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Bioactive compounds of rice bran and their potential health benefits in the development of functional foods: A review

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ABSTRACT

Rice bran is a by-product produced from the milling and polishing process of rice, which makes up about 10% of the whole grain. In 2021, the amount of rice bran produced in Indonesia can reach up to 3 million tons. Researchers have been intrigued to study rice bran as an ingredient for foods because it is considered underutilized despite its abundance and functional properties. Rice bran is rich in nutrients such as fat, protein, dietary fiber, ash, and bioactive compounds. There is an increase in the use of rice bran following consumers' search for healthier consumption. Bioactive compounds in rice bran include phenolic acids, such as ferulic acid; flavonoids and anthocyanins, such as cyanidin glucoside; steroidal compounds, such as gamma-oryzanol; gamma-aminobutyric acid (GABA); etc. Rice bran's wax contains wax esters and aliphatic alcohols, namely policosanol. Bioactive compounds in rice bran have been known to have beneficial effects on health as antioxidants, antidiabetic, and anti-inflammatory agents. The bioactive compounds of rice bran as well as its antioxidant activity are influenced by rice variety, degree of milling, and processing method. This paper aims to review the bioactive compounds of rice bran, including pigmented rice bran, to support the development of functional foods.

Introduction

Rice bran is produced as a by-product of the dehulling and polishing of rice grains. This process is intended to produce white rice that is more likeable in terms of sensory acceptance than brown rice. High consumption of white rice significantly increases the risk of type 2 diabetes. The risk is higher in Asian populations, especially Chinese and Japanese, than in Western populations due to the consumption of rice as the staple food for most of the population (Hu et al., 2012). The nutrient content of brown rice, such as protein, fat, and vitamins, is higher than that of white rice; even the mineral content of potassium is almost three times higher in brown rice (Saleh et al., 2019). These data show that polishing the rice or removing the bran would eliminate of most of the health-promoting substances.

The rice production in Indonesia last year was about 31.69 million tons of grain (BPS, 2021) making about 3 million tons of rice bran. Rice bran composes of about 10% of whole-grain (Phongtha et al., 2017), consisting of pericarp, aleurone, sub-aleurone, and a small amount of endosperm and germ (Justo et al., 2013; Sharif et al., 2014). Rice bran contains 12–22% fat, 11–17% protein, 6–14% fiber, 10–15% moisture, and 8–17% ash, as well as anthocyanins in red and black rice bran (Chen et al., 2012; Pengkumsri et al., 2015). Colored rice began to gain popularity among consumers as a healthier alternative to white rice. Colored rice contains potent antioxidants such as cyanidin glucoside and peonidin glucoside that have beneficial effects on health. The color of pigmented rice bran is a phenolic compound in the rice's pericarp, which is part of the rice bran (Ramos et al., 2022).

Rice bran is a good source of fatty acids that is dominated by oleic acid, linoleic acid, and palmitic acid (Phan et al., 2021). The oil fraction of rice bran contains vitamins, 1.5–2%

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phytosterols, 1.2–1.8% oryzanol, 0.15– 0.2% tocopherols and tocotrienols (Liang et al., 2014). Tocotrienols in rice bran are rarely found in other edible oils (Capellini et al., 2017). Protein in rice bran is mainly water-soluble protein, and albumin at the higher percentage (Hu et al., 2019). Rice bran’s protein is a potential substitute for animal protein with hypoallergenic properties (Fabian et al., 2011; Kim et al., 2015). The removal of the bran exacerbates the lack of dietary fiber in polished rice. About 27% of total dietary fiber, 24% insoluble dietary fiber, and 3.5% soluble dietary fiber are contained in rice bran (Nandi et al., 2019). They are crucial to protect the body from colon cancer, diabetes, and many more (Yao et al., 2022). The pigment in colored rice bran comes from phenolic compounds known to have antioxidant activity (Ramos et al., 2022).

Because of these compounds, rice bran has a high potential to be developed as a functional food ingredient instead of just utilizing it as animal feed and waste. There is an increased application of rice bran in the food industry, nutraceuticals, and pharmaceuticals as there is a change in consumption patterns toward healthier options (Gul et al., 2015). The bioactive compounds in rice bran can be divided into phenolic and cinnamic acids; flavonoids and anthocyanins; steroidal compounds; carbohydrate polymers; and proteins (Friedman, 2013). Other compounds, such as gamma-aminobutyric acid and policosanol that are found in rice bran have advantageous effects on health and well-being. This review article aims to go through the bioactive compounds found in rice bran and their health benefits in the midst of functional foods’ mass development.

Phenolic and Cinnamic Acids

Phenolic acids in rice bran exist in free soluble, free conjugated, and bound insoluble forms. Plant vacuole cells contain free phenolic acids, whereas soluble esters or conjugates are esterified with sugars or other low molecular weight compounds. Additionally, bound forms of phenolic acids are covalently bound to cellulose, hemicellulose, lignin, pectin, and protein. The most potent antioxidant capacity is found in the insoluble, bound form of phenol. Ferulic acid is rice bran's most abundant phenolic compound, with high antioxidant activity (Wang et al., 2015). Most phenolic acids (more than 80%) in rice bran were present in bound form (Huang and Lai, 2016).

The separation or extraction of these phenolic compounds can be done by various techniques, such as extracting with water or combinations of water and organic solvents. This technique only separates soluble phenolic compounds while overlooking the bound phenolics, essential for evaluating rice bran's physicochemical, nutritional value, etc (Wang et al., 2015). Wang et al. (2015) used organic solvents to extract phenolic compounds, which were then separated into four fractions using silica gel. Setyaningsih et al. (2015) extracted phenolic compounds using the microwave at 1000 W power for 20 minutes, and it was concluded that the microwave application was suitable for extracting these compounds.

Ferulic acids in black rice bran can be found in concentrations greater than 4800 g/g dry weight (DW) and vary depending on rice variety and milling degree (Zhang et al., 2022). *Trans*- and *cis*-ferulic acid had the highest DPPH and ABTS+ radical scavenging activity (Wang et al., 2015). Ferulic acid in the black rice bran was more plentiful than white and red rice bran (Ghasemzadeh et al., 2018). The study by Zhang et al. (2022) disclosed that the second most abundant phenolic acid after ferulic acid was ferulic acid methyl esters, which are not commonly reported to be contained in black rice bran, with an amount of 483.99 µg/g DW.

P-coumaric acid is another abundant phenolic acid in rice bran that ranges from 16.71 – 33.35 mg/100 g. *P*-coumaric acid was found in both free and bound forms in white, red, and black rice bran (Ghasemzadeh et al., 2018). In line with that, about 353.29 µg/g DW of *p*-coumaric acid was in the black rice bran sample as the third-highest phenolic compound, followed by protocatechuic acid (Zhang et al., 2022). Then, about 416 µg/g DW of *p*-coumaric acid was found in defatted rice bran as the second-highest phenolic compound after ferulic acid (Zhao et al., 2018). The total phenolic compounds in white and red rice bran are 1.57 and 4.39 mg gallic acid equivalent (GAE)/g, respectively (Moongngarm et al., 2012).

Other phenolic acids that were known to exist in rice bran are gallic acid, protocatechuic acid, chlorogenic acid, *p*-hydroxybenzoic acid, vanillic acid, caffeic acid, syringic acid, epicatechin, vanillin, quercetin, and vanillic acid (Zhao et al., 2018; Zhang et al., 2022). Cinnamic acid was identified in both free and bound forms in black rice bran, while only the free form of cinnamic acid was found in white and red rice bran. Cinnamic acid in rice bran ranges from 9.61–25.53 mg/100 g. Overall, black rice bran was superior in terms of phenolic compound content compared to white and red rice bran

(Ghasemzadeh et al., 2018). The antioxidant properties of ferulic acid significantly reduced oxidative stress in rat models that were given a high-fat diet (Perez-Ternero et al., 2017). The mechanism that probably takes place is that the phenolic compound in rice bran reduces lipid biosynthesis along with increasing the oxidation of fatty acids in the liver (Zhang et al., 2020).

Flavonoids and Anthocyanins

Like phenolic compounds, flavonoids can be extracted using organic solvents or a combination of organic solvents and water. It can also be done with the assistance of ultrasound, as was done by Das et al. (2017). The process is called UAE, which stands for ultrasound-assisted extraction. Under optimum conditions (temperature, pH, solvent concentration, and time), UAE produced more anthocyanin content than to conventional extraction. MAE has been applied to assist in the extraction of flavonoids. The optimum conditions of MAE compared to conventional solvent extraction required less time and a smaller amount of solvent to extract the flavonoids (Halee et al., 2020).

Rice bran contains flavonoids, namely quercetin, apigenin, catechin, luteolin, and myricetin. Quercetin, apigenin, and catechin were found in free and bound form in white, red, and black rice bran, whereas luteolin and myricetin were only found in free form. Quercetin total in rice bran ranges from 2.87–15.55 mg/100 g. Apigenin in rice bran can be found in the range of 4.22–15.31 mg/100 g. Catechin had the highest flavonoid compound content, with a whole range of 8.96–22.05 mg/100 g. Luteolin and myricetin have a range of 2.35–10.72 and 5.68–12.85 mg/100 g, respectively. Black and white rice bran have the highest and lowest flavonoid contents respectively (Ghasemzadeh et al., 2018).

Peanparkdee et al. (2019) study with rice bran from many cultivars showed that the total flavonoids in pigmented rice bran (purple) were almost ten times higher than they are in white rice bran. The total flavonoids were composed of rutin, myricetin, and quercetin-3-glucuronide. Quercetin-3-glucuronide was discovered as the highest flavonoid compound in an ethanol extract of pigmented rice bran at a concentration of 163.88 µg/g rice bran. The total flavonoids of white and pigmented rice bran were 20.33 and 167.40 µg/g rice bran, respectively.

Total flavonoid, free flavonoid, and bound flavonoid in rice bran are about 40.15–240.88; 28.52–135.18; and 11.63–105.70 mg quercetin equivalent (QE)/100 g, respectively. On the other hand, red rice bran contains multiple times more total flavonoid, free flavonoid, and bound flavonoid in the amount of 332.98–457.00; 218.24–324.92; and 85.51–238.75 mg QE/100 g, respectively, compared to white rice bran. Then, black rice bran contains the highest total flavonoid, free flavonoid, and bound flavonoid in the amounts of 452.08–823.88; 340.78–526.68; and 111.30–297.20 mg QE/100 g, respectively (Ghasemzadeh et al., 2018).

The two most abundant anthocyanins found in rice bran are cyanidin-3-glucoside and peonidin-3-glucoside. About 88% and 67% of the total anthocyanins in black and red rice, respectively, are from cyanidin-3-glucoside, followed by peonidin-3-glucoside. Cyanidin-3-glucoside and peonidin 3-glucoside vary amongst rice varieties, ranging from 0–470 and 0–40 mg/100 g, respectively (Deng et al., 2013). Anthocyanins in white rice bran were the lowest, with a number of 2.18–10.72 mg cyanidin-3-glucoside equivalent (Cy3-GE)/100 g. Anthocyanins found in red rice bran were about twenty-five times higher than they are in white rice bran, in the amount of 51.88–77.87 mg Cy3-GE/100 g. Black rice bran has the highest anthocyanin content, ranging from 84.04–294.62 mg Cy3-GE/100 g (Ghasemzadeh et al., 2018).

Proanthocyanidin is the main pigment of red rice, whereas cyanidin-3-glucoside and peonidin-3-glucoside are the main contributors to black rice pigment. Proanthocyanidins were not detected in black rice bran, while they were found in the amount of 0.75–19.13 mg catechin equivalent/g dry matter. Total anthocyanins in some of the black rice varieties were 0.20–11.27 mg Cy3-GE/g dry matter. Black rice bran had multiple times more anthocyanin content compared to red rice bran (Huang and Lai, 2016). Anthocyanins of rice bran have been known for their health benefits, one of them is anti-cancer for prostate cancer by reducing enzyme activity in PC3 cells (Jongsomchai et al., 2020). Anthocyanins from black rice bran have antidiabetic properties by inhibiting the enzyme that catalyzes the release of glucose entering the hexosamine pathway (Bhuyan et al., 2020).

Steroidal Compounds

As stated before, rice bran oil (RBO) is considered excellent as it contains a good profile of fatty acids. RBO is also considered a “healthy oil” with its bioactive compounds (Fraterrigo et al., 2021). The oil fraction of rice bran contains

1.2–1.8% gamma-oryzanol (γ-oryzanol) (Liang et al., 2014). Rice bran has the highest content of gamma-oryzanol among edible oils. Chemically, gamma-oryzanol is a mixture of a ferulic acid ester with phytosterol and triterpene alcohol (steryl ferulic). Steryl ferulic in RBO is composed of campesterol, β-sitosterol, cycloartenol, and 24-metilenecycloartenol ester (Lemus et al., 2014).

Gamma-oryzanol exists in the non-polar fraction of rice bran, especially in RBO. The extraction of this compound requires non-polar solvents such as hexane, isopropanol, chloroform, etc. Research by Heidtmann-Bemvenuti, Nora and Badiale-Furlong (2012) revealed that extraction using hexane:isopropanol with the ratio 1:3 (v/v) at 40 ^{o}C produced high gamma-oryzanol content. The RBO extraction has been done using subcritical carbon dioxide Soxhlet (SCDS) extraction. This process showed higher oxidative stability of RBO with about a 10-fold higher content of tocopherols, tocotrienols, and oryzanols compared to RBO extracted with hexane (Chia et al., 2015). The use of alcalase in aqueous enzymatic extraction (AEE) produced higher contents of tocopherol, tocotrienol, and oryzanol than Soxhlet extraction (Xu et al., 2021).

Many studies have revealed gamma-oryzanol and its benefits to health, such as anti-inflammation, anti-hyperlipidemia, anti-carcinogenicity, and many more (Lemus et al., 2014; Gul et al., 2015). The antioxidant activity of oryzanol is ten times higher than that of tocopherol. Crude RBO has about 15 g/kg of gamma-oryzanol, and the amount can be reduced during processing, such as degumming and dewaxing of RBO (Friedman, 2013; Gul et al., 2015). White and red rice bran contains gamma-oryzanol in amounts of 3.5 and 8.58 mg/g, respectively (Moongngarm et al., 2012). Black rice bran has an amount of 10.92–12.89% of RBO, which varies among rice varieties (Pengkumsri et al., 2015).

Besides gamma-oryzanol, RBO contains vitamin E derivatives, namely tocopherol and tocotrienol. The majority of tocopherol exists as α- and γ-tocopherol, whereas tocotrienol exists as γ-tocotrienol. Rice bran contains tocotrienol, which is rarely found in edible oils (Capellini et al., 2017). Tocotrienol has neuroprotective, antioxidant, anticancer, and cholesterol-lowering properties. It has 40-60 times higher levels of antioxidant activity than α-tocopherol (Alauddina et al., 2017). White rice bran has both α- and γ-tocopherol of more than 40 µg/g. Red rice bran contains approximately 44 and 25 µg/g of α- and γ-tocopherol, respectively (Moongngarm et al., 2012). Total tocols in black rice bran is 0.29 mg/g, composed of 40.7% α-tocopherol; 23.2% α-tocotrienol; 8.9% γ-tocopherol; and 27.2% γ-tocotrienol (Zhang et al., 2013).

Some studies go into how these compounds interacted if exist together. According to research, α-tocopherol reduces tocotrienol's triglyceride-lowering and cholesterol-lowering properties (Shibata et al., 2016). According to the findings of Liu et al. (2021), a binary mixture can have an antagonistic or synergistic interaction depending on the ratio and concentration of these minor substances, such as α-tocopherol, which did not work well with gamma-oryzanol.

Polymeric Carbohydrates

Polished rice has a poor dietary content because rice bran is discarded. Rice bran's dietary fiber is dominated by insoluble dietary fiber and consists of cellulose, hemicellulose, and lignin with low solubility (Liu et al., 2021). Rice bran also contains arabinoxylan, which is a non-starch polysaccharide derived from cereals and has many functions that are related to health (Chen et al., 2019). Many studies utilized arabinoxylan from rice bran to reveal its effects on some diseases, such as cancer (Pérez-Martínez et al., 2015; El-Din et al., 2020; Ooi et al., 2020), and also revealed that its interaction with gut microbiota is beneficial to human health (Chen et al., 2019). Arabinoxylan is extracted from rice bran and requires enzymes and various reagents to separate it from fat, starch, and hemicellulose. The hemicellulose A can be obtained by reducing the pH of de-oiled and de-starched rice bran to 4.0–4.5 (Li et al., 2021).

Hemicellulose has the second-highest content among the dietary fibers, at about 20–35%. Hemicellulose is advantageous for use in the food, medicine, and energy industries because it is highly branched and amorphous, allowing it to be easily converted (Luo et al., 2019). Beta-glucan (β-glucan) is a type of soluble fiber found in cereals, oats, and a variety of bacteria and fungi. Beta-glucan acts as a prebiotic that is important to boost microbiota in the gastrointestinal tract, which will affect the immune system. It will be further beneficial for preventing or as a therapy for diabetes mellitus (Jayachandran et al., 2018).

Other Compounds

Another compound that exists in rice bran is gamma-aminobutyric acid (GABA). Rice bran contains an enzyme called glutamic acid decarboxylase (GAD), which converts glutamic acid residue to GABA. GABA is a non-protein amino acid found in bacteria, plants, and other vertebrates. GAD in rice bran acts as a potential source that produces GABA that helps with brain function, depression disorders, and blood pressure. Anaerobic treatment with 30% electrolyzed oxidizing water for 5 hours at 40 ^{o}C and 5 mM glutamic acid added produced approximately 523 mg/100 g of GABA from rice bran (Kim et al., 2015). GABA can be obtained with ultrasound and solvents, such as water and ethanol (Kim et al., 2013).

Pokkanta et al. (2019) reported bioactive compounds found in rice bran, including squalene, in of 3189 µg/g. RBO also consists of wax, which is a waste of wax esters and aliphatic alcohols such as policosanol. The main components of the policosanol mixture are 66% octacosanol, 12% triacontanol, 7% hexocosanol, and 15% of other alcohols, namely tetracosanol, heptacosanol, nonacosanol, and tetratriacontanol Policosanol supports human health in areas such as anti-aging, fat-lowering, cell regeneration, Parkinson’s disease, inflammation, and cancer (Shen, Luo and Lin, 2019). The crude wax from RBO improved the oxidative stability and properties of oleogel (Wang et al., 2021). The amount of policosanol in rice bran and bran’s wax is 9.81 g/100 g of rice bran and 10.82 g/100 g of bran’s wax, respectively (Ishaka et al., 2014). This compound is extracted after the wax separates from RBO using petroleum ether and NaOH, assisted by sonication. The yellowish middle layer is policosanol, while the upper and lower layers are the petroleum ether layer and NaOH layer, respectively (Ishaka et al., 2014).

Peptides consist of short-chain amino acids (2–9) linked by peptide bonds that generate distinctive functional properties related to physiological functions (Wang et al., 2017; Shobako and Ohinata, 2020). Functional peptides such as Leu-Arg-Ala, Tyr-Tyr, and Tyr-Ser-Lys are beneficial peptides derived from rice bran protein that are functional as anti-hypertensives (Shobako and Ohinata, 2020). The peptide fraction of rice bran has antioxidant activity (Mineo et al., 2021). On molecular docking simulation, pentapeptides of Glu-Aln-Arg-Pro-Arg isolated from rice bran proteins exhibit anti-COVID-19 activity and indicate anticancer activity (Gasymov et al., 2021). The study conducted by Wattanasiritham et al. (2016) showed the isolation of antioxidant peptides from rice bran hydrolysates. RP-HPLC fractionated the lyophilized rice bran hydrolysates, and the elution fractions were collected to obtain peptides.

Factors Affecting Bioactive Compounds In Rice Bran

The amount, ratio, bioavailability, and bioactivity of bioactive compounds differ greatly based on many factors. Rice varieties, milling degree and method, pre-treatment, and other processing all have an impact on the attribute and composition of rice bran, such as its physicochemical properties and bioactive compound content (Gul et al., 2015; Kalpanadevi et al., 2018; Kaur et al., 2021). The bioactive compounds are diverse among rice varieties, as shown by Huang and Lai (2016) where Tailabang black waxy rice bran has the highest total anthocyanins. The study also concluded that the degree of milling affects the rice bran’s bioactive composition, where the outer bran has high proanthocyanidins. Black rice bran has a thicker layer than red rice bran and thus requires a higher degree of milling to eliminate fat content. Removing the bran will also degrade the protein content of black rice and the bran in particular (Paiva et al., 2014).

The pre-treatment of rice bran, including the stabilization process, also affects the bioactive profiles of rice bran. Rice bran has a high-fat content and will be easily degraded because of endogenous lipase. This lipase can catalyze hydrolytic and oxidative oxidation that causes off-flavors and limits the utilization of rice bran (Liu et al., 2019). The stabilization process using a microwave at 78 ^{o}C for 6 minutes could retain the mineral composition of rice bran (Faria et al., 2012). Other processing methods used by Kim et al. (2014), such as dry-heating, freeze-drying, and autoclaving, affect free fatty acids and improve bioactive compound availability.

Unfortunately, there are not only favorable effects caused by processing, depending on the method of processing, but it can also lead to the opposite effects. The research by Zhao et al. (2022) revealed that soaking, heating, and high hydrostatic pressure could bring down the flavonoid contents of rice bran. Although it was said that phenolic content was increasing, those treatments caused diverse effects if applied together. The fermentation process could also boost the rice bran’s bioactive compounds. The fermentation process can produce many substances that are beneficial to health, such as amino acids, phenolic acids, and vitamins, subsequently increasing rice bran’s antioxidant activity (Jung et al., 2017; Nisa et al., 2019).

Conclusion

Rice bran contains bioactive compounds that have the potential to go much further than has been done thus far. It contains phenolic acids, flavonoids, anthocyanins, polymeric carbohydrates, GABA, etc., that were disclosed by many studies to have advantageous effects on health. Other than conventional solvent methods, green technology can be applied, such as UAE and MAE for compound separation from rice bran. In application, rice bran will go through processing that will affect the final product's bioactive compounds. It is critical to choose rice varieties, milling, and processing methods as they will determine the bioactive substance content at the end.

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Declarations

Conflict of interests The authors declare no competing interests.

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