

# Phytochemicals of Whole Grains and Effects on Health



Mehmet Sertaç Özer and Gamze Nil Yazici

**Abstract** Grains are important raw materials for staple food products in the diet. Since they are not only a good source of carbohydrate content, provides for daily energy intake, but also protein, vitamins B-complex source for an adequate and balanced diet. Moreover, in recent times, it was elucidated that whole grains involve several bioactive compounds namely phytochemicals. Phytochemicals are non-nutritive dietary bioactive compounds and secondary metabolites generated by plants to protect themselves against environmental stress or threats. Whole grain phytochemicals comprise of dietary fiber as  $\beta$ -glucan, arabinoxylan, inulin, resistant starch; phenolic compounds as phenolic acids, anthocyanins, tocopherols (tocotrienols and tocopherols), lignans, alkylresorcinols, carotenoids (lutein, zeaxanthin, etc.) and other phytochemicals as phytic acid, phytosterols,  $\gamma$ -oryzanol, avenanthramides, benzoxazinoids. Phytochemicals could improve health and/or hinder some chronic diseases by means of whose antioxidant, anticarcinogenic, antimicrobial, antimutagenic, and anti-inflammatory activities. Epidemiological studies support that consumption of whole grains and food products are related to decreasing the risk of coronary heart disease, type 2 diabetes, obesity, oxidative stress, and some cancer types. The phytochemicals are mainly present in outer layers of grains as germ and bran parts. For this reason, the content of whole grains phytochemical is higher than refined ones owing to the milling process. In some cases, the processing negatively affects the bioactive components but there are contradictory remarks and studies about the stability of phytochemicals during processing. This chapter will briefly discuss not only phytochemicals of whole grains and effects on health but also the effect of processing on whole grain phytochemicals.

**Keywords** Phytochemicals · Grains · Health · Processing · Bioactive compounds

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M. S. Özer (✉) · G. N. Yazici

Department of Food Engineering, Faculty of Agriculture, Cukurova University, Adana, Turkey

e-mail: [msozer@cu.edu.tr](mailto:msozer@cu.edu.tr)

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## Introduction

Cereals are edible seed and taxonomically belongs to *Poaceae* namely *Gramineae*, in other words, grass family (Jones and Engleson 2010; Gani et al. 2012). Dates from commencing of civilization, cereals are staple foods not only for human consumption but also livestock feed (Poutanen 2012; Gani et al. 2012). Since cereals are one of the main raw food material and fundamental energy sources which supply almost half of the energy for humans throughout the years in the world. Cereal-based foods could supply mostly the intake of the carbohydrate and dietary fiber (Poutanen 2012).

The main cereal grains are composed of wheat, rice, maize (corn), rye, barley, oats, triticale, sorghum, and millet (Slavin 2004). Among them, the most consumed ones are wheat, rice, and maize, despite oats, rye, barley, millet, and sorghum are more extensive in some countries based on cultural, climate (Seal 2006) and regional differences (Schaffer-Lequart et al. 2017). In this regard, the most important cereals for human nutrition are wheat in Europe, rice in Asia which corresponds to nearly half of the cereal consumption annually, maize in Central America and South America, millets and also sorghum in Africa (Poutanen 2012). According to recent data of the Food Agricultural Organisation, the ultimate forecast for production of cereal around the world in 2018 stands at 2595 million tonnes (Anonymous 2018a).

Whole grains comprised of three primary parts as the bran, endosperm, and germ (Jacobs and Gallagher 2004; Seal 2006) from outside to in and the relative ratios of these parts vary from one species to other species (Seal 2006). In this regard, all cereal grains contain a preservative hull and also the endosperm, bran, germ parts underneath of it. The germ part involves plant embryo and contributes lesser to the dry weight in many grains as 4–5% in wheat and barley typically, whereas the germ part in maize comprises higher ratios of the total grain quantitatively than other grains as wheat, oats, and barley (Slavin 2004). The germ fraction supplies critical nutrients which are needed to develop new plant and, rich in vitamin E, antioxidants, other phytochemicals and lipid-soluble compounds (Jones and Engleson 2010). The endosperm part is composed of about 75–80% of the kernel weight (Liu 2007), viz. the largest part of the grain (Jacobs and Gallagher 2004) and main energy sources for growing plants (Jones and Engleson 2010), during germination due to its high amount of starch content about 50–75% of the endosperm (Slavin 2004). The second largest part of the grain is the bran part (Jacobs and Gallagher 2004), which surrounds and covers the endosperm and germ fractions and preserves the grain from the weather, insects, molds, and bacteria (Slavin 2004). The outer bran layer is comprised of non-digestible, insoluble, inadequate fermentable carbohydrates like cellulose, hemicellulose, arabinoxylan and also other phytonutrients like polyphenols whereas germ and starch endosperm involve soluble fiber, resistant starches, fermentable oligosaccharides, lignin, polyphenols, oils, vitamins and minerals (Slavin et al. 2013).

Earlier times, the entire grains in other words whole grains were used by human (Poutanen 2012) and were the part of diet nearly for 10,000 years ago (Slavin 2004).

During those dates, people utilized gristmills which could not able to separate the bran and germ fractions from the endosperm completely (Slavin 2004). The endosperm was the most important fraction in terms of technological and scientific attention for food processing until the end of the past century (Kong and Singh 2008; Poutanen 2012). In the 1830s, Sylvester Graham was suggesting whole grain food beforehand the common availability of refined flour (Jacobs and Gallagher 2004). However, subsequent to using roller mill which separates more effectively bran and germ parts from the endosperm than gristmills by 1870s, it created a great demand for refined grain products (Slavin 2004), particularly in Western industrialized countries (Seal 2006). The utilizing of the rolling miller was a not only effective, profitable and simple way to supply refined grains (Jacobs and Gallagher 2004), but also they were thought higher characterization about nutritional, sensorial and also hygienical when comparing unprocessed grains (Vitaglione et al. 2008). Thus, most of the population has intake generally refined grain products for the last 100 years (Slavin 2004).

Health sides of whole grains are known for a long while. Dates back to fourth century BC, Hippocrates discerned the health benefits of whole grain bread. In the early 1800s to mid-1900s, scientists suggested whole grains could hinder constipation (Slavin 2004). In the early 1900s, there was claims and discussions about whether refining was proper. Refined grains made a contribution to vitamin deficiency diseases as pellagra and beri-beri. In 1937, discoveries of thiamin and niacin were the lacking factors cause these ailments was surprising. The restorative power of these substances causes a belief that nutritional value could be restored by enriching of refined grain products, what could be called as the “Wonder Bread” phenomenon. Walker, Burkitt, Cleave, and Trowell countered to this view by developing the notion that whole foods were healthful, yet they interpreted their ideas into statements about dietary fiber (Jacobs and Gallagher 2004).

Then, Trowell first proposed the ‘fiber hypothesis’, published in 1972, suggested that whole grain enable dietary fiber including derived from whole grains with other components which have affirmative effects on human health and therewith intake of whole grains augmented slightly. After that, this hypothesis has become ‘high fiber food’ hypothesis with the result of that ‘fiber’ has become the focus of public health suggestions (Seal 2006). Nowadays, there is a growing interest to outer layers of grains. Therefore, the importance of the whole grains was getting well understood on the health due to whose phytochemicals, vitamins and minerals content (Kong and Singh 2008; Poutanen 2012).

The progression of milling technologies could control extractions rates. The average extraction rate is nearly 75% in wheat and the rest of it namely, the bran fraction is separated and generally utilized for animal feed. The extraction rate also defines the composition of flour with regard to nutritional value (Hemery et al. 2007; Poutanen 2012). The relation between consumption of cereal based food and health outcomes is depends on various factors such as the variety of cereal, the form of the cereal such as whole grain or refined, the fiber and polyphenol content, micro-nutrient composition, and glycemic index. Epidemiological studies pointed consistently out that there is an association between cereal consumption, particularly

whole grain and preclusion of many epidemics of non-communicable diseases, but the mechanisms involved are still not well elucidated (Gibson et al. 2013).

Many different terms and explanations were utilized to define whole grains in the world, and these disparities made it difficult to comprehend of whole grains (Slavin 2004). “Whole grain” is an abbreviation of “whole cereal grain” for an American term (Jacobs and Gallagher 2004). The European countries were generally used ‘wholemeal’ term to describe a finely ground whole grain flour or whole grain bread. On the other hand, ‘whole grain’ term was utilized and described not only bread, cereal products, and also both finely and coarsely ground flour in the USA. In this regard, several definitions of whole-grain have been defined to provide a common comprehension of whole grains (Slavin 2004).

First of all, AACC (American Association of Cereal Chemists) members defined and agreed on whole grain term in 2000. According to this term, ‘whole grains should include intact ground, cracked or flaked caryopsis (seed or kernel), whose principal anatomical components endosperm, germ, and bran are present in the same relative proportions as they exist in the intact caryopsis’ (AACC 2000; Slavin et al. 2013). In this regard, whole grains involve all cereals and pseudocereals (Anonymous 2018b). In 2004 this description was adopted by the ‘Whole Grains Council’ (WGC) as whole grains or whole grains foods are made from kernel, in other words entire grain seeds, that comprise whose all main parts as germ, endosperm, and bran from the inside out, and nutrition values in the same ratios even if they expose to some processes like cracking, crushing, cooking, and/or extruding and rolling. In respect to this, they claimed that whole grains are composed of wheat and whose varieties such as spelt, einkorn, emmer, farro, Khorasan wheat, Durum wheat and also whose forms as wheatberries and bulgur; rye, oats (involving oat-meals), barley, maize (involving popcorn and whole cornmeal), rice (brown and coloured rice), millet, sorghum stated in other words milo, triticale, teff; pseudocereals (amaranth, buckwheat, quinoa) and some *Gramineae* members as Job’s tears, canary seed, fonio and montina (Anonymous 2004). In 2006, the AACC International Whole grains Task Force in a letter to FDA (US Food and Drug Administration) confirmed that whole grains are referred to not only whole grain cereals but also pseudocereals whose overall macronutrient composition is analogue with cereals (Jones and Engleson 2010). In 2009, the FDA identified whole grains ecologically with AACC but only endosperm part explained as most of the inner part of the kernel. In terms of FDA, whole grains include all grains and pseudocereals in a similar vein with AACC (Anonymous 2018b). Pursuant to term, whole grains may embody following cereals like wheat, rye, oats, barley, maize, rice, millet, sorghum, triticale, teff, bulgur and some pseudocereals such as buckwheat, amaranth, and quinoa. Nevertheless, in an agreement with AACC, WGC and FDA, legumes as soybean, chickpea; oilseeds as *sunflower seed, flax and chia* (Anonymous 2004). For regulation of the European Parliament and of the Council, whole grains describes as irrespective of characteristics produced at each stage of milling and end of the part has been only removed (Anonymous 2018b). Also, there is not a common idea about the extent of whole grains between other issuing bodies. According to Sweden health claim code of practice, whole grains comprise of only some cereals like wheat, rye,

oats, and barley. Danish Task Force added that different milling fractions of these grains are allowable on the condition that relative ratios of germ, endosperm, and bran must be the same as in the intact germ. In addition, pseudocereals, fresh maize flour, and popcorn are not accepted as whole grains. Health authorities of three Scandinavian countries (Sweden, Norway, and Denmark) approved some rules about the declaration of healthy foods as an intitle of Scandinavian Keyhole. Taking into consideration that they accepted the same cereals as whole grains except triticale. Furthermore, within this context, they declared the parts of whole grains which are exposed to dehulling, grounding, cracking, flaking as processed fractions should adding back to final product even if they are separated (Frølich and Åman 2010). Even though EFSA (European Food Safety Authority) elucidated health claims related to whole grains in 2010 (EFSA 2010). EU countries organized a consortium as 'HEALTHGRAIN' and come to an agreement with definition and content of whole grains, a nutritional recommendation as a guidance and labeling objectives in 2010 (Van der Kamp et al. 2014). In contrary to the updated AACCI definition, minimal losses during the processing of whole grain-based foods are allowed vis à vis this definition (Seal and Brownlee 2015). In this regard, during processing, only fewer than 2% of the grain and 10% of the bran losses are permissible for consistent quality (Anonymous 2018b).

Ever since the early 1980s, epidemiological studies continuously showed that people who eat more whole grains reduced the risk of certain chronic diseases (Schaffer-Lequart et al. 2017). Therefore, intake of whole grains and/or whole grain-based food products in the diet regularly is related with enhancing health and playing a role with preventing the risk of some health diseases such as cardiovascular disease, hypertension, obesity, type 2 diabetes, metabolic syndrome and some types of cancer (Borneo and León 2012). This notion is still remarkable, even after adjustment for dietary fiber (Ye et al. 2012; Schaffer-Lequart et al. 2017). Moreover, recent studies showed that intake of plant-based bioactive compounds as a complex mixture of whole grains, fruits, and vegetables could be more beneficial and healthful than individuals isolated compound (Liu 2007; Slavin 2013) by showing synergistic effects (Gani et al. 2012). Thus, it is recommended that people should consume a wide variety of plant-based foods daily in order to get the highest health benefits (Liu 2013). Therefore, several states, non-profit organizations, trade, and industrial communities non-profit health, and industrial and trade groups have supported the consumption of whole-grains more than the last 35 years (Slavin 2004). Nevertheless, there has been no worldwide standard of what involves a “whole-grain food in spite of defining the “whole grain” term properly. Thus, it is creating challenges for not only researchers, the food industry, regulatory authorities, but also consumers all over the world (Ferruzzi et al. 2014). To develop a definition for whole-grain foods that could be accepted worldwide and applied to dietary recommendations and planning was issued by the U.S. Dietary Guidelines Technical Advisory Committee (DGTAC) as part of the 2010 Dietary Guidelines for Americans (DGA)” (Ferruzzi et al. 2014). In 2010, the Dietary Guidelines Advisory Committee (DGAC) calls for the development of criteria for labeling whole grain foods to reduce confusion both for researchers and consumers. To ensure that products labeled with a whole grain

health claim will provide substantive amounts of whole grains, it must be the first ingredient listed on the ingredient label, meaning it makes up 51% of the product by weight. Also, most of the whole grains could be processed as grinding, cooking, parboiling, extruding, pearling, rolling, and milling and terms are not put in order, therefore, it could be ambiguous. Due to most whole grains are processed, the FDA acts in concert with the AACC and established a labeling definition. To be considered a “whole grain,” each of the principal components of the grain as endosperm, germ, and bran must be present in the same relative proportions as they exist naturally in the seed (Harris and Kris-Etherton 2010). So the ratios of whole grains in whole grain foods for the health claims are different between some countries (Van der Kamp et al. 2014). Therefore, many countries try to find a common way to describe whole grain food products (WGFP) to be labeled (Slavin et al. 2013). In the USA and the UK, WGFP must contain equal or greater than 51% whole grain ingredients on a wet weight basis. In Denmark and Sweden, the minimum level of whole grains is 50% whole grain in dry weight basis. Moreover, this level is higher than others in Germany and their whole grain wheat and rye bread includes 90% whole grain (Van der Kamp et al. 2014), whereas pasta 100%. Recently, AACCI approved that WGFP must contain equal or more than 8 g whole grain for per 30 g end product (Slavin et al. 2013).

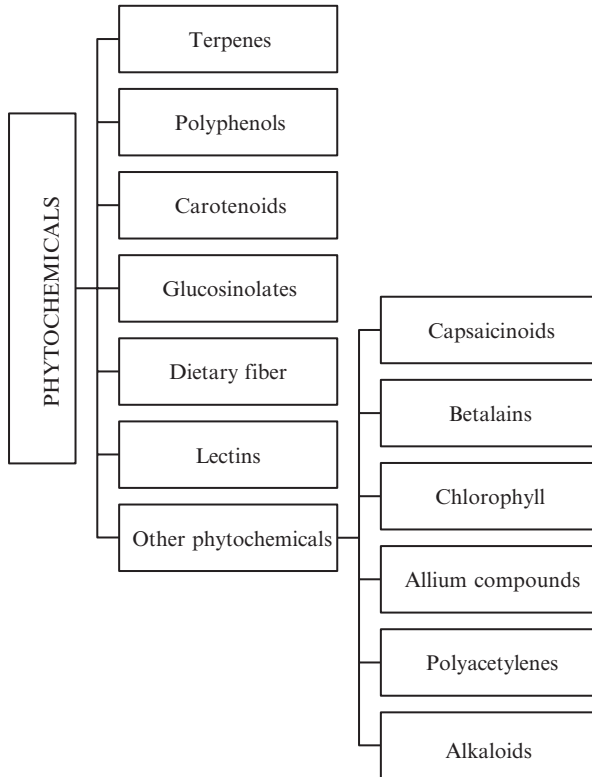
## Whole Grain Phytochemicals

“Phytochemical” term is derived from the league between the words “chemical” and *phyto*, which means plant in Greek (Liu 2013), and named as also plant bioactive substances (Gani et al. 2012). They are plant-based non-nutrient bioactive compounds that have health-enhancing benefits to decrease the risk of major chronic disease beyond whose nutritional values (Slavin et al. 2013; Liu 2013; Rebello et al. 2014; Abuajah et al. 2015; Zhu and Sang 2017). Upwards of 5000 phytochemicals have been isolated and defined in plants like grains, fruits, and vegetables however it is predicted that wide range and a large quantity of them are still remains unknown (Liu 2013). According to another study, this value is over 900 (Abuajah et al. 2015).

As seen in Fig. 1, phytochemicals are generally divided into terpenes, polyphenols, carotenoids, glucosinolates, dietary fibers, lectins and other phytochemicals such as capsaicinoid, betalains, chlorophyll, allium compounds, polyacetylene, and alkaloids.

Health beneficial whole grain phytochemicals are mostly present in germ and bran parts (Liu 2007; Slavin et al. 2013) and distributed as bound, free and soluble-conjugated forms (Liu 2007).

Many studies stated that the combination of biologically active compounds in whole grains which are generally located in germ and bran fractions could be more effective than individual isolated compounds (Gani et al. 2012). In many epidemiological researches, analysis of data attained that intake of whole grains and its compounds, namely bran, germ, and endosperm, demonstrated an independent relation



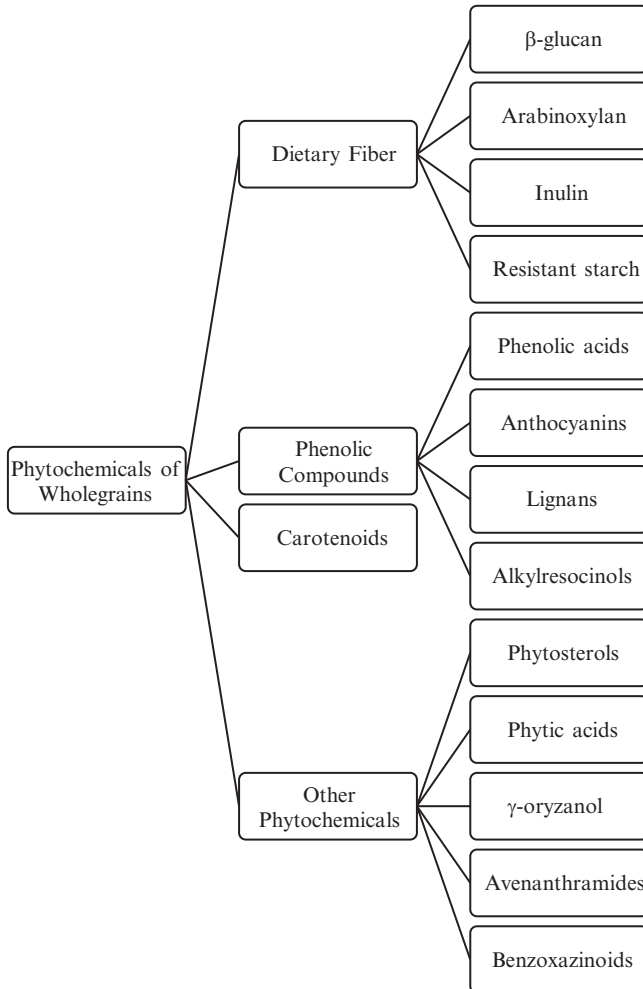
**Fig. 1** The general classification of phytochemicals

only for the wheat bran (Stevenson et al. 2012). Thus, the bran is a key factor in identifying the health benefits of whole grain (Călinoiu and Vodnar 2018).

The phytochemicals present in fruit and vegetables are analogue to whole grains (Craig 1997; Craig and Beck 1999). Phytochemicals of whole grains are generally subdivided as dietary fiber, phenolic compounds, carotenoids and other phytochemicals such as phytic acid and phytosterols as seen in Fig. 2.

### ***Dietary Fiber***

The carbohydrates which are found in whole grains could be separated into two different groups, based on the ability of digestion in the human digestive system. Principally, the small bowel enzymes are not capable of the digest any complex carbohydrates present in whole grains except starch. Starch could only digestive by amylases that present in the human digestive system. In fact, non-digestibility is based upon the definition of dietary fiber. Non-digestible complex polysaccharides



**Fig. 2** The general classification of whole grain phytochemicals

are constituted non-starch polysaccharides (NSPs) and oligosaccharides (OS). Also, non-starch polysaccharides of whole grains are subdivided into two main groups due to whose solubility in water as soluble and insoluble non-starch polysaccharides, or in other names “soluble fiber” and “insoluble fiber” (Borneo and León 2012).

NSPs involve all the plant polysaccharides except that starch which is the key compounds of the cell walls of grains. The main NSPs are cellulose,  $\beta$ -glucans, pentosans, pectins, heteroxylans, and xyloglucan that could not be hydrolyzed by the human endogenous enzymes. NSPs together form a major part of the dietary fiber of grains, dietary fibers is chemically described as non-starch polysaccharides by a majority. The physiochemical features of NSPs such as water dispersibility and



water holding capacity, viscosity and fermentability into short chain fatty acids (SCFAs) correspond to dietary fiber (Kumar et al. 2012).

Dietary fibers (DF) are the edible fragments of plants or similar carbohydrates that are resistive to digestion by human digestion enzymes, absorbed in the small intestine and partially or completely fermented in the large bowel (Okarter and Liu 2010; Bartłomiej et al. 2012). According to the dietary fiber definition of AACCI, DF includes “cell wall polysaccharides (polysaccharides, oligosaccharides), lignin and associated substances resistant to hydrolysis by the digestive enzymes of humans”. In this definition, “associated compounds” are subsumed for the first time in an official definition of dietary fiber (Vitaglione et al. 2008; Borneo and León 2012). Definition of dietary fiber was updated in 2008 by the Codex Committee on Nutrition and Foods for Special Dietary Uses (CCNFSDU). In their definition, the dietary fiber involves also polysaccharides composing of ten or more monomers but it could be reduced to three depending on local regulations. Dietary fiber composes of three main categories of polysaccharides as the first one is polymers which are intake in the natural form with foods, the second one is polymers extracted from raw foods by physical, chemical and enzymatic methods and the last one is synthetic polysaccharides (Cummins et al. 2009; Bartłomiej et al. 2012). Dietary fibre could be subdivided into two main categories due to whose water solubility as water soluble and water insoluble (Charalampopoulos et al. 2002). The water-soluble fibres are mainly composed of  $\beta$ -glucans, arabinoxylan, gums, pectin and mucilage whereas the water-insoluble fibres are comprised of lignin, cellulose, and hemicellulose (Charalampopoulos et al. 2002; Abuajah et al. 2015). Among the cereals, rice involves almost no soluble fibre and wheat has a low level in soluble fibre than most grains (Slavin 2004). Each category ensures different therapeutic effects. In this regard, soluble fibre decelerates intestinal transit, retards gastric emptying, and decreases glucose and sterol absorption by forming a viscous solution. Also, soluble fibre reduces serum cholesterol, insulin and postprandial blood glucose contents (Charalampopoulos et al. 2002) and improves glucose response, whereas insoluble fibre is related to enhance laxation (Slavin 2004).

Whole grains are good reserves of dietary fibers (Liu 2007). Rye, oats, and barley involve approximately one-third soluble fibre and residual part is insoluble fibre when comparing the content of dietary fibre in whole grains (Slavin 2004). The fiber content of the whole wheat grains ranges between 11.6% and 12.7% in dry weight based and most of them are located in the outer layers of the grain as pericarp and seed coat which is usually known as bran (Stevenson et al. 2012). According to another study, dietary fiber contents in wheat grains range from 11.6 to 17.0 g/100 g and lower than wheat bran (36.5–52.4 g/100 g) based on dry matter (Zhu and Sang 2017). Also, the content of soluble fiber in wheat is considerably fewer than in other cereal grains such as barley and oats, 3–11% and 3–7%, respectively (Stevenson et al. 2012). The content of soluble fibre in barley, rye, and oats is much higher than wheat (Seal 2006). Additionally, the refining process results in removing proportionally more of the insoluble fibre than soluble fibre in grains (Slavin 2004).

Dietary fibers are important compounds for a healthy diet. Consumption of whole grain-based dietary fibers are related with lowering the risk of chronic

diseases and has a protective role on coronary heart disease some type of cancers, diabetes, insulin resistance, weight gain, and metabolic syndromes. All these effects are associated with several physiological mechanisms that contain eliminating or binding cholesterol and bile acids, alleviation of hormonal activity, induction of the immune system, enabling toxicant transit through the digestive system, generation of SCFAs in the colon, reducing glycemic index and calorific value of foods, developing insulin response, providing scavenging free radicals and bulk in foods (Liu 2007).

Whole grains are reserves of fermentable carbohydrates as dietary fibre, resistant starch, and oligosaccharides. Indigested carbohydrate which arrives the colon is fermented to SCFAs and gases by the intestinal microflora. SCFAs involve butyrate, acetate, and propionate. Among them butyrate is mainly favored by the colonic mucosa cells (Slavin 2004) because of being fuel for them and also contributes to faecal pH, affecting colonic function (Stevenson et al. 2012). Production of SCFAs results in physiological alters to the colonic contents influencing water retention capacity, bulking and viscosity (Stevenson et al. 2012) therefore, reducing serum cholesterol and cancer risk (Slavin 2004). Cereal-based foods are also a significant source of dietary fiber. For instance, a slice of 40 g of white bread could supply approximately 1 g of dietary fiber, whereas a similar slice of whole grain bread could supply about 3–4.5 g of dietary fiber. In this regard, the different choice of bread type has an important effect on obtaining dietary fiber. Also, by taking into consideration of these data, consumption of six portions of whole meal bread could provide close to the suggested intake of dietary fiber of 25–35 g/day (Poutanen 2012).

## **$\beta$ -Glucan**

(1 $\rightarrow$ 3,1 $\rightarrow$ 4)- $\beta$ -D-Glucans, which are generally known as  $\beta$ -glucans, consist of D-glucopyranose residues (Bartłomiej et al. 2012).  $\beta$ -glucan is a complex carbohydrate that consists of linear polymers of glucose molecules linked each other by account for 70% of  $\beta$ -(1–4) and 30% of  $\beta$ -(1–3) glycosidic bonds (Liu 2007; Okarter and Liu 2010; Borneo and León 2012). Due to these bonds,  $\beta$ -glucan is more soluble, viscous and flexible than cellulose (Liu 2007; Gani et al. 2012). Put it differently,  $\beta$ -glucans are polysaccharides which are comprised of glucopyranosyl units (Zekovic et al. 2005; Okarter and Liu 2010).

In cereals,  $\beta$ -glucan is one of the non-starch polysaccharides which is the component of cell walls (Ahmad et al. 2012) and content is affected by mainly genetic as their genotypes or waxy, non-waxy varieties; and also environmental factors like heat stress, available water content during maturation, moisture content, fertilizer implantation (Brennan and Cleary 2005), the existence of hull fraction and amylose content (Fardet 2010).

$\beta$ -glucan content of whole grain wheat is generally lower than 1% on a dry weight based, and so whole grain wheat is not recognized as a source of  $\beta$ -glucan (Charalampopoulos et al. 2002). Among the cereals, particularly barley and oats are

dietary fiber source (Ahmad et al. 2012). Therefore it could be assumed as a marker for whole barley or whole oats because this compound is the characteristic phytochemical for them (Okarter and Liu 2010). Barley and oat  $\beta$ -glucans present in the walls of the endosperm cells which environ starch, protein matrix and lipid sources of the grain (Gangopadhyay et al. 2015). The ratio of dry matter based total  $\beta$ -glucan content is 3.0–27.17% (w/w) in whole grain barley. The water-soluble  $\beta$ -glucan in whole grain barley is 0.5–8.3%, whereas higher in whole grain oats 3.9–7.5%, and also the water-insoluble  $\beta$ -glucan content is 1.2–21.7% (w/w) in barley, while 5.2–10.8% in dehulled oats (Fardet 2010). Moreover, it is indicated that  $\beta$ -glucan is mainly located in the aleurone layer in oats whereas becoming intense in the endosperm fraction in barley. Besides, fewer amounts of the  $\beta$ -glucan present in rye (1–2%) wheat less than 1%, and also only trace quantity of  $\beta$ -glucan are stated in maize, rice, sorghum and other cereals (Liu 2007; Gani et al. 2012). Beforehand,  $\beta$ -glucan is only known as a component of the cell wall, but today  $\beta$ -glucan is linked with beneficial effects on human health.

$\beta$ -glucan is the primary bioactive component an which is liable for reducing the serum and plasma cholesterol, particularly from oat bran (Liu 2007; Gani et al. 2012). Relevant researches are encouraged that intake of  $\beta$ -glucan during 1 month could reduce total cholesterol level account for 10% and LDL cholesterol for 8% (Liu 2007).

In generally, researches indicate that  $\beta$ -glucan could also reduce or attenuate postprandial glycemic and insulin responses (Wood 2007; Gani et al. 2012; Sibakov et al. 2013). In this regard, consumption of  $\beta$ -glucan could be related with lowering risk of insulin sensitivity, type 2 diabetes by, controlling blood sugar in diabetes (Gani et al. 2012), and also coronary heart disease and metabolic syndrome (Wood 2007). These are attributed to whose feature of high viscosity as a soluble fiber to bind cholesterol and facilitate their elimination from the body (Liu 2007), and retarding gastric emptying that permitted dietary sugar to absorb stepwise, as well as by probably augmenting insulin sensitivity, respectively (Liu 2007; Gani et al. 2012). Also, it is predicted that a reduction in cholesterol content in blood serum by 1% eventuate in decreasing the coronary heart disease risk by 2% (Bartłomiej et al. 2012).

Other researches also identified that  $\beta$ -glucan, especially obtain from oats plays a role in the management of body-weight and reducing blood pressure (Gani et al. 2012). Like arabinoxylans,  $\beta$ -glucans could be fermented by bacteria localize the large bowel which could enhance the SCFAs formation (Bartłomiej et al. 2012). It was elucidated that oat-based foods are proper for the lactic acid bacteria which are capable of producing exopolysaccharides (EXP). This attributes to behaving like dietary fiber because of whose capacity of withstanding to degradation by gastrointestinal enzymes (Lambo et al. 2005). Moreover,  $\beta$ -glucans have a high water-binding capacity (WBC) thereby contributes to removing detrimental carcinogenic substances from colons faster, thereby scanting the colorectal cancer risk (Bartłomiej et al. 2012).

Therefore, the Food and Drug Administration (FDA) declared that consumption of oat and its products should be used to decrease hazard of heart disease and

advanced that 3 g of  $\beta$ -glucan from oats could reduce total cholesterol. After that FDA permitted to utilize  $\beta$ -glucan in food products in case of made taking part in label compulsory (Liu 2007; Okarter and Liu 2010; Ahmad et al. 2012).

## Arabinoxylan

Arabinoxylans (AX) are polymers of pentoses and herewith they are titled with 'pentosans' term (Bartłomiej et al. 2012). AX is hemicellulose which is one of the most plenteous cell wall polysaccharides of cereal grains after cellulose (Ragaei et al. 2013). Also, total arabinoxylans and water extractable arabinoxylans are most abundant in the bran fraction of whole grains (Bartłomiej et al. 2012). Arabinoxylans (AX) was for the first time defined in wheat flour in 1927 (Bartłomiej et al. 2012). Arabinoxylan is the main component of wheat, rye and rice bran fiber complex (Sibakov et al. 2013). Quantification of AX in wheat, rye, barley and oat bran range between 9.0–18%, 12.1–14.8%, 4.8–9.8% and 4.0–13.0% in dry based, respectively (Bartłomiej et al. 2012). According to another research, AX content is higher in rye correspond to 9.1% and following with wheat (7.3%) (Ragaei et al. 2013), barley, oats, rice and sorghum (Cui et al. 2013). When comparing with the flour forms the whole rye grains flour has the highest AX content varied from 3.1% to 4.3% in dry weight based following with whole wheat grain flour, barley grain flour and oats grain flour account for 1.7–2.0%, 1.4–2.25% and 0.35–1.25% in dry matter based, respectively (Bartłomiej et al. 2012). Arabinoxylans have the health improving effects and also antioxidant capacity based upon the presence of phenolic groups of ferulic acid that is mainly comprised of AX. Ferulic acid could be the ester form and either bond. Therefore it could participate in cross-links between polysaccharides or between polysaccharides and lignins that cause AX more resistant to digestion. The cross-linking arises from dimerization of ferulic acid residues caused by photochemical reactions or reactions between free radicals (Bartłomiej et al. 2012).

## Inulin

Inulin is a polymer of fructose units whose degree of polymerization ranged between 2 and 60 (Ragaei et al. 2013), and the link between fructose units in inulin is a  $\beta$ -(2–1) glycosidic bonds (Liu 2007).

Inulin non-digestible dietary fiber and so has prebiotic properties which enable to grow benefits probiotics also known as microorganisms are good for the gastrointestinal system (Liu 2007; Borneo and León 2012). Because inulin puts up resistance to hydrolyzation by human digestive enzymes due to its glucosidic bridge (Ragaei et al. 2013). Therefore, inulin is a source for probiotics as lactobacilli, and bifidobacteria in the intestine because induce the growth and enhance the balance of these bacteria in the bowel. Among them, bifidobacteria could hinder the growth of detrimental bacteria, to promote the immune system, and to the synthesis of vitamins

B complex and enable the absorption of minerals. When bifidobacteria digest inulin, short chain fatty acids, like propionic acid, acetic acid, and butyric acids emergence. Acetic acids and propionic acids contribute as an energy source for the liver, whereas butyric acids have cancer prohibiting properties in the bowel. Beside, inulins could enable the absorption of some minerals such as magnesium, calcium, and iron in the colon because of the formation of SCFAs. Among them, calcium and magnesium are significant regulators for cellular activity. In high concentrations calcium could assist the formation of insoluble bile or salts of fatty acids and so could decrease the harmful effects of fatty acids or bile on colon cells (Liu 2007).

### **Resistant Starch**

Starch is a polymer of glucose units linked by  $\alpha$ -(1–4) bonds and composes of amylose and amylopectin fractions. Starch could be degraded by  $\alpha$ -amylases yet, some of them could not easily digest and put up “resistant” to amylolysis (Borneo and León 2012). Resistant starch (RS) is resistant to digestion in the upper intestinal and so pass through the large intestine to be fermented by the colonic microflora (Liu 2007). And similar with oligosaccharides, particularly fructooligosaccharides supply fermentable carbohydrates for colonic microflora (Charalampopoulos et al. 2002). By this means, they produce short-chain fatty acids like acetate, butyrate, and propionate to enhance colon health (Liu 2007). Therefore, resistant starch act as prebiotics for reducing the risk of intestine diseases (Charalampopoulos et al. 2002). Besides, they use to reduce the caloric content of foods by not only providing lower calorie intake but also modulating lipid metabolism by promoting lipid oxidation in human subjects (Higgins et al. 2004). Moreover, they moderate blood sugar levels and in this way, they could decrease the risk of diabetes, heart disease, and other chronic health diseases (Liu 2007). Resistant starches subdivided into four types as RS1, RS2, RS3, and RS4. RS1 states for physically inaccessible trapped starch and mainly present in and unprocessed cereal grains, seeds, and legume; RS2 express to ungelatinized starch and natural raw starch; RS3 represents for retrograded starch form and RS4 refers to chemically modified starches (Borneo and León 2012). In recently, RS5 is also included and originates in formation of amylose-lipid complexes (Raigond et al. 2015).

### ***Phenolic Compounds***

Phenolic compounds have chemically one or more aromatic rings with one or more hydroxyl groups. They are the outputs of secondary metabolism and have crucial roles as in the growing up and reproduction of plants, behaving as defensive mechanisms against parasites, pathogens, predators, UV radiation and also making a contribution to the color of plants. Together with their functions in plants, in human diet

obtain health benefits related to protection and/or decrease in risk of chronic diseases (Liu 2007, 2013; Gangopadhyay et al. 2015).

Phenolic compounds are mainly classified into phenolic acid flavonoids stilbenes, coumarins, tannins, and anthocyanins. Phenolic acids and flavonoids are the most common phenolic composites which are present in whole grain cereals (Liu 2007; Gani et al. 2012; Gangopadhyay et al. 2015).

The content of phenolic compounds in whole grains vary by depending on grain type, genotype/varieties, part of the grain sampled, handling, and processing types of grains (Liu 2007; Gangopadhyay et al. 2015). Bran fraction, phenolic compound content is approximately 15–18-fold higher than the endosperm fraction that composes of 17% from the content of total phenolics. Thus, total phenolic content and implicitly the total antioxidant activity slightly reduce from the aleurone layer to the internal parts of the grain (Călinoiu and Vodnar 2018).

## Flavonoids

Flavonoids are constituted C6–C3–C6 skeleton that comprises of aromatic rings. They are a large group of polyphenolic compounds (Gangopadhyay et al. 2015) and classified into five main subgroups as anthocyanins, flavones, flavanones, flavonols, and isoflavonoids (Gani et al. 2012). Until today, more than 4000 flavonoids determined in nature (Liu 2013) and notified that they have antioxidant, anticancer, anti-inflammatory, anticarcinogenic, antiallergic properties and preservative feature of the gastrointestinal system (Gani et al. 2012). Flavonoids correspond with nearly two-third of the phenolics in our diet and the remaining one third are from phenolic acids (Liu 2013).

Nevertheless, cereals contain a few amounts of flavonoids (Gangopadhyay et al. 2015) except barley that includes measurable contents of catechin and some procyanidins (Gani et al. 2012). Up to the present, there are a few researches about flavonoid contents of whole wheat grains. Latest studies stated that flavonoids are mainly C-glycoside form as particularly apigenin-C-diglycosides (Zhu and Sang 2017). Flavonoids are present in the pericarp fractions of all cereals. It was reported that among cereals, sorghum has the broadest varieties of flavonoids (Gani et al. 2012). Flavonoid contents in different wheat varieties are varying between 740 and 940  $\mu\text{mol}$  of catechin equiv/100 g, whereas 60 and 80  $\mu\text{mol}$  of catechin equiv/100 g in endosperm fraction (Zhu and Sang 2017).

## Phenolic Acids

Phenolic acids are classified into two main groups as hydroxycinnamic acid and hydroxybenzoic acids and whose derivatives (Liu 2013), based on C3–C6 and C1–C6 skeletons, respectively (Călinoiu and Vodnar 2018). Hydroxybenzoic acid derivatives contain protocatechuic, *p*-hydroxybenzoic, vanillic acid, gallic acid, syringic acid, besides the hydroxycinnamic acid derivatives involve in ferulic acid,

*p*-coumaric acid, caffeic acid, and sinapic acid (Liu 2007, 2013; Călinoiu and Vodnar 2018).

The phenolic acids in cereals could be in both bound and free form. Free phenolic acids are mainly present in the outer layer of the pericarp whereas bound phenolic acids are esterified to cell walls and also acidic or basic hydrolysis is needed to set free of these bound compounds from the cell matrix (Gani et al. 2012; Gangopadhyay et al. 2015). Hydroxybenzoic acid derivatives are generally found in the bound form and they are typically compounds of complex structures like lignins and hydrolyzable tannins. They could also present as derivatives of organic acids and sugars in plant-based foods. Hydroxycinnamic acid derivatives are also found in the bound form and linked to cell wall structural compounds like cellulose, lignin, and proteins through ester bonds (Liu 2007).

The widest variety of phenolic acids found in millet and sorghum (Gani et al. 2012). One of the main phenolic compounds of whole grain cereals is phenolic acids and predominantly ferulic acid (trans-4-hydroxy-3-methoxycinnamic acid) which is hydroxycinnamic acid derivatives and mainly present in aleurone, pericarp, and embryo cell wall in whole grains (Ragaee et al. 2013). Ferulic acids are mainly present in the leaves and seeds of plants, generally covalently combined with plant cell wall polysaccharides as insoluble carbohydrate biopolymers, lignin, fibers, glycoproteins and polyamines (Liu 2013). In whole grain cereals, ferulic acid could be present in free, soluble (conjugated) or insoluble (bound) forms (Borneo and León 2012; Călinoiu and Vodnar 2018), and generally bound ferulic acids are the dominant form in grains (Liu 2013) account for more than 93% of the total ferulic acid content (Okarter and Liu 2010). The ferulic acid concentration is highest in whole grain corn when comparing with other grains and following by wheat, oat and rice and correspond to (Ragaee et al. 2013), 906  $\mu\text{mol}$  ferulic acid/100 g, 333  $\mu\text{mol}$  ferulic acid/100 g, 185  $\mu\text{mol}$  ferulic acid/100 g, and 154  $\mu\text{mol}$  ferulic acid/100 g, respectively (Okarter and Liu 2010). After the ferulic acid, the most common phenolic acids are vanillic acid, syringic acid and *p*-coumaric acid in wheat bran (Ragaee et al. 2013). The content of total vanillic acid is ranged between 8.4 and 12.7  $\mu\text{g/g}$ , total syringic acid is ranged from 8.9 to 17.8  $\mu\text{g/g}$ , and the total *p*-coumaric acid is ranged from between 10.4 and 14.1  $\mu\text{g/g}$  (Moore et al. 2005; Okarter and Liu 2010). The almost total content of ferulic acid (98%) is localized the aleurone and the pericarp fractions of wheat grain (Călinoiu and Vodnar 2018). The concentration of ferulic acid ranges from 535 to 783 mg/kg in mature grains. Ferulic acid could be present in free and also esterified forms as ferulic acid dehydromers (DiFA) whose relative concentration is 808 mg/kg (Shahidi and Nacz 2003).

The antioxidant activity of wheat grain fractions is adversely relevant to the aleurone content owing to its high concentration in hydroxycinnamic acids, the principal one being the ferulic acid. The bioavailability of the ferulic acid is restricted because of whose powerful boundary with indigestible cell wall material in grains (Călinoiu and Vodnar 2018). Stages of food processing, like fermentation and thermal processing such as pasteurization, and freezing unleash free and

soluble-conjugated ferulic acids from bound phenolic acids (Dewanto et al. 2002; Liu 2013). In a study, subject to wheat whole grain to alkaline hydrolysis showed that germination could increase phenolic acid content. According to results ethanol soluble ferulic acid, *p*-coumaric acid and syringic acid composition are 3 mg/kg, 1 mg/kg, 2 mg/kg respectively in ungerminated grains whereas 26 mg/kg, 8 mg/kg, 8 mg/kg in a consequence of 48 h germinated grains. Moreover, it was added that the highest phenolic acid content is reached after nine days of germination process (Shahidi and Naczki 2003).

Phenolic acids are known as their antioxidant activity and that is an association with health benefits (Borneo and León 2012).

### Anthocyanins

Another study pointed out that cyanidin-3-galactoside and peonidin-3-glucoside are also determined in purple and blue wheat as anthocyanins. Average total anthocyanins content is approximately 100 mg/kg in purple whole wheat, 150 mg/kg in blue whole wheat whereas 5 mg/kg in red whole wheat (Zhu and Sang 2017).

In colored maize, the most common anthocyanins are cyanidin, pelargonidin, and peonidin, which are mainly present in the pericarp and aleurone layer of the endosperm (Suri and Tanumihardjo 2016).

### Tocols

Tocopherols and tocotrienols, which are widely named as tocols are chemical components also known as vitamin E (Bartłomiej et al. 2012). They are lipid-soluble compounds that involve a phenolic-chromanol ring bond to an isoprenoid side chain that could be saturated viz. tocopherols or unsaturated viz. tocotrienols (Abuajah et al. 2015). Also, tocols are a group which composes of whose four forms of tocopherols as  $\alpha$ -tocopherols ( $\alpha$ TP); and  $\beta$ -tocopherols ( $\beta$ TP),  $\gamma$ -tocopherols ( $\gamma$ TP),  $\delta$ -tocopherols ( $\delta$ TP) and four forms of tocotrienol as  $\alpha$ -tocotrienols ( $\alpha$ TT),  $\beta$ -tocotrienols ( $\beta$ TT),  $\gamma$ -tocotrienols ( $\gamma$ TT),  $\delta$ -tocotrienols ( $\delta$ TT) which all have vitamin E and antioxidant activity (Ragaei et al. 2013).

It is revealed in many reports that tocols have vitamin E activity which depends on physiological factors and chemical structure. In this regard isomers of tocols have different vitamin E activities as follows:  $\alpha$ -tocopherols >  $\beta$ -tocopherols >  $\alpha$ -tocotrienol >  $\gamma$ -tocopherol >  $\beta$ -tocotrienol >  $\delta$ -tocopherol or no activity for  $\gamma$ -tocotrienol and  $\delta$ -tocotrienol. Among them, the  $\alpha$ -TP has the highest vitamin E activity whereas,  $\alpha$ -TT exhibits the highest antioxidant activity (Gani et al. 2012; Gangopadhyay et al. 2015). In accordance with dietary guidelines, the estimated average requirement of vitamin E is 12 mg and the suggested dietary allowance is 15 mg of 2R- $\alpha$ -tocopherol in a day (Gani et al. 2012).

Tocols are mainly found in plant-based foods. The major reserve of tocols are vegetable oils, yet great amounts of these compounds are also found in most cereal



grains (Gani et al. 2012; Gangopadhyay et al. 2015). The distribution of tocol isomers is irregular in the kernel. Nearly almost tocotrienols are present in the bran whereas particularly  $\alpha$ -tocopherol and  $\gamma$ -tocopherol are located in germ fraction (Gangopadhyay et al. 2015). Therefore, refined cereals have less vitamin E content due to the refining process (Fardet et al. 2008). According to a study, whole grain maize and rye have higher tocol contents than other cereal grains (Fardet et al. 2008). The contents and profiles of tocols are different in grains. Another study revealed that wheat and rye, which contained 27.81  $\mu\text{g}$  and 27.78  $\mu\text{g}$  in dry weight based and have higher amounts than barley (18.73  $\mu\text{g}$ ) and oats (11.59  $\mu\text{g}$ ), respectively. Also rye, wheat, and barley were the rich in  $\alpha$ -tocopherol,  $\beta$ -tocotrienol and  $\alpha$ -tocotrienols, respectively (Bartłomiej et al. 2012).

Tocols act as a radical scavenger, therefore, it is known as its antioxidant activity and hindering polyunsaturated oxidation in particularly cell membranes (Fardet et al. 2008). Aside from antioxidant activities, whole grain tocols could have many human health benefits involves modulating some degenerative diseases like cardiovascular diseases (CVD), cancer, and also decreasing blood cholesterol levels by prohibiting biosynthesis of cholesterol and lipid peroxidation, and act as a potential anti-inflammatory agent (Gani et al. 2012). They have been found stable in unprocessed groats for a period of 7 months at room temperature. Nevertheless, they undergo degradation in all the processed products (Gangopadhyay et al. 2015).

## Lignans

Lignans are one of the polyphenolic bioactive compounds which are composed of a group of dietary phytoestrogen components consist of two coupled C6–C3 units (Liu 2007). Dietary lignans are comprised of seven different phytoestrogen compounds as lariciresinol, matairesinol, 7-hydroxymatairesinol, medioresinol, pinoresinol, secoisolariciresinol, syringaresinol that are mainly located in outer layers of grains. Some of these plant-based dietary lignans as matairesinol and SDG could be metabolized in the gastrointestinal system and converted into mammalian lignans as enterolactone (EL) and enterodiol (ED), respectively (Ragae et al. 2013; Thompson et al. 2001). Lignans have a diphenolic structure which is analogue to that estrogenic component (Slavin et al. 1999).

Lignans are dietary phytoestrogens which are found in a widespread variety of plant-based foods involving flaxseeds, fruits, vegetables, legumes and also whole grains as corn, oats, wheat, and rye (Gani et al. 2012). Among them, flaxseeds are the highest content of dietary source in plant lignans (Liu 2007). The concentration of whole grain lignans from high to low as rye, oats, and wheat which are in between 2500 and 6700  $\mu\text{g}/100\text{ g}$ , 820 and 2550  $\mu\text{g}/100\text{ g}$ , 340 and 2270  $\mu\text{g}/100\text{ g}$ , respectively (Ragae et al. 2013). Another study mentioned that wheat and rye bran fractions have a higher concentration of lignans as 92.24  $\mu\text{g}/\text{g}$  than other grains. Another research revealed that different cultivars of the wheat concentration of total lignans varied from 2.60 to 5.00  $\mu\text{g}/\text{g}$  in dry seed weight based (Zhu and Sang 2017). In vitro studies showed that secoisolariciresinol diglycoside (SDG) could reduce early

biomarkers of colon cancer, also the new precursors of mammalian lignans as ED and EL could diminish spreading colon tumor cells in conjunction SCFAs (Thompson et al. 2001). The ED and En with  $\text{Ca}^{2+}$  and L are abundant in whole grain rye. In a study, dry matter based SDG level in wheat pasta samples is ranging between 34.20 and 58.81  $\mu\text{g/g}$  (Zhu and Sang 2017).

Lignans are phytoestrogens and lately related to reducing the prevalence of hormone-dependent health problems (Heinonen et al. 2001). Because, lignans are hormonally active compounds in grains and so, they could protect against hormonally mediated diseases (Slavin et al. 1999). ED and EL which have high antioxidant activity and less estrogenic activity make them very beneficial in promoting health benefits and combating various chronic diseases (Liu 2007; Gani et al. 2012). The mammalian lignans as ED and EL which are the metabolites of lignans may prevent against heart disease and hormone-related breast cancer and prostate cancers. Also, they could inhibit cell growth of colon cancer (Liu 2007; Gani et al. 2012).

### Alkylresorcinols

5-n-Alkylresorcinols, namely alkylresorcinols are synthesized by higher plants of families as *Gramineae*, *Myristicaceae*, *Proteaceae* and *Anacardiaceae* (Bartłomiej et al. 2012). Alkylresorcinols are plant-based phenolic lipids (Fardet 2010) and amphiphilic compounds (Ross and Kamal-Eldin 2001). Amphiphilic characterization is related to being a 1,3-dihydroxybenzene derivative with an alkyl chain at position 5 of the benzene ring (Fardet 2010; Gani et al. 2012). They are mostly found in aleurone fractions of whole grain cereals (Ross and Kamal-Eldin 2001) and especially dominated in rye between other whole grains. The content of alkylresorcinols could almost two times more in rye than wheat (Fardet 2010; Gani et al. 2012).

The content of alkylresorcinols in dry weight based is higher in the rye and mainly located in its bran fraction as 734  $\mu\text{g/g}$  among other cereals and keep up with wheat account for 583  $\mu\text{g/g}$  and barley as 45  $\mu\text{g/g}$ , respectively (Ragae et al. 2013). The content of alkylresorcinols in whole grain wheat especially bran fraction is 2110 mg/kg and higher by a long way than wheat flour (380 mg/kg) (Shahidi and Nacz 2003). On the other hand, the total amounts of whole grain wheat breads are ranged between 422 and 609  $\mu\text{g/g}$  in the dry matter based (Zhu and Sang 2017). According to other research, the alkylresorcinols content of rye grains vary between 360 and 3200  $\mu\text{g/g}$  in dry weight based, whereas 317–1430  $\mu\text{g/g}$  and 41–210  $\mu\text{g/g}$  in wheat and barley, respectively (Bartłomiej et al. 2012).

Alkylresorcinols have antifungal and antibacterial features and also antioxidant activity *in vitro* (Ragae et al. 2013). Their antibacterial and antifungal activities are attributed to whose hydrophobic alkyl chain that enables to react with proteins involving enzymes and therefore hinders their catalytic activities (Bartłomiej et al. 2012). Alkylresorcinols are biologically active antioxidants and whose absorption levels are high be a counterbalance up to 80%. Also, their potential antioxidant activities are proved in in-vivo studies that are protective to lipid oxidation.

Alkylresorcinols are provided to antioxidant activity that is subject to chain lengths such as incorporation with cell membranes and whose amphiphilic characters. However, it is remarked that their radical scavenging activities are less efficient than vitamin E and also sensitive to some production processes as fermentation, baking, and extrusion (Fardet et al. 2008). In vitro studies stated that alkylresorcinols have positive effects on reducing cholesterol level and anticancer cytotoxic effects (Fardet 2010). Their antioxidant activity is associated with the anticancer effect, but it is not certain in vivo studies (Ross and Kamal-Eldin 2001). For instance, in vivo studies on mice with implemented cells of prostate cancer, alkylresorcinols demonstrated no effect on cancer cells (Bartłomiej et al. 2012).

## Carotenoids

Carotenoids are natural pigments of fruits, vegetables, whole grains and responsible for yellow, red and orange colors which are synthesized by microorganisms and plants (Borneo and León 2012). They are lipid-soluble compounds (Abuajah et al. 2015) and including at least 40 carbon skeleton (Okarter and Liu 2010) could be present esterified to fatty acids or unesterified in plant tissues (Abuajah et al. 2015). In nature, it is defined more than 600 different carotenoids (Gani et al. 2012) and generally present in the all-trans form (Okarter and Liu 2010), yet, among them, only 40 are present in the human diet (Borneo and León 2012). Carotenoids are subdivided into two main groups as carotenes as hydrocarbons and whose oxygenated derivatives as xanthophylls (Borneo and León 2012). The most prevalent carotenoids which have antioxidant activity and source of yellow pigments are lutein, zeaxanthin, and  $\beta$ -cryptoxanthin in whole grain cereals (Ragaee et al. 2013).

Cereals are a major reserve of carotenoids. On the contrary to other bioactive compounds such as polyphenols, carotenoids are located mainly in endosperm fraction (Fardet et al. 2008). Among whole grain cereals, maize has the highest carotenoids content account for 11 mg/kg in the dry matter based totally, also particularly lutein and zeaxanthin are dominant correspond with 6–18  $\mu\text{g/g}$ ; 4–8  $\mu\text{g/g}$ , respectively. In accordance with whole grain soft wheat contain about only 1.5 mg/kg carotenoids while wheat germ has approximately 5.5 mg carotenoids/kg concentration of carotenoids in the dry matter based. Lutein concentration is depend on different wheat varieties such as 0.3–1.4  $\mu\text{g/g}$ ; 1.2–5.8  $\mu\text{g/g}$ ; 0.8–1.1  $\mu\text{g/g}$  (Fardet et al. 2008). Zeaxanthin contents of 11 wheat varieties from around 8 to 27 mg/g grain, and  $\beta$ -cryptoxanthin contents from around 1.0 to 13.5 mg/g grain (Fardet et al. 2008). The content of major carotenoids range from 26.4 to 143.5  $\mu\text{g}/100\text{g}$ ; 7.0 to 27.1  $\mu\text{g}/100\text{g}$ ; 1.1 to 13.3  $\mu\text{g}/100\text{g}$  respectively, in wheat. Among the wheat species concentration of carotenoids particularly lutein is higher *Triticum durum* and *Triticum monococcum* (Einkorn) than *Triticum aestivum* (Ragaee et al. 2013). *Triticum durum*, *Triticum turgidum* have intermediate levels of lutein account for 5.41–5.77  $\mu\text{g/g}$ , whereas one of the most common wheat namely *Triticum aestivum* had the lowest content correspond to 2.01–2.11  $\mu\text{g/g}$  (Abdel-Aal et al. 2002). On the

other hand, corn flours contain reasonable concentrations of the different carotenoids like  $\beta$ -cryptoxanthin (3.7 mg/kg), lutein (11.5 mg/kg), and also zeaxanthin (17.5 mg/kg) (Brenna and Berardo 2004; Ragaee et al. 2013).

Carotenoids have antioxidant and pro-vitamins functions (Gani et al. 2012). Antioxidant activities of carotenoids are attributed to whose several characteristic features as enable to cyclized one or both ends of the structure and could be hydrogenated to different degrees. They also have oxygen involving groups and a long series of alternating single and double bonds. Thus, carotenoids could scavenge free radicals and so being free and remain stable radicals in the process, due to whose capability of localization delocalize the free radical amongst its alternative single and double bonds (Okarter and Liu 2010). Despite the fact that fruits and vegetables known as a main source of carotenoids, there is a growing interest of whole grain carotenoids (Borneo and León 2012).

### *Other Phytochemicals*

Phytic acid or stated in other words inositol hexaphosphate (IP6) is bioactive compounds. Also, its salt form is called phytate (Gani et al. 2012). Phytic acid is majorly present in the bran parts of whole-grains, particularly in the aleurone layer (Fardet et al. 2008; Gani et al. 2012), correspond to 90% and 10% in the embryo (Dost and Tokul 2005; Stevenson et al. 2012) while mainly present germ fraction in corns (Gani et al. 2012). The amount of phytic acid in whole grain wheat, maize, sorghum are 82 mg/100 g, 635 mg/100 g, and 829 mg/100 g respectively (Ragaee et al. 2013). Phytic acid is a principal phosphorus storage components in cereal grains correspond with approximately 1–7% in the dry matter based (Fardet et al. 2008). That contributing more than 70% of the total phosphorus content of the kernel (Fardet et al. 2008; Gani et al. 2012). It is generally known that phytic acid has an antinutritional effect which is related to chelates minerals and trace elements such as Fe, Ca, Zn and/or Mg and so limiting whose bioavailability (Fardet et al. 2008; Gani et al. 2012). Besides this, it is revealed that phytic acid has antioxidant activities not only in vitro by suppressing iron-catalyzed oxidative reactions due to whose ability to chelate free Fe and may be a potent antioxidant but also in vivo by blunting lipid peroxidation (Fardet et al. 2008). Thus, there is a potential health problem about nutritional deficiency particularly iron and zinc deficiency for populations whose diets are based on cereals and legumes (Raboy 2001; Stevenson et al. 2012). On the other hand, it was revealed in recent studies that phytic acid could prevent some health problems such as coronary heart disease, atherosclerosis, formation of kidney stone and some cancer types respectively (Ragaee et al. 2013). Researches are detected that endogenous or purified in other words exogenous phytic acid has a protective effect to colon cancer. This effect is explained by the antioxidant effect of phytic acid which has the capability to bind iron which is a catalyst for lipid peroxidation. Moreover, it was enlightened that purified phytic acid is more effective than endogenous phytic acid about this issue (Thompson et al. 2001). The

phytic acid content is effected during milling. In this regard, refined flour has almost no phytate although wheat involves about 1.13% phytate in dry weight based. In refined flour, phytic acid content varies from 200 to 400 mg/100 g while these values are 600–1000 mg/100 g in whole flour (Febles et al. 2002). Moreover, it is higher in n wheat bran account for 3116–5839 mg/100 g in the dry matter based (Stevenson et al. 2012).

Phytosterols are secondary metabolites (Liu 2007; Ragaee et al. 2013), and collective term to state plant sterols and stanols that have an analogue structure with cholesterol. Plant-based sterols involve stigmasterol, sitosterol, campesterol in other respects stanols include as stigmastanol from only in the side chain groups (Liu 2007; Gani et al. 2012). In whole grains, plant sterols could be found in different forms as free sterols, steryl esters with fatty acids, or phenolic acids, steryl glycosides, and acylated steryl glycosides (Gani et al. 2012). The most abundant plant sterol is  $\beta$ -sitosterol in Western diets (Kris-Etherton et al. 2002). Plant sterols and stanols are mainly present in oilseeds, vegetable oils, whole grains, legumes and nuts (Slavin 2004; Liu 2007). Moreover, cereals are recognized as significant plant sterol sources than vegetables (Gani et al. 2012). Among the cereals, the highest amounts of phytosterols are present in rye (80–90 mg/100 g) and following with wheat (70 mg/100 g), barley (70–80 mg/100 g) and oats (45–50 mg/100 g), respectively (Bartłomiej et al. 2012). Also, the phytosterol level is moderate in whole grain cereals but high in pearling fines, namely outer kernels of barley (Gangopadhyay et al. 2015).

In many researches, it is indicated that phytosterols reduced the absorption of serum cholesterol and it is attributed to a similar structure with cholesterol and phytosterols (Bartłomiej et al. 2012). Another study reported that less than 1 g/day, intakes of phytosterols have a significant effect on lowering cholesterol level and recommended consumption of 1–2 g phytosterols in a day (Slavin 2004). According to other epidemiological studies, ingestion of 1–3 g phytosterols in each day reduced the low-density lipoprotein (LDL) cholesterol level by 10% on average in blood serum, whereas triacylglycerols and the high-density lipoprotein (HDL) cholesterol levels and were not affected (Lagarda et al. 2006; Bartłomiej et al. 2012). Nevertheless, the estimated plant sterols content is about 200–300 mg/day in the Western diet (Slavin 2004). According to another source, the typical consumption of plant sterols is nearly 200–400 mg/day (Kris-Etherton et al. 2002). Also, it is stated that a non-vegetarian diet involves about 250 mg of unsaturated phytosterols whereas a vegetarian diet includes more than 500 mg (Abuajah et al. 2015). Therefore, it is difficult to fulfill the recommended phytosterol intake levels (Rebello et al. 2014). Yet, still, it is suggested that increased consumption of whole-grain implicitly total phytosterol intake contribute to a reduction in cholesterol (Slavin 2004) and potentially perform a protective effect on cardiovascular diseases (Rebello et al. 2014). Therefore, the beneficial health effects of plant sterols induce to the improvement of functional foods fortified with sterols. The eventuality of utilizing sterols as an adjunctive therapy to cholesterol decreasing pharmaceuticals has been recommended lately (Gangopadhyay et al. 2015).

$\gamma$ -Oryzanol is a mixture of at least ten phytosterol ferulates such as methyl sterols esterified to ferulic acid (Fardet et al. 2008). The  $\gamma$ -oryzanol is mainly specified in whole grain rice and particularly its bran fraction as 18–63 mg/100 g and 185–421 mg/100 g in the dry matter based, respectively (Fardet 2010). Another study is expressed that  $\gamma$ -oryzanol content of rice bran is corresponded to 3000 mg/kg following with wheat bran as ranges from 300 to 390 mg/kg (Ragaei et al. 2013). The content of  $\gamma$ -oryzanol is depended on several factors such as a variety of rice, milling procedure, extraction methods (Fardet 2010).  $\gamma$ -oryzanol is a strong inhibitor of iron driven hydroxyl radical formation. Antioxidant activity of  $\gamma$ -oryzanol has been proved not only in vitro (Juliano et al. 2005) but also in vivo studies (Suh et al. 2005). It is demonstrated that  $\gamma$ -oryzanol has favorable effects on CVD, hyperlipidemia and also reduction in cholesterol level and lipid peroxidation (Fardet 2010).

Avenanthramides (AVs) are a group of hydroxycinnamoyl anthranilate alkaloids. They have been found specifically in oats and particularly in oat groats and oat hulls. AVs are mostly localized in the oat bran when comparing with oat groat yet, more uniformly distributed throughout the oat groat (Gangopadhyay et al. 2015). Also, the content of oat flakes avenanthramides are higher than oat bran corresponds to 26–27  $\mu\text{g/g}$  and 13  $\mu\text{g/g}$ , respectively (Gani et al. 2012). The main avenanthramides are avenanthramide-1, avenanthramide-3, and avenanthramide-4, in other words, avenanthramide B, avenanthramide C and avenanthramide A, respectively. AVs have antioxidant antiatherogenic and anti-inflammatory properties (Gani et al. 2012).

Benzoxazinoids (BXs) is a group of nitrogen inclusive secondary metabolites is mainly stored as glucosides in plant cells. The presence of BXs in whole grain products discovered recently and it was stated that BXs are generally localized in the germ of wheat seeds, a part of the bran fraction. Yet, the content of total BXs in whole grain wheat products is very low correspond to about 5  $\mu\text{g/g}$  in the dry matter based (Zhu and Sang 2017).

## Whole Grain Phytochemicals and Effect on Health

Several metabolic diseases have an association with daily lifestyle, namely lifestyle disorders, being in the first place an unbalanced diet, intake of inadequate fiber and bioactive components as phytochemicals and micronutrients (Gani et al. 2012; Călinoiu and Vodnar 2018).

By-products of grain processing are cereal brans that source of nonstarch carbohydrates such as beta-glucan, arabinoxylan; phenolic acids mainly ferulic acid, flavonoids particularly anthocyanin and also tocopherols, carotenoids, folates, oligosaccharides, and sterols. Therefore, the bran parts obtained from cereals such as wheat, oats, barley, rye, rice, maize, millet, and sorghum have been qualified to provide with plenty of health-enhancing compounds are about antiatherogenic, hypoglycaemic, antihypertensive and antilipemic features (Patel 2015). Epidemiological

prospective studies, randomized controlled trials and cohort studies on humans demonstrate that the consumption of whole grain and whole grain-based foods are preservative against to various health diseases which are related with an increment of oxidative stress. Kind of cardiovascular diseases, type 2 diabetes, obesity and some cancer types (Călinoiu and Vodnar 2018). These health benefits are acquired by way of several multifactorial physiological mechanisms subsuming antioxidant capacity and/or activity, procuration of hormones, improvement of the immune system and enable of substance transit via the digestive system, and absorbing and/or diluting of substances in the intestinal system (Gani et al. 2012).

It is generally agreed that the synergistic action of the components present in the bran and germ fraction of whole grain cereals have a preservative role because of whose antioxidant activities (Călinoiu and Vodnar 2018).

### *Cardiovascular Disease*

Cardiovascular disease (CVD) involves mainly coronary heart disease (CHD), stroke, hypertension, peripheral vascular disease (Zhu and Sang 2017). CVD is a charge of one out of three mortality in all around the world, particularly in the industrialized world. The World Health Organization (WHO) is apprised of the increase of CVD in developing countries (Borneo and León 2012).

Whole grain consumption and total dietary fiber constantly related to preservation from coronary heart disease (CHD). It is indicated that the effect of fruit or vegetable fiber consumption was intermediate whereas whole grain cereal fiber intake had a lower frequency of substantial adverse association with CHD (Anderson et al. 2000).

The preservative effect of whole grain cereals CHD has come forward for nearly 60 years. Burkitt, Cleave, Trowell, and Walker lead the notion that highly refined foods are principal contributors to western diseases involving coronary artery disease. Over 45 years ago Trowell highlighted the fiber hypothesis linked with CHD. The first scientific research to corroborate the hypothesis was conducted by Morris et al. (1977) stated that higher cereal fiber intake resulted in a reduced rate of heart attacks in British men. After that several epidemiologic studies have the same view about this hypothesis and got strengthen in the following years. “Whole grain” hypothesis was supplanted by “dietary fiber” hypotheses. Burkitt also gave attention to wheat bran as a principal preservative food and support consumption of whole grain-based bread and bran cereals (Anderson et al. 2000). Trowell’s hypothesis was interpreted as a “fiber hypothesis” rather than as a “high-fiber food hypothesis” (Anderson 2004). They insisted on whole foods should get the emphasis. Recent findings of the “whole grain story” validate their vision (Anderson et al. 2000).

First of all, it is mentioned that high amounts of consumption natural starchy carbohydrates, with their whole fiber parts, is preservative versus ischemic heart disease and hyperlipidemia. After that, this notion was encouraged with another

study that interrelates intake of high levels of cereal-based dietary fiber and relation with reducing ratios of heart attacks among British men. This researches lead to affirmation by FDA and stated that diets rich in whole-grain foods could decrease the risk for heart disease. Furthermore, subsequent studies revealed that whole grain consumption has a stronger relationship with preservation from CVD than the intake of cereal fiber and other plant-based fibers as vegetables or fruits (Anderson et al. 2000). In 2010, the Dietary Guidelines Advisory Committee (DGAC) rated the evidence for the preservative association between whole grains and CVD as “moderate” (Harris and Kris-Etherton 2010).

Main risk factors of CVD are high levels of serum LDL cholesterol and fasting serum triacylglycerol, low levels of HDL-cholesterol, and also hypertension, diabetes, and obesity. Whole grain cereals and foods could be one of the healthiest preference to reduce the CVD risk. Epidemiological researches stated that high amounts of whole grain consumption could reduce the risk of CVD account for 29% than individuals with low levels of whole grain intake. Diets rich in whole grain foods are prone to reduce serum LDL-cholesterol and triacylglycerol levels also blood pressure whereas rising serum HDL-cholesterol levels (Anderson 2003).

Besides to dietary fiber several studies focused on relation between some bioactive compounds particularly carotenoids and cardiovascular health (Voutilainen et al. 2006; Giordano et al. 2012; Ciccone et al. 2013; Gammone et al. 2015; Di Pietro et al. 2016; Kulczyński et al. 2017) and also lignans (Peterson et al. 2010), ferulic acids (Alam et al. 2013).

## *Type 2 Diabetes*

Whole grain intake is adversely related to type 2 diabetes risk, and this relationship is stronger for bran fraction than germ fraction. Results from prospective cohort studies constantly encourage the increased consumption of whole grain for the prevention of type 2 diabetes (De Munter et al. 2007).

Diets which are rich in whole grains are related with a nearly 20–30% decrease in risk of type 2 diabetes, that is accredited with whole grain components, particularly dietary fiber, phytochemicals, vitamins, and minerals. Major phytochemicals such as phenolics and flavanoids have antioxidant activity in vitro and have the potential to attenuate inflammation and oxidative stress which are involved in the pathogenesis of type 2 diabetes. However, their bioavailability is frequently limited because of these compounds are bound firmly to the cell wall. Clinical trials as postprandial and medium-term intake researches demonstrated that phytochemical compounds of cereals obtained a restricted benefit for prohibiting the development of type 2 diabetes. On the other hand, consumption of whole grains in the diet may cause an increment phenolic contents of postprandial plasma. Nonetheless, the magnitude of the response is generally impermanent and smidgeon. In addition, clinical relevance with the effect of whole grain cereals and their fractions are not improved biomarkers to decreasing risk of type 2 diabetes are still fewer (Belobrajdic and Bird 2013).



There are many possible mechanisms about the effect of whole grains and whose bioactive components on diabetes. These are related to the capability of reducing insulin resistance and enhance insulin sensitivity, improvement in glucose tolerance and the high levels of magnesium in whole grain. However, the exact mechanism is not identified yet, that is related to a low glycemic index of whole grains (Borneo and León 2012).

To detect the association of whole-grain consumption with glucose and insulin metabolism needs biomarkers. In this regard, the glycemic index (GI) could be a marker to compare the glycaemic response of foods (Slavin 2004). The glycemic index of whole grains such as barley, oats, corn, rice, rye, buckwheat, and wheat range between 36 and 81. Among them, barley and oats having the lowest glycemic indexes values. According to results, concentrations of blood glucose and insulin secretion decreased in subjects with and without diabetes mellitus who consumed a low-glycemic index diet (Slavin et al. 1999; Slavin 2004).

According to a report of Dietary Guidelines Advisory Committee (DGAC) in 2010, it is mentioned that there is a little or no relation between glycemic index, type 2 diabetes, weight loss, and cancer, also an inconclusive relation with cardiovascular disease (CVD) (Harris and Kris-Etherton 2010).

Andersson et al. (2011) studied on suppression effect of alkylresorcinols which is isolated from rye bran on hormone-sensitive lipase activity and adipocyte lipolysis. They pointed out that constantly high intake of ARs, in the format of whole grain rye, could cause to decrease lipolysis in vivo and so reduce the levels of circulating free fatty acids (FFAs). Liu et al. (2000) aimed to examine the relationship between consumption of whole grain or refined grain and the risk of type 2 diabetes mellitus in 75,521 U.S. women aged 38–63 years without a previous diagnosis of diabetes or cardiovascular disease. Throughout the 10 years follow up, results showed that replacement of refined grain products with whole grain-based products could reduce diabetes mellitus risk. Montonen et al. (2003) researched the association between the Consumption of whole grain and fiber and the incidence of type 2 diabetes in 2286 men and 2030 women aged 40–69 years without initially diabetes diagnosed. There is an adverse relationship between type 2 diabetes risk and persons with high whole-grain intake. This is attributed to cereal fiber intake and other bioactive components present in whole grain products, such as tocotrienols, lignans, phytic acids, and other antinutrients. The following research should address the mechanisms and which compounds are responsible for the effects, the exact amounts of whole grain needed to decrease type 2 diabetes risk (Murtaugh et al. 2003).

### ***Obesity and Weight Management***

Obesity arises from the consequence of a long-dated imbalance between energy expenditure and energy intake. To increase energy intake, one of the ways is raising the intake of whole grains (Mikušová et al. 2011). Epidemiological studies stated that there is an adverse relationship between consumption of dietary fibre with

weight gain and obesity. It is expressed that fibre dietary intake is related to reduced energy intake, increased satiety. Researches indicated that wheat bran could decrease in food consumption following a test meal with wheat bran (Stevenson et al. 2012). However, it is not clear yet whether this effect is long-lasting with regards to the management of obesity (Freeland et al. 2009; Stevenson et al. 2012).

Whole grain and whole grain-based foods reduce weight, body-mass index (BMI), the waist circumference and also waist-to-hip ratio by decreasing the amount of accumulated body fat due to whose dietary fiber content (Mikušová et al. 2011). It is hard and complex to identify a specific mechanism by which whole grains have a benefit on weight reduction or weight management. Moreover, intake of whole grains is also related to the acceptance of other healthy habits like increasing intake of fruits and vegetables and also physical activities (Borneo and León 2012). So, there is lack of accurate explanations of underlying mechanisms of the relation between them but it has been proven that the obesity risk could be diminished by substituting of refined cereal-based foods with, low glycaemic index and high-fiber content whole grains. The possible mechanisms are an enhancement of satiety and satiation, an extension of gastric emptying time while deceleration of nutrient absorption and impact on gut hormones like leptin, ghrelin, cholecystokinin, glucagon-peptide-1 (GLP-1) and peptide tyrosin-tyrosin (PYY). Moreover, the synergistic effect of dietary fiber between antioxidants could be a charge of slowing down the rate of glucose absorption, putting off insulin release and blunting glycaemic response, what may affect weight management (Mikušová et al. 2011). The reduction in markers of obesity such as insulin, leptin, and C-peptide are related to increased levels of whole grains ingestion (Borneo and León 2012). Diets which abound in whole grains pretend to affirmative effects on health comprising body weight management. Dietary recommendations declared that whole grains have several worthwhile bioactive compounds than refined grains. Many epidemiological researches verified invariably that intakes of whole grain instead of refined grains are related with lower body mass index (BMI). Nevertheless, some clinical trials are still inconsistent and/or incomplete to encourage the role of whole grain in enhance weight loss and/or weight control-regulation-maintenance (Karl and Saltzman 2012). In a study, wheat alkylresorcinols increased insulin sensitivity and also glucose tolerance by blunting intestinal cholesterol absorption and hepatic lipid accumulation, which subsequently suppresses diet-induced obesity (Oishi et al. 2015).

It was proven that effect of consuming whole grains decrease daily calorie intake, it was noted that merely randomized, placebo-controlled double-blind studies could show the evidence of phytochemicals and whose exact potential about weight loss and/or management at least up to 24 weeks of consuming (Tucci 2010). Observational studies highly recommend that consuming approximately three servings per day whole grain is related with lower body mass index, diminish weight gain, abdominal adiposity, increase in the dietary fiber and energy intake (Karl and Saltzman 2012). Moreover, it was mentioned that the people who intake more whole grains in their diet tend to have a healthier lifestyle as getting more dietary fiber intake but less fat intake, often exercise, more fewness of them smoke. For this reason, whole grains could be as a marker of healthy body weight but the underlying mechanism

of between them have inadequate proof to show up clear favorable effects of WG consumption on body weight management (Harland and Garton 2008).

## *Cancer*

The guidelines of the American Institute for Cancer Research and the American Cancer Society, suggested consumption of whole grains instead of refined grains for as part of a comprehensive lifestyle approachment to decrease the incidence of cancer (Makarem et al. 2016). Case-control studies based on whole grain is the main reserve of dietary fiber, which associated with a decreased risk of several types of cancer, particularly associated with the digestive system (Xiao et al. 2018) such as colorectal, pancreatic, gastric and hormone-related cancer types (Mourouti et al. 2016). Potential preservative effect of whole grains and cereal fiber is limited to some cancer types such as head and neck cancers, renal cell carcinoma but these results require approval following researches (Makarem et al. 2016). Yet it was also demonstrated that intake of refined cereal-based products such as bread and pasta have been related with enhanced some kind of cancer types as the digestive tract, thyroid, larynx, pharynx, cancers (Gani et al. 2012).

Cell wall materials are resistant to upper gastrointestinal digestion, thus they could reach large intestine without digestion. Then, they could be fermented here by microflora and thus, bioactive components which have antioxidant activity are released (Gani et al. 2012). The antioxidant activity of insoluble phenolic acids could attribute the trapping oxidative components in the whole digestive system. For instance, a few amounts of ferulic acid (0.5–5%) which is typical phenolic acid in whole grain wheat, could be absorbed in the small bowel, majorly the soluble fraction and would perform possibly a major action for preservation from colon cancer (Gani et al. 2012). Kruk et al. (2017) reviewed that some *in vitro* and observational researches based on anticancer activities of natural or synthetic alkylresorcinols. According to *in vitro* studies, interception of some types of cancer cell lines as colon cancer, breast cancer, lung cancer and ovarian cancer at micromolar alkylresorcinols content. Prospective studies proved that there is an adverse relation between whole grains consumption and risk of colon cancer. According to prospective researches, approximate 52–66% reduction of distal colon cancer risk at nanomolar alkylresorcinols concentration in plasma whereas 40% increase in the risk of prostate cancer (Kruk et al. 2017). However, some meta-analyses stated an inverse relationship between dietary fiber and whole grain consumption and the risk of colorectal cancer. Some epidemiological studies have pointed out that a possible inverse relation, while other studies have found no clear relation between whole grain intake and risk of breast cancer (Xiao et al. 2018). The unsteady results could be due to some factors as different research designs, different assessment methods of dietary intake, the quantity of whole grain intake in different populations, and a range of contradicting factors that were adjusted in previous studies and were not place in forefront in early studies (Mourouti et al. 2016; Xiao et al. 2018).

The first meta-analysis to research a potential nonlinear relation of dietary fiber intake with breast cancer risk was conducted by Aune et al. (2012). Despite they could not find proof of nonlinearity with the statistical tests used, substantial inverse relations were monitored only among studies with a high level or large range of consumption. Farvid et al. (2016) examined the risk of breast cancer and lifelong grain consumption and remarked that consumption of higher amounts of whole grain foods could act a role in the hindrance of premenopausal breast cancer. Bakken et al. (2016) have investigated that intake of whole grain bread and colorectal cancer risk among Norwegian women. According to findings there was found no relation between whole grains consumption and colorectal cancer that supports the results of Swedish research. However, outcomes of study do not corroborate an early meta-analysis, which remarked that there could be an inverse relationship between the intake of whole-grains and the CRC risk. The differences between studies are attributed to CRC incidence, whole grains type, and whose contents. On the other hand, a recent study found no clear relation regarding the possibly different effects of grains as wheat, rye, or oats among Norwegians, Danes, and Swedes (Bakken et al. 2016). Mourouti et al. (2016) examined case-control research in women based on whole grain consumption and breast cancer. According to findings more than seven times whole grain consumption in a week was coherently related with decreased breast cancer risk, especially among premenopausal and normal weight women patients. Also, it was emphasized that randomized clinical and epidemiological trials are needed to approve or disprove the relationship between them (Mourouti et al. 2016). Also, there are controversial views in this regard. For instance, In the Danish Diet, Cancer and Health Cohort Study, the analysis of a cohort of Danish postmenopausal women consumption of whole grain products was not related to breast cancer risk (Mourouti et al. 2016).

There are many potential mechanisms for the conservation effect of whole grains against breast cancer. It could be first attributed to whose be sources of dietary fiber that enable to augment the amount of fecal bulk and reduce whose transition time. So it causes the decrease interaction fecal mutagens with the epithelial tissue of intestinal. In addition, dietary fibers could dilute or bind bile acids, which are thought to promote cell proliferation, so enabling an increased opportunity for mutations to occur. Besides, whole grains are rich in antioxidant content and phenolic compounds, which have a key role in cancer prevention. In addition, many antinutrients such as phytic acid, protease inhibitors, and saponins could also act as cancer preventers by counteracting the formation of carcinogens and via blocking the interaction of carcinogens with cells. Moreover, whole grains are important sources of phytoestrogens, which appear to have a role as natural cancer-protective composites, by whose antioxidant activity, ability to hinder cell proliferation and give rise to cell apoptosis. Furthermore, taking into consideration that in many epidemiological researches, it was revealed that higher serum insulin levels have been related with breast cancer an indirect way owing to whole grains have enabled to decrease insulin levels (Mourouti et al. 2016).

## Processing Effect on Whole Grain Phytochemicals

In the beginning, recommendation and encouragement of whole grains consumption of cereals were related with those only high dietary fiber contents which provided health benefits. Nonetheless, recent studies demonstrated that the phytochemicals of cereals are mainly located in the outer layers and so their removal would enable products that are less beneficial to health (Shahidi 2009). There are three main key factors affect the content of macronutrients and micronutrients in whole grains are variety and cultivars; growing conditions such as climate, weather and soil; processing type and conditions such as milling, baking, extruding (Jones et al. 2015). Among them, processing of foods mostly presents a major impact on their constituents consisting of their bioactivities (Shahidi 2009). Despite, generally known that the processing has a negative aspect of nutritional value, several factors encourage the significance of processing of grains to develop grain consumption (Slavin et al. 2001). In developed countries, like Europe and the USA, cereal grains are generally exposed to some processing types like milling, heat extraction, cooking, parboiling, or other technique. Commercial cereals are extruded, puffed, flaked, or modified (Slavin 2004) to get the desired product in general by optimizing appearance, texture, flavor, color, and shelf-stable end products (Slavin et al. 2001). Therefore the important thing is not only the content of phytochemicals in whole grains but also determination effect of the processing on end product with regard to pros or cons.

Processing could open up the food matrix, therefore enabling the unleash of strictly bound phytochemicals from the structure of grain (Slavin 2004). Food processing could lead give rise to the decrease phenolic components in the final products, but also food processing could determine physical or chemical modifications in food in the matter of increases the absorption and release of phenolic components in the gastrointestinal system (Călinoiu and Vodnar 2018). In the milling process, the nutritional quality of grain decreases as a result of separating bran and germ fractions from the endosperm. On the other hand, fiber and phytates could increase the bioavailability of minerals and vitamins (Harris and Kris-Etherton 2010) as a result of germination, fermentation and baking cause to phytate hydrolysis (Stevenson et al. 2012). Thermal processing such as cooking, baking, boiling, and parboiling could release antioxidants from the bran into the endosperm and so enhance the bioavailability of phytochemicals, and form resistant starch. The sourdough fermentation or the adding of organic acids to grains enhance glycemic response in the absence of fiber (Harris and Kris-Etherton 2010). In some rye-based studies, biologically active compounds are stable during food processing and also whose content may be increased with proper conditions (Slavin 2004). For instance, Liukkonen et al. (2003) examined the impact of some processes like milling, germinating and sourdough fermentation on whole grain rye. Results showed that after the 6-day germination at three different temperatures (5 °C, 10 °C, 25 °C) the amount of easily extractable phenolic compounds and folates increased and highest values were obtained in the highest temperatures. The amount of bioactive com-

pounds as easily extractable phenolic compounds, phenolic acids, lignans, sterols and alkylresorcinols slightly increased while tocopherols reduced after the fermentation process.

Despite some of these compounds could be substituted into the refined flour through compulsory enrichment policies, there is a prevalent view; that intake of the fortified product is not the same as intake of the original grain product with its more complicated structure. In the generality of modern milling methods, the individual compounds of the grain are removed, yet then re-constituted to re-form the whole grain flour (Seal 2006).

## *Germination*

The main function of the endosperm is to provide energy to the seedling (Jacobs and Gallagher 2004). The germinated grain is a raw material as a fermentable sugar and nitrogen source eventuate in raising in bioactive compounds level. Also, grain germination commences with a soaking process which leading to synthesize several cell wall degrading enzymes to metabolize some molecules results synthesis of some bioactive compounds. Germination causes augmentation in the level of nutritional compounds and whose bioavailability and also, reduce in the content of antinutritional compounds (Alvarez-Jubete and Tiwari 2013), such as phytic acid and tannins. Besides, germination improves the nutritional value of the grains by increasing the content of  $\alpha$ -tocopherol and vitamin C as vitamins and  $\beta$ -carotene, polyphenols, ferulic acid, and vanillic acid as antioxidants (Yang et al. 2001; Schaffer-Lequart et al. 2017). Many in vitro studies supported that phenolic content and relevant with antioxidant capacity augments with germination process (Alvarez-Jubete and Tiwari 2013). However, germination could also degrade  $\beta$ -glucan in oats and barley by decreasing the average molecular weight of  $\beta$ -glucan (Wolever et al. 2010; Schaffer-Lequart et al. 2017). The important point is the optimization of germination conditions as sprouting time and temperature to minimize lack of phytochemicals (Alvarez-Jubete and Tiwari 2013). For instance, although it is declared that generally  $\beta$ -glucan is affected adversely during germination; optimize germination temperature and time as 72 h, 15 °C respectively could end up with higher retain  $\beta$ -glucan content (Wilhelmson et al. 2001).

## *Milling*

Milling is a process of whole grains ends with refined flour (Slavin et al. 2013). Conventional milling of grains is based upon separate the endosperm, which generates white flour, from the bran and embryo fractions (Stevenson et al. 2012). In other words, the milling term generally refers to removing the germ and bran fraction (Alvarez-Jubete and Tiwari 2013). The bran and germ fractions are

corresponded to 14% and 2.5% in whole wheat, respectively while lower than about 0.1% in refined wheat. Therefore, starch content is higher in refined grains than whole grains (Slavin et al. 1999).

Flour types could be defined by the extraction rate. In this regard, white flour is identified by 75% and/or less extraction rate whereas wholemeal or whole grain flour is specified by 100% extraction (Pedersen et al. 1989). Bran, along with germ is carried out for appearance, organoleptic properties and extend shelf life by discarding generally bran and germ fractions. These components have been characterized to include a large amount of dietary fibre, antioxidants, phenolic lipids as alkylresorcinol, phytosterols, vitamins, minerals and other phytochemicals (Patel 2015). Thus, the milling process causes remarkable losses as dietary fibre and other phytochemical compounds especially carotenoids, tocopherols and also phenolic acids, particularly ferulic acids (Alvarez-Jubete and Tiwari 2013). For instance, refining wheat led to approximately 200–300-fold loss in phytochemical content (Craig 1997; Craig and Beck 1999).

Milling method, process parameters, the degree of milling are also had an effect on phytochemical contents, means high extraction rate flours related with high antioxidant capacity. Increasing the degree of milling is a particularly adverse effect on tocopherols (Alvarez-Jubete and Tiwari 2013). For instance, whole grain wheat is possible to lose more than half of dietary fiber and folates about, 58% and 79%, respectively and also most of the minerals (Mg, Zn, Se) and vitamins (vitamin B3, vitamin E) (Fardet 2010). In other words, refined the grains not only have lower phytate and fiber contents but also lower mineral contents. The reducing availability of minerals is attributed to mineral-binding capabilities of phytic acid and fiber content. Consumption of whole grains and fiber in recommended amounts as 20–35 g in a day for fiber and three servings in a day for whole grains were not found to have any negative influences on mineral status (Slavin et al. 1999). Therefore it is known that consuming whole grains have more potential health benefits than refined flours (Alvarez-Jubete and Tiwari 2013).

The particle size of the whole grain is a significant factor in determining the whose physiological effect. For instance, coarse wheat bran retards gastric emptying and small intestine transition by having a high faecal bulking effect than finely ground wheat bran. Thus, beyond composition differences coarse whole grains as has a unique physiological effect (Slavin 2004).

When comparing with refined wheat flour and whole grain wheat flour, it is determined that refined wheat flour lost whose 83% of total phenolics, 79% total flavonoids, 93% ferulic acids which is one of the phenolic acids compound, 78% zeaxanthin and 51% lutein content (Slavin et al. 2013). Conversely, some researches notified that operations as milling and the thermal process could increase bioaccessibility of phytochemicals (Slavin et al. 2013). Some researches notified that the phenolic content increased by the milling process. It is reported that the addition of 5% micronized fractions in the fermentation process to wheat flour based dough increased the content of dietary fiber, total phenols, antioxidant activities and free amino acids of dough and improved sensory properties of the end product in bread making process. Another experimental research reported that there is an adverse

relationship between the bioaccessibility of phenolic compounds and the bran particle size (Călinoiu and Vodnar 2018).

### ***Fermentation***

Sourdough fermentation is using traditional bread production to enhance nutritional value and some quality parameters as a flavor and textural properties in contribution to LAB and yeasts. Besides sourdough fermentation improves the bioavailability of minerals and also reduces the glycemic index. From the point of view phytochemical content, sourdough fermentation could affect positively or negatively based on the type of phytochemical compound and sourdough process. Studies mentioned that sourdough fermentation increases the content of folates and total free phenolic compounds, namely extractable phenolics thereby antioxidant capacity. In addition, decreasing in pH levels consequential of sourdough fermentation increases pronyl-L-lysine in end products. Whereas reduces  $\beta$ -glucan and also particularly oats and barley flours, and also tocols because of oxidation. Conversely, the fermentation process causes minimal decreasing in carotenoid content that is related to the preservative effect of bakery yeast by reason of consuming O<sub>2</sub> throughout fermentation which results in the inheritance of lipoxygenase related carotenoid degradation. In addition, it is reported that there could be a synergist effect between germination and fermentation processes on phytochemical content. In this context, the combination of these two processes increase folates, lignans, sterols and ferulic acids in whole grain rye. This could be explained by the same pH ranges of fermentation (pH: 4.5–6.0), and cell wall degradation which is carried out by indigenous grain or microorganisms enzymes levels (Alvarez-Jubete and Tiwari 2013). Anti-nutritional compounds like phytic acid, tannins, and flatulence sugars could be reduced by fermentation (Soetan and Oyewole 2009; Schaffer-Lequart et al. 2017).

### ***Thermal Process***

Thermal processes as baking are generally causing to a reduction in the content of tocols, flavonoids,  $\beta$ -glucans, carotenoids and also antioxidant which results in decreasing antioxidant capacity in the final product. Loss of polyphenolic compounds is associated with extraction rate, substrate and baking process parameters. Reduction in tocol content is related to oxygenation throughout dough making and heat devastation throughout the baking process. Tocol content in the final product depends on several factors such as initial tocol content, tocol profile, other compounds which have antioxidant activity. As carotenoids polyphenolic compounds particularly flavonoids are heat sensitive and so adversely affected by thermal processing as baking. The whole breadmaking process affects the stability of carotenoids adversely. In this regard, the highest decrement is shown in dough making



due to oxygen inclusion during kneading and hereout eventuating carotenoid degradation, following by baking and then fermentation processes. From the point of carotenoid content view, the baking process cause to decrease in carotenoid content because of high sensitivity to heating and seen in more crust structure than crumb (Alvarez-Jubete and Tiwari 2013). On the other hand, despite Maillard reaction and whose products are generally known as having a harmful influence on health, many researches have indicated that some of these compounds show antioxidant activities as well and so could affect the final antioxidative features of baked products, particularly in the crust part (Alvarez-Jubete and Tiwari 2013; Slavin et al. 2001). For instance, when comparing with flour as a raw material or crust-free bread, it is remarked that the crust of white bread has double the antioxidant activity (Slavin 2004). Also, among boiling, microwave heating, and pressure cooking, roasting is the best cooking way to maintain and/or in some cases increase the phenolic compounds bioaccessibility in wheat, sorghum, finger millet and pearl millet (Călinoiu and Vodnar 2018).

Bioactive compounds are sensitive to extrusion process parameters and could be influenced in a negative or positive way. A number of researches noticed that content of phytochemicals, particularly tocols, anthocyanins, and phenolic acids are reducing during extrusion cooking in whole grain wheat, barley, oats and rye (Alvarez-Jubete and Tiwari 2013). In a study, extrusion cooking treatment of wheat, oat, and brown rice were implied and the findings revealed that total antioxidant activity and total phenolic content stemming from the free forms were reduced whereas the total bound phenolic acids were significantly increased (Călinoiu and Vodnar 2018). In another study, extrusion cooking, which was applied between 120 and 200 °C, increased the phenolic content of oats and sorghum bran, while wheat, rye, and barley had an increment of 200–300% of ferulic acids, vanillic acids, and syringic acids as free forms suggesting that hydrothermal processing could raise the releasing rate of phenolic acids and whose derivatives. This increment could be a result of the combination of high temperature and water-stress (Călinoiu and Vodnar 2018). According to another study, dietary fiber through Klason lignin content of wheat increased after extrusion by catalyzing the Maillard reaction (Poutanen 2001). Zieliński et al. (2001) studied on the effect of extrusion cooking in three different temperatures (120 °C, 160 °C, 200 °C) on bioactive compounds of wheat, barley, rye, and oats. According to results, the content of tocopherols and tocotrienols decreased whereas phenolic acids which are free and released from ester bonds increased. On the other hand, also it was reported that the extrusion process caused degradation of the dietary fiber polysaccharides (Poutanen 2001). Also, the decrease in antioxidant activity and total phenolic content of end products as extrudates was reported. This decrease could be attributed to whose low resistance to heating and evaporating processes temperatures (Călinoiu and Vodnar 2018).

The extrusion process results in the mechanic breakdown of the glycosidic bonds and could cause increasing the amount of soluble dietary fiber. Actually, the mechanical stress through the extrusion process could be in charge of the breaking down polysaccharide glycosidic bonds, causing to the release of oligosaccharides. Because of this reason, it could increase the soluble dietary fiber. Nevertheless,

there are controversial opinions in some cases about increasing insoluble dietary fiber. These differences are attributed to the different process conditions as shape and speed and shape of the extrusion screws. In addition, both of the starch gelatinization and starch retrogradation, the formation of the protein-polysaccharide complex during Maillard reaction and also oxidation of dietary fiber-phenolic compounds could account for the increase of insoluble dietary fiber by the formation of diferulates and results in dietary fiber cross-linking (Vitaglione et al. 2008).

Parboiling is comprised of three different processes like soaking, heating, and drying, relatively. The effect of this hydrothermal process on phytochemical of whole grain rice is associated with stability and migration of carotenoids. Particularly brown rice parboiling decrease content of carotenoids to trace levels (Alvarez-Jubete and Tiwari 2013).

## Conclusion and Future Remarks

Cereals are one of the main raw materials for the staple foods in many countries. Also, awareness about the relationship between health and food is increasing day by day. In this regard, whole grains are rich in several phytochemicals involving dietary fibre, phenolic compounds and other phytochemicals as phytic acid,  $\gamma$ -oryzanol, avenanthramides, and benzoxazinoids which are linked with reducing some chronic diseases like cardiovascular disease, cancer, diabetes, and obesity. Therefore, raising awareness, education of consumers about the health benefits of whole grains and designated daily intake of whole grains is so important regarding public health policy, which should be mediated by government in collaboration with health organizations, media, academic researchers and industry. Moreover, one of the most significant factors for choosing foods is the sensory properties of foods. For this reason, future studies should focus on advanced processing techniques to develop palatability of wholegrain products, and so, increasing the consumption of whole grain-based baked foods. Further, while choosing the processing technology, its advantages and disadvantages on the end product should be taken into consideration. Besides, further epidemiological studies should enlighten the plausible mechanisms of the protection of these compounds and health problems.

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