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Review Article

Bioactive Compounds from Cereal and Pulse Processing Byproducts and Their Potential Health Benefits

Saini A, Panwar D, Panesar PS* and Bera MB
Food Biotechnology Research Laboratory, Department of Food Engineering & Technology, Sant Longowal Institute of Engineering and Technology, India

***Corresponding author:** Parmjit S. Panesar, Food Biotechnology Research Laboratory, Department of Food Engineering & Technology, Sant Longowal Institute of Engineering and Technology, India

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Abstract

An enormous amount of byproducts (bran, husk, germ meal etc.) is generated worldwide during the processing of cereals and pulses, which are a rich source of bioactive compounds. The major components include phenolic acids (ferulic, gentisic, p-hydroxybenzoic, gallic, sinapic, syringic, vanillic, caffeic, p-coumaric), dietary fibers (β-glucan), vitamins (thiamin, riboflavin, niacin, pantothenic acid) etc. These bioactive components are associated with various health benefits such as anti-inflammatory, antioxidant and anti-diabetic, anti-carcinogenic etc as well as modulation of the metabolic processes. This review provides comprehensive information about different types of bioactive compounds present in the byproducts produced from cereal and pulse processing industries and their health benefits.

Keywords: Bioactive Compounds; Cereal and Pulse Byproducts; Health Benefits

Introduction

Bioactive compounds are the phytoconstituents that are a part of food chain and are responsible for numerous beneficial changes in the human health such as antioxidant properties, anti-cancer, anti-inflammation, anti-allergenic, anti-atherogenic and anti-proliferative agents, depending upon the pathway and their bioavailability in the body. These compounds are found in plant, animal, marine and their byproducts, which are associated with various factors such as bioactivity, chemical structure, and dose etc [1]. Also, these compounds are known for their preventive action from many diseases.

In context to this, cereal and pulses are the major sources of energy and protein in the diet. Also, these bioresources contain a wide range of different bioactive compounds, vitamins, fibres and minerals. Most of the existing studies have focused on the bioactive compounds in fruits, vegetables and in their byproducts. However, some of the bioactive compounds are unique in nature and only present in cereals but cannot be obtained from fruits and vegetables [2].

Cereals (wheat, oat, rice, corn and barley) and pulses generate valuable byproducts during dry, wet milling, malting and pearling such as aleurone, pericap, germ, coat, husk, germ meal, shorts, spent grain, testa, hyaline and part of the endosperm which are a good source of potentially marketable bioactive compounds. These byproducts are intensely utilized in first valorization by extracting the bioactive compounds such as polyphenols, vitamins, flavonoids, dietary fibres etc. After that, it proceeds for the another valorization where it is generally associated to biorefinery concept [3]. This concept is involved to produce minimum waste and maximum utilization of different bioresources during processing. since, these cereal and pulse byproducts are the major sources for the production of value-added products such as functional foods, nutraceuticals and food additives and further it can be utilized in production of biofuels and energy etc rather than downgraded by using as a cattle feed or/and dispose in the environment directly [4] as shown in Figure 1. This review is focused on the bioactive compounds from the byproducts which are produced during milling and processing of cereal and pulses along with their health benefits.

Major Categories of Bioactive Compounds Present in Cereals and Pulses

Bioactive compounds are often produced in small quantities while their chemical structures, properties and functions vary widely. These compounds are synthesized by some primary metabolites (e.g. amino acids) or from intermediates obtained by primary metabolism in specialized cell types and only during a particular growth stage, or under specific conditions, make their extraction and purification quite difficult [5]. Commercially, the useful bioactive compounds (secondary metabolites) are terpenoids, polyphenols, vitamins, alkaloids etc. [6], which are utilized in the production of functional foods and pharmaceuticals.

Phenolic compounds

Phenolic compounds are important for their antioxidant properties and protection from degenerative diseases like cancer and heart diseases [7]. Phenolic acids are a group of the derivatives of benzoic and cinnamic acid such as capsaicin, ellagic, salicylic, tannic, vanillin, gallic, syringic, p-coumaric, o-coumaric, m-coumaric, caffeic, ferulic, sinapic, chlorogenic acids which occur in both forms (free and bound) [8]. Flavonoids are the compounds that consist of two aromatic rings joined by a three-carbon link. Also, flavonoids belong to different sub-classes such as anthocyanins, flavonols, flavanones, flavones and flavonols. Furthermore, lignans are a group of the dietary phytoestrogen compounds that are present in the cereals such as wheat, oat, corn and rye [9]. These polyphenolic bioactive compounds include lariciresinol, sacoisolariciresinol, pinoresinol, matairesinol and syringaresinol [8]. Another important group is alkylresorcinols (5-n-alkylresorcinols) which are 1, 3-dihydroxybenzene derivatives with an alkyl chain at position 5 of the benzene ring, indicate the

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Table 1: Some selected studies of bioactive compounds from cereal byproducts.

(Phytochemicals Categories) Compounds	Concentration	Sources	References
Vitamins		Wheat Bran	[39,40]
Thiamin	0.65 mg/100g		
Riboflavin	0.51 mg/100g		
Niacin	28 mg/100g		
Pantothenic acid	3.15 mg/100g		
Pyridoxine	1 mg/100g		
Folate	0.23 mg/100g		
Vitamin E		Coloured rice bran	
γ-tocopherol	10.76-28.43 mg/g DM		
α-tocopherolH	13.12-67.30 mg/g DM		
γ-tocotrienol	16.91-53.09 mg/g DM		
Total carotenoids	57.9 µg/g 32.0 µg/g 4.2 µg/g	Corn germ meal Corn bran Wheat bran	[41]
Lignan Betaine Phytosterols Choline	4.75 mg/100g 868 mg/100g 158 mg/100g 172 mg/100g	Wheat bran	[39]
Total carotenoids Caotenoid β-carotene	9.11 µg/g 0.74 µg/g 101 µg/100 g	Wheat germ Wheat bran Whole rice bran	[42,43]
Total anthocyanins	294.62 mg Cy3-GE/100 g DM 77.87 mg Cy3-GE/100 g DM 10.72 mg Cy3-GE/100 g DM	Black rice bran Red rice bran Brown rice bran	[27]
Total Flavonoids content	262.4 to 681.6 mg/100 g	Cereal milling byproducts (Bran, germ, shorts, husk, germ meal)	[41]
	358 ± 7.2 mg CE/100g dw	Defatted Rice bran	[44]
	3000-4300 µg/g	Wheat bran	[45]
	40.15-823.88 mg QE/100 g DM	Rice bran fractions	[27]
Phytosterols	4.73-2020 µg/g	Wheat Bran	[39]
Alkylresorcinol	489-1429 µg/g	Wheat bran	[46]
Dietary Fibre Soluble dietary fibres β-glucan	33.4-63.0% dm 344-2050 µg/g	Wheat bran Barley Bran	[47,48]
Phenolic compounds ferulic, gentisic, *p*-hydroxybenzoic, gallic, sinapic, protocatechuic, syringic, vanillic acids, and vanillin, Caffeic, *p*-coumaric	-	Rice bran biomass	[49]
Phenolic acid Ferulic acid	 1376-1918 µg/g	Wheat bran	[50]
Polyphenols Total phenolics Total flavonoids Caffeic acid Ferulic acid *p*-hydroxybenzoic acid *p*-coumaric acid	 14.90 ± 0.70 mg GAE/g 3.08 ± 0.17 mg CE/g 3.68 ± 0.14 mg/100g 33.64 ± 1.01 mg/100g 12.55 ± 0.93 mg/100g 265.4 ± 2.4 mg/100g	Rice Husk	[51]
Total monomeric phenolics	3454.4 ± 98.7 µg/g dw	Defatted Rice bran	[44]
Total phenolic content	1861.9 mg GAE/100 g 844.7 mg GAE/100 g 698.2 mg GAE/100 g 1925 mg GAE/100 g	Wheat germ Wheat bran Wheat shorts Corn bran	[41]
	10.55 mg GAE/g.	Defatted wheat germ	[52]
	4206.16 µg/g.	Wheat bran	[53]
	5698.8 to 6820.3 mg Ferulic acid/kg dw.	Different wheat bran fractions	[54]
	769.7±17.2 mg GAE/100g dw	Defatted Rice bran	[44]
	269.85 to 1214.7 mg GAE/100 g DM.	Rice bran fractions	[27]

GAE=Gallic Acid Equivalents

amphiphilic properties.

Carotenoids

Carotenoids are a class of more than 600 naturally occurring tetraterpenoid organic pigments synthesized by plants, algae, and photosynthetic bacteria which occur commonly in transform. These molecules are the source of colour like yellow, orange, and red [10] and have received attention because of their role as pro-vitamins and antioxidants. These compounds are classified into two classes, carotene (β-carotene, γ-carotene, α-carotene and β-cryptoxanthin) and xanthophylls (lutein, astaxanthin and zeaxanthin). Carotenoids are present in whole-grain cereals [11] whereas fruits and vegetables are the principal sources of carotenoids and its deficiency can cause many diseases such as night blindness, keratomalacia, xerophthalmia, corneal ulceration, scarring and at last irreversible blindness [12].

Phytic and oxalic acid

Phytic acid (myoinositol hexaphosphate; IP6) is the major source of phosphorus and its salts known as the phytates which can result in various health beneficial effects such as anticarcinogen and decreasing the risk of heart diseases or diabetes [13,14]. Phytic acid is an important seed constituent, which is present in all nuts, cereals (aleurone layer), legumes and oil seeds about 1-3% [15].

Oxalic acid [$(COOH)_2$] is present in many plants which occurs in the cell sap of the plant in the form of K or Ca salts. Legumes are the source of minerals but due to the phytates and oxalates, their bioavailability was observed lower than other food [16].

Phytosterols

Phytosterols are the combination of plant sterols and stanols, which are present in small quantities. Their structures are similar to cholesterol, differing only in the side chain group and/or presence or absence of the double bond. The most common phytosterols are β-sitosterol, stigmasterol and campesterol. These compounds are present in different legumes such as kidney bean, pea, chickpea and butter bean. Cereal products contain significant amount of plant sterols than vegetables. The level of these compounds varies in different cereals and in various parts of the kernel [17]. Various studies have shown that sterols and stanols are beneficial in preventing the colon cancer and decrease the cholesterol level [18].

Saponins

The ‘saponin’ term is derived from the Latin word sapo, means ‘soap’, because saponin molecules produce soap-like foams when shaken with water. These molecules are known as non-volatile, surface active compounds that are composed of lipid-soluble aglycone consisting of either a sterol or triterpenoid which are attached to water-soluble sugar residues differing in type and amount of sugars. Saponins have been reported in lupin, lentil, pea, black gram and beans while major sources of saponins are soybean and chickpea in the human diet [19-23]. Various studies suggest that saponins possess different properties such as anti-carcinogenic, hypocholesterolemic and immune-stimulatory [24,25].

Bioactive Compounds of Cereal Byproducts

Cereals mainly contain three parts such as endosperm, germ and bran. The main cereals are rice, oats, maize, barley, rye, sorghum, wheat, millet which consist of different phytochemicals including

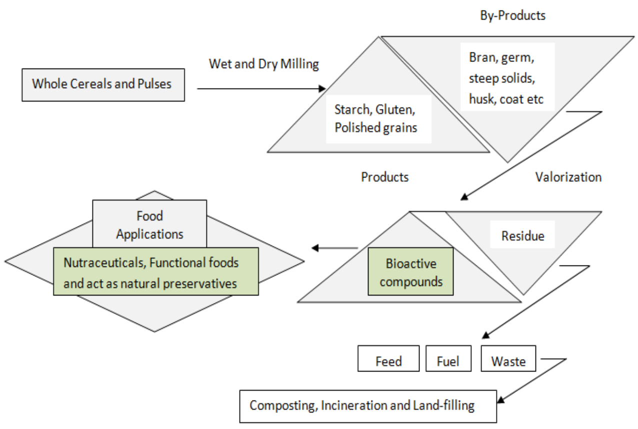

Figure 1: Schematic representation of bioactive compounds from cereal and pulse byproducts.

polyphenols, flavonoids, anthocyanin, carotenoids etc. Whole grains and their byproducts consist of dietary fibers (lignin/lignans, cellulose, β-glucans, and arabinoxylans), alkylresorcinols, phytic acid, avenanthramides, cinnamic acid, inositols, ferulic acid, γ-oryzanols, phenolic compounds, tocols and betaine and phytosterols which are present in small quantity as shown in Table 1. These polyphenolic bioactive compounds include lariciresinol, sacoisolariciresinol, pinoresinol, matairesinol and syringaresinol [8]. Generally, two main phenolic acids present in cereals are ferulic and p-coumaric acids [26]. Also, other phenolic acids and flavonoids are present in black, red and brown rice bran i.e. syringic acid, protocatechuic acid, cinnamic acid, myrecitin, catechin, luteolin, quercetin and apigenin [27]. Generally, concentration of flavonoids in cereals is less, except for barley that has the measurable amount and wide range of flavonoids present in sorghum [28].

Alkylresorcinols (5-n-alkylresorcinols) are plant-derived phenolic lipids that are synthesized by higher plant families and found in rye, wheat, wheat-rye and barley while they are absent in oats and edible parts of rice [29]. Moreover, avenanthramides are substituted cinnamic acid amides of anthranilic acids and these specific polyphenols are reported in oats which have anti-atherogenic, anti-inflammatory and anti-oxidant properties [30,31].

Dietary fibre like beta-glucan is the linear polymer which consists of glucose molecules connected by 70% of β-(1-4) and 30% of β-(1-3) linkages and found in the aleurone layer cells, endosperm and bran of grains [8,32]. Skendi et al. [33] and Marconi et al. [34] reported the range of β-glucan in cereal bran, which contains 5-24% (barley), 3-7% (oat) and 1% (wheat). Carotenoids are also present in whole-grain cereals such as alpha-carotene, beta-cryptoxanthin, beta-carotene, lutein and zeaxanthin [35].

Bioactive compounds are specific for some cereals in quantity such as beta-glucans in barley and oats, alkylresorcinol in rye and γ-oryzanol in rice etc. The outer layer of grains contains higher level of bioactive compounds [36]. Generally, bran and germ are removed during cereal processing. However, these byproducts are an important source of bioactive compounds and play a vital role in performing health benefits [8]. Products which have no bran and germ in their composition are often supplemented with such substances which

Table 2: Some selected studies of bioactive compounds from pulse byproducts.

Categories (Phytochemicals)	Concentration	Sources	References
Total phenols Free phenolics	1.75 ± 0.02 mgCatE/g 1.50 ± 0.05 mgCAE/g	Soybean hull Chickpea hull	[59,63]
Bound phenolics	0.33 ± 0.04 mgCatE/g 0.11 ± 0.02 mgCAE/g	Soybean hull Chickpea hull	
Total flavonoids Free flavonoids	0.73 ± 0.02 mgCatE/g 0.42 ± 0.02 mgCatE/g	Soybean hull Chickpea hull	
Bound flavonoids	1.21 ± 0.07 mgCatE/g 0.94 ± 0.03 mgCatE/g	Soybean hull Chickpea hull	
Total flavonoid content	1730 mg QE/100g 31.68-85.17 mg CE/g 104 mg CE/100g 2651 mg CE/ 100g	Black cowpeas seed coat Peanut seed coat Pea seed coat Pigeon pea seed coat	[64,65]
Carotenoids	0.415 mg/100g	Black gram seed coat	[60]
Anthocyanin	87 mg/100g	Black gram seed coat	[66]
Total Phenolic content	146 to 5798 mg/100 g DW 0.2 to 32.6 mg CE/g DW	Bean Coat Chickpea seed coat	[64,67]
C-Glycosylated flavonoids Vitexin	536.54 ± 7.94 μg/g 29.99 ± 2.36 μg/g 202.89 ± 5.57 μg/g 91.46 ± 1.39 μg/g	Black gram Husk Black gram Germ Black gram Aleurone Black gram Plumule	[68]
Isovitexin	1221 ± 15.47 μg/g	Black gram Husk	
	71.94 ± 4.34 μg/g	Black gram Germ	
	518.61 ± 10.13 μg/g	Black gram Aleurone	
	214.51 ± 5.64 μg/g	Black gram Plumule	

GAE= Gallic Acid Equivalents; RE= Rutin8 Equivalents; CE= Catechin Equivalents; QE=Quercetin Equivalents.

are biologically active [37,38]. Furthermore, research is required to identify the unknown bioactive compounds from waste and their utilization in value added products, their various properties and functions in the body.

Bioactive Compounds in Pulse Byproducts

India is the largest producer of pulses (around 25%) in the world and according to the United Nations general assembly, year 2016 has been declared as the international year of pulses [55]. Pulses are the important source of valuable nutrients such as carbohydrates, proteins and low in calories. It also supplies bioactive compounds, which have health benefits, and it may be negative and positive depending on the pathways, which perform their specific function in the body. The major pulses comprise of lentil (*Lens culnaris*), pigeon pea (*Cajanus cajan*), black gram (*Vigna mungo*), lupin (*Lupinus* spp.), kidney bean (*Phaseolus vulgaris*), green gram (*Vigna radiate*), chickpea (*Cicer arietinum*), moth bean (*Vigna acontifolia*), fieldpea (*Pisum sativum*), lima bean (*Vigna lunatus*) and rice bean (*Vigna umbellata*) and their waste, contains many bioactive components such as phytosterols, phytates, phenolic compounds, phytosterols, saponins and lectins (Table 2). Pulses are the foods which have a very low glycaemic index (GI: 28-52) and numerous studies have indicated that low GI foods in diet, decrease the risk factors for coronary heart diseases and benefits in dietary treatment [56,57]. Recent research is mainly focused on the development of value added products using pulses and replacement of energy intense products, which are the responsible for many negative health effects such as obesity etc [58]. Moreover, polyphenols of the pulses contribute to the colour, sensory characteristics as well as numerous biological properties [59]. These compounds are mainly present in seed coat of the pulses, which is generally removed during milling. During processing of the black gram, 25% of the black gram is removed as the by-product, which is rich source of polyphenols [60]. Authors are continuing their research in the direction towards the identification and quantification of bioactive compounds in pulses for their beneficial health effects. Choung et al. [61] reported the concentration of phenolic compounds in seed coats of kidney beans such as petunidin 3-glucoside, cyaniding 3,5-diglucoside, delphinidin 3-glucoside, pelargonidin 3-glucoside and cyaniding 3-glucoside are 0-0.17, 0-0.04, 0-2.61, 0-0.59 and 0-0.12 mg/g dry basis respectively. Another study has been investigated the research on the defatted lentil samples and reported that total phenolic content in free form (1.37-5.53 mg GAE/g), esterified form (2.32-21.54 mg GAE/g) and insoluble form (2.55-17.51 mg GAE/g) [62].

Health Benefits of Cereal and Pulse Byproducts

The byproducts are obtained after processing of cereal and pulse, which are rich source of various bioactive compounds. These compounds are allocated in free, bound and soluble-cojugated form in whole cereal grains. Numerous studies have been done for recovering the bioactive compounds from byproducts and their antioxidant properties which have high potential for providing various health benefits, e.g. anti-inflammation and anti-tumor activity by black rice bran. Although the incorporation of byproducts directly in different food products acts as the functional ingredient e.g. the wheat bran of four varieties have been added at different levels of concentration (0%, 12.5%, 25%, 37.5%) into the wheat flour and prepared snacks showed the improved oxygen radical absorption capacity due to addition of wheat bran [69]. The main reason for having interest in these functional compounds (polyphenols) is due to their synergistic antioxidative action, which protect from different diseases e.g.

neurodegenerative diseases. Another study was conducted in which different test foods samples such as high soluble fibre (barley alone), medium soluble fibre (mixture of barley and brown rice/whole wheat) and low soluble fiber (brown rice/whole wheat) were taken by the hypercholesterolemic men. The results concluded that total and LDL-cholesterols level were decreased significantly in high-soluble fiber diet (barley β-glucans) as compard to other diets [70].

The various pharmacological effects of rice bran derived products involve in decrement of total cholesterol, triglycerides, low-density lipoprotein cholesterol, aortic ester accumulation, hepatic thiobarbituric acid and increased in the high density lipoprotein cholesterol [71,72]. On the other hand, numerous epidemiological and intervention studies have concluded that whole cereals (germ and bran layer) are attributed for their combined effects which are beneficial for human health e.g. epidemiological data has recommended the consumption of dietary fibre (mixture of soluble and insoluble) which lowers the risk of cancer especially colon cancer [73,74]. Furthermore, phenolic lipids like alkylresorcinols (5-n-alkylresorcinols) which perform many functions by improving intestinal peristalsis, reduce the glucose absorption to blood and controlling the cholesterol transfer into blood [75,76]. Moreover, these compounds show the antibacterial and antifungal activities [77].

According to different studies, pulse consumption in diet, reduces the risk of cancer because of the presence of antinutrient content, fibre, antioxidant and micronutrients [78,79] Moreover, coronary heart diseases are related to the elevation in the triglycerides and cholesterol level in body and by consumption of pulses in diet, it has reduced the risk factors which are correlated with coronary heart diseases [80].

Many studies have indicated that regular use of pulses is associated with the weight management [81-83]. These bioactive compounds have potential health benefits such as anti-microbial, anti-inflammatory, anti-allergic, antioxidant and anti-diabetic, anti-ulcer, anti-carcinogenic, anti-atherogenic and anti-thrombotic which prevent from many infectious, cardiovascular, degenerative diseases and promote the vascular health [84-87]. These health effects are observed by consumption of pulses four times or more in a week compared with less than once a week, was associated with 11% lower risk of cardiovascular disease and 22% lower risk of CHD [88]. Therefore, bioactive compounds have various health benefits can be potentially used in nutraceutical, cosmetic, food, pharmaceutical applications.

Summary

Cereal and pulse processing industry is an important part of food industry, which generates the huge volume of byproducts throughout the year. These byproducts are generally considered as wastes and are either dumped or utilized as cattle feed. However, for their better utilisation, these can be used for recovering the bioactive compounds or can be directly used as natural preservatives in different food systems to increase their functional properties. Further, lot of research is being carried out in processing of food industry byproducts for production of functional foods either by using these byproducts as whole or using extract of bioactive compounds as replacer of synthetic additives.

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