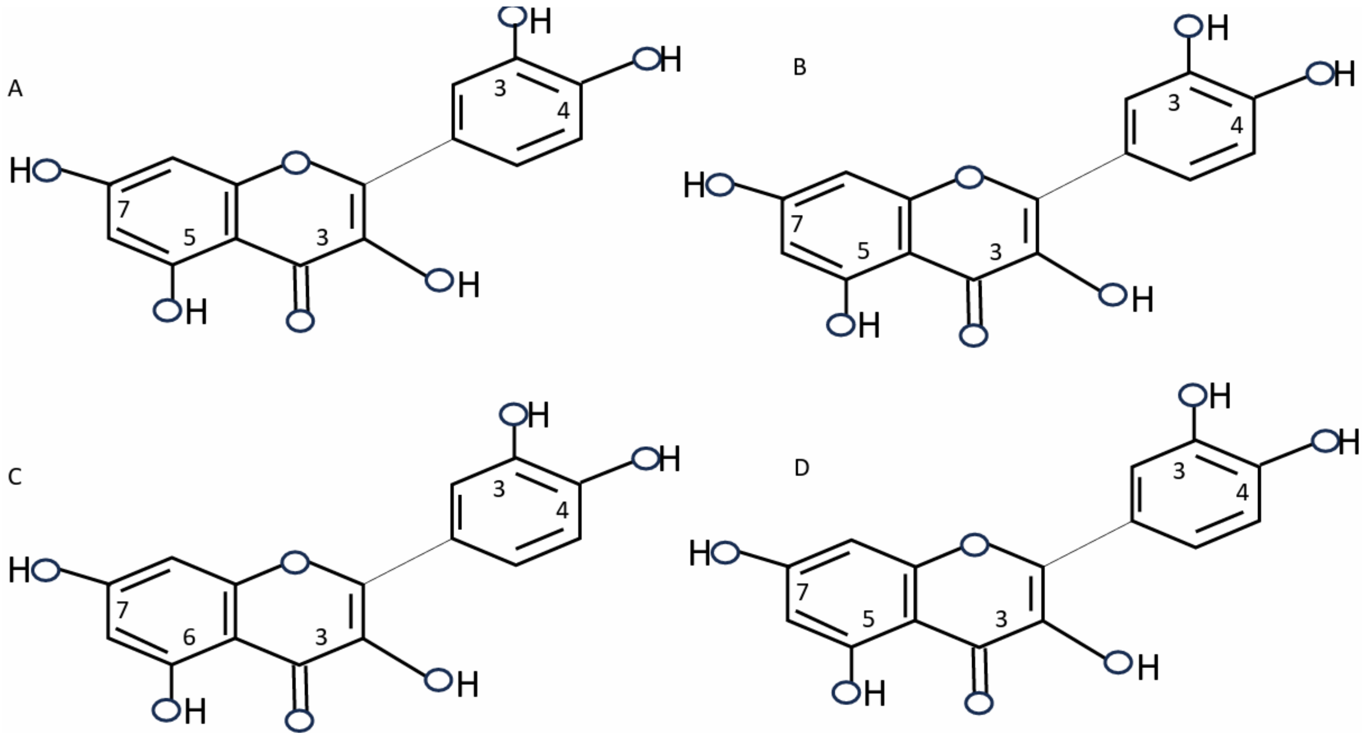
Figure 3. Catechin and epicatechin structure chemistry.

wastes of the agro-food industry. Gallic acid/chitosan fibers have already been suggested for manufacturing food packaging (Sun et al., 2014).

Gallic acid is a flat molecule chemically derived from 3,4,5-trihydroxybenzoic acid. The structure contains an aromatic ring; three hydroxyl groups are attached to the ring in an ortho position about each other, which is essential for the strong antioxidant capacity of phenolic compounds. Its n-alkyl esters, also known as gallates, especially propyl, actin, and dodecyl gallate, are used as antioxidant additives in foods to prevent changes in flavor and nutritional value due to the oxidation of unsaturated fats (Ow & Stupans, 2003).

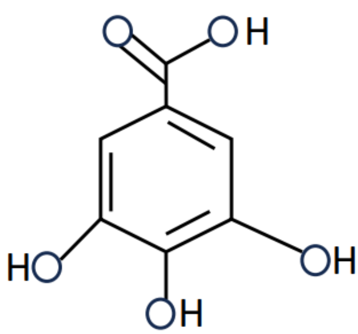
7 HEALTH EFFECTS

Pinhão seed almonds are of great nutritional interest, as they are rich in starch, fiber diets with low glycemic index, and



Source: Based on Cunha et al. (2017).

Figure 4. Structures of glycosylated quercetins: (A) quercetin-3-rutinoside, (B) quercetin-4′-glycoside, (C) quercetin-3-glycoside, and (D) quercetin aglycone.



Source: Based on Punithavathi et al. (2011).

Figure 5. Structure chemistry of gallic acid.

low levels of lipids. Some compounds present in pinhão have a functional character, such as resistant starch and antioxidant compounds (phenolics, flavonoids, and proanthocyanin), potentially promoting health for the consumer. The film is an important component of pinhão kernels as it has a high content of phenolic compounds (Koehnlein et al., 2012).

It is common to find products made with pinhão, such as beer, bread, flour, pickled pinhão, and cooked pinhão frozen all year round. In addition, different processing techniques applied to pinhão were studied. A study on the extrusion of pinhão flour to produce gluten-free ready-to-eat snacks showed that extrusion cooking suits pinhão processing. This study about the extrusion of pinhão flour presented good texture properties and a well-accepted natural flavor. They also had a high dietary fiber content and increased slow-digesting starch content compared to flour, with potential health benefits for people with diabetes (Zortéa-Guidolin et al., 2017). Daudt (2016) studied the applicability of pinhão starch and bark extract as ingredients in topical formulations (gel) and edible films. Topical formulations showed good storage stability, similar spreadability to controls, and high antioxidant activity. Edible films showed that pinhão starch is an option for producing edible films similar to commercial ones made with cassava starch (Daudt, 2013).

8 PHENOLIC COMPOUNDS AND AFFINITIES WITH DAIRY PRODUCTS (BIOAVAILABILITY OF MILK PROTEINS + PREBIOTICS + ANTIOXIDANTS)

Bioavailability is directly related to the bioaccessibility of the food matrix during digestion. Through bioaccessibility, it is possible to determine the amount of the compound of interest that is released and is available for absorption during the gastrointestinal process. Bioaccessibility can be evaluated *in vitro* through simulated gastrointestinal digestion by an artificial membrane, cell culture, and Caco-2 culture (cell lines from human colorectal epithelium), among other methods (Barba et al., 2017; Galanakis, 2018). Information regarding bioaccessibility is valuable to determine the dosage and ensure the nutritional efficiency of foods (Fernandez-Garcia et al., 2009).

Bioavailability, in turn, is part of a more complex process, corresponding not only to the number of compounds released ready for absorption but also includes metabolic processes, genetic predisposition, nutrient distribution in the body, and bioactivity, which may vary from individual to individual (Granato, 2016). The action of bioactive compounds present in foods in the body depends not only on their physicochemical nature but also on their bioaccessibility and bioavailability in the face of biological barriers, making the target compound available for use by organs and tissues, aiming to perform certain physiological functions. Parameters such as heat treatment, packaging, and technological processes can influence the bioaccessibility of foods (Barba et al., 2017).

Bioavailability, on the other hand, is part of a more complex procedure, representing not only the number of released compounds ready for absorption but also metabolic processes, genetic predisposition, nutrient distribution in the organism, and bioactivity, which may vary from individual to individual (Granato, 2016).

The activity of bioactive compounds present in foods in the body results from their physicochemical nature and their bioaccessibility and bioavailability in the face of biological barriers, making the target compound available for use by organs and tissues, aiming to perform certain physiological functions. Parameters such as heat treatment, packaging, and technological processes can influence the bioaccessibility of foods (Barba et al., 2017).

Antioxidants are important for preventing and treating such chronic conditions, and functional foods contain many phytochemicals that serve as bioactive drugs and positively impact the organs. (Shashirekh et al., 2015). Functional compounds are chemicals synthesized by plants and are usually found in fruits, vegetables, grains, beans, and other plants. They include tannins, alkaloids, steroids, saponins, flavones, and other groups. About 10,000 phytochemicals fall into these categories. However, it has been reported that phytochemicals with antioxidant activity, such as phenolics, carotenoids, flavonoids, and other compounds such as vitamin C, prevent chronic disease conditions. These antioxidant compounds decrease reactive oxygen and nitrogen species, preventing damage to organs and cells (Zhang et al., 2019). Antioxidant compounds are commonly found in many plant products such as fruits, vegetables, grains, leaves, roots, and other organisms such as macrofungi. However, fruits and vegetables are the most studied plants regarding their antioxidant capacity. Fruit peels and seeds contain numerous functional compounds such as chlorogenic acid, gallic acid, catechin, and epicatechin, to name a few. Likewise, vegetables contain phenolics, quercetin, kaempferol, caffeic acid, lutein, and zeaxanthin, to name a few. Thus, fruits and vegetables are favorite products for food fortification because of their taste, nutrition, appearance, and antioxidant properties (Shashirekh et al., 2015). Currently, yogurt is among the most favored food products enriched with various plant and animal products.

Probiotic strains are widely studied and commercially exploited in different products worldwide (Soccol et al., 2010). These microorganisms represent a large part of the worldwide sales of functional foods. Probiotics are live microorganisms that confer a health benefit on the host when administered adequately (Hill et al., 2014). The most used probiotics involve the genera *Lactobacillus* and *Bifidobacterium*; however, yeasts, such as S*accharomyces boulardii*, have also been explored for their probiotic potential (Szajewska & Mrukowicz, 2005). For a microorganism to be used as a probiotic, several studies must assess its resistance capacity, efficacy, and technological aptitude (De Dea Lindner et al., 2007).

The beneficial influence of probiotics on the human intestinal microbiota includes factors such as immunological effects, control of intestinal infections, stimulation of intestinal motility, better absorption of certain nutrients, better use of lactose and the relief of symptoms of intolerance to this sugar, the decrease in cholesterol levels and its effect, and by stimulating the production of antibodies against pathogens in the intestine and other tissues of the host, in addition to the production of antimicrobial compounds increasing resistance against pathogens. Thus, using probiotic bacterial cultures stimulates the multiplication of beneficial bacteria to the detriment of the proliferation of potentially harmful bacteria effects, reinforcing the host's natural defense mechanisms (Puupponen-Pimia et al., 2002).

According to Hill et al. (2014), a probiotic microorganism must reside in the gastrointestinal tract, survive through the stomach, maintain viability and activity in the intestine, and present good technological properties, promoting adequate sensory characteristics for the product and remaining stable, and viable during storage, so the minimum amount needed to be considered a probiotic is at least 10^6–10^7 colony forming units (CFU) per gram.

9 FINAL CONSIDERATIONS

This review demonstrates that pinhão is a food with antioxidant capacity and rich in too many phenolic compounds, in addition to the nutritional properties already proven in several articles. Innovations using pinhão are highlighted in several products, such as pinhão flours, which show nutritional improvement in their composition and increased antioxidant activity. More studies are needed, however, regarding the technological viability of its use in industrialized products, mainly as an alternative source of flour or as a substitute or alternative to commonly used flour. At least, it seems clear from the preliminary results that there is still much to be gained from a systematic and targeted continuation of investigations. In addition to this technology used in by-products, we have to highlight the beneficial health effects of pinhão from the seed to the bark, where all of their characteristics have positive properties for health. The bioavailability of pinhão compounds for dairy products, in turn, is part of a more complex process, corresponding not only to the number of compounds released ready for absorption but also includes metabolic processes, genetic predisposition, distribution of nutrients in the body, and bioactivity, which may vary from individual to individual. However, due to the other phenolic compounds found in pinhão, we can relate that bioactives and prebiotics would have affinities with dairy products.

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