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Chapter 7

Antioxidant-Rich Natural Grain Products and Human Health

Afam I.O. Jideani, Henry Silungwe, Thakhani Takalani, Tonna A. Anyasi, Henry Udeh and Adewale Omolola

Additional information is available at the end of the chapter
http://dx.doi.org/10.5772/57169

1. Introduction

Over the years, several definitions have been used to describe whole grains. Though these definitions exist, a harmonized definition is yet to be agreed upon with many nations rather adopting the definition of whole grains as used by the American Association of Cereal Chemist (AACC) international due primarily to its comprehensiveness [1]. Accordingly in 1999, the AACC defined whole grains as grains that consist of an intact, milled, cracked or flaked caryopsis whose primary components; starchy endosperm, germ and bran are present in the same relative proportions as they exist in the intact caryopsis. Plant produce that can be classified as whole grains include amaranth, brown and coloured rice, sorghum, teff, wheat, faro, wild rice, triticale, millet, quinoa, oats, buckwheat, whole rye, barley, corn (including popcorn) and bulgur. According to the Food and Drug Administration (FDA) of the United States, foods such as soybeans, oilseeds (sunflower seeds), roots and corn flour or corn meal without the pericarp and other essential fractions cannot be classified as whole grains [1,2]. The term grains can also be used as a collective name given to seeds of cereals (wheat, barley, oats, corn/maize and sorghum) and legumes like peanuts and cowpea (Cajanus cajan) [2].

Whole grains are rich in phytochemicals and provide unique bioactive compounds that are complementary to those in fruits and vegetables when consumed together. The additive and synergistic effects of phytochemicals in fruits, vegetables and whole grains are responsible for their health benefits [3]. Important groups of phytochemicals with great beneficial nutritional and health effects are phenolics, carotenoids, vitamin E compounds, lignans, β-glucan and insulin. Phenolic compounds are the most common antioxidants in whole grains and are
generally categorized as phenolic acids, flavonoids, stilbenes, coumarines and tannins [4]. The most abundant phenolic compounds found in whole grains are phenolic acids and flavonoids (Figure 1).

![Structures of common phenolic compounds](image)

**Figure 1.** Structures of common phenolic compounds

<table>
<thead>
<tr>
<th>Minerals mg/kg</th>
<th>Wheat</th>
<th>Rye</th>
<th>Barley</th>
<th>Corn</th>
<th>Oats</th>
<th>Rice</th>
<th>Buckwheat</th>
<th>Millet</th>
<th>Sorghum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus</td>
<td>1170</td>
<td>3010</td>
<td>2460</td>
<td>990</td>
<td>4110</td>
<td>1030</td>
<td>1550</td>
<td>2400</td>
<td>350</td>
</tr>
<tr>
<td>Potassium</td>
<td>1550</td>
<td>4380</td>
<td>3290</td>
<td>1200</td>
<td>4000</td>
<td>1500</td>
<td>2420</td>
<td>2200</td>
<td>240</td>
</tr>
<tr>
<td>Magnesium</td>
<td>250</td>
<td>930</td>
<td>670</td>
<td>470</td>
<td>1170</td>
<td>350</td>
<td>1010</td>
<td>1000</td>
<td>188</td>
</tr>
<tr>
<td>Calcium</td>
<td>170</td>
<td>330</td>
<td>270</td>
<td>60</td>
<td>530</td>
<td>60</td>
<td>110</td>
<td>100</td>
<td>27</td>
</tr>
<tr>
<td>Sodium</td>
<td>20</td>
<td>50</td>
<td>40</td>
<td>10</td>
<td>40</td>
<td>20</td>
<td>10</td>
<td>NA</td>
<td>5</td>
</tr>
<tr>
<td>Zinc</td>
<td>8</td>
<td>28</td>
<td>13</td>
<td>5</td>
<td>30</td>
<td>17</td>
<td>25</td>
<td>34</td>
<td>3</td>
</tr>
<tr>
<td>Iron</td>
<td>12</td>
<td>28</td>
<td>24</td>
<td>11</td>
<td>38</td>
<td>12</td>
<td>15</td>
<td>48</td>
<td>11</td>
</tr>
<tr>
<td>Manganese</td>
<td>5</td>
<td>22</td>
<td>13</td>
<td>NA</td>
<td>58</td>
<td>9</td>
<td>15</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>Copper</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>NA</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Table 1.** Mineral content of whole grains

According to the FDA, a whole grain food is said to meet the whole grain health claim when it contains 51% whole grain flour by weight of its final product. It is also said to meet the whole grain health claims when it contains all components of the intact grain, has about 1.7 g of dietary fibre and also contains 16 g whole grain per serving [5]. *In vitro* minerals (Table 1) and phytochemicals in grains can act as antioxidants and used as nutraceuticals when consumed, by providing the body with protection against cardiovascular, anticancer, antidiabetics and...
antiobese agents, immune boosters, chronic inflammatory disorders and degenerative diseases [6]. Epidemiological studies have also revealed that regular consumption of whole grains and their products have been associated with reduced risk of developing chronic diseases [7]. Therefore, dietary modification by increasing the consumption of a wide variety of fruits, vegetables and whole grains daily, is said to be a practical strategy for consumers to optimize their health and reduce the risk of chronic diseases.

2. High antioxidant grains

Whole cereal grains contain a wide range of bioactive components with antioxidant effect [10] such as dietary fibre (DF) and phytochemicals [11,12] that are beneficial against diabetes, colon cancer and cardiovascular disease (CVD) [13,6,14]. Antioxidants present in whole grain cereals act in defense to remove the reactive oxygen species (ROS) thereby preventing and curing oxidative stress-related diseases. In [15], it was reported that vitamin E, folates, polyphenols, minerals, trace elements, carotenoids, phytic acid, lignin and alkylresorcinols are the bioactive compounds available in cereal grains. Polyphenols that are predominant in cereals are hydroxycinnamic, ferulic, gallic, vanillic and ρ-coumaric acids, of which, ferulic acid is the most potent. Phenolic compounds [16] are said to be present in cereal grains in free and bound form, as conjugates with sugars, fatty acids or as proteins. These polyphenols have several biological functions such as antioxidant, anti-inflammatory and anti-cancer activities that can protect the human body, which is constantly exposed to endogenous and exogenous free radicals [17]. Plant sterols, also called phytosterols, found in plants, have been clinically shown to lower low-density lipoprotein (LDL) cholesterol by about 8 to 15% as part of a heart-healthy diet. Also, wholegrains that serve as source of DF are useful in the prevention and treatment of constipation, CVD and hypertension [8,12].

Grains can be classified as typical and pseudo-cereals. Typical cereals include sorghum, wheat, rice, barley, millet, rye, oat, maize, buckwheat, triticale, fonio, canary grass. Pseudo-cereals include amaranth, buckwheat, quinoa, kaniwa, and pitseed. Cereals reported with high antioxidant capacity include sorghum, wheat, barley, millet and amaranth. It has also been reported that bioactive substances occur in grains at different concentrations and identities depending on genotypes and phenotypes [9]. Sorghum, millet and barley adapted to the UAE environment, were found to contain reasonable levels of DF and antioxidant properties [9]. Experimental evidence has shown that certain cereals such as sorghum are rich in antioxidants that are comparable to those in fruits and vegetables [19]. Varieties of sorghum such as black sorghum, have been shown to contain significant amount of antioxidants; condensed tannins, anthocyanins (Figure 2 and 3) and other phytochemicals with properties that complement the phytochemicals present in fruits and vegetables [19]. Whole wheat and wheat bran-based ready-to-eat breakfast cereals have also been reported to be an important source of dietary antioxidants [20]. It has been shown [21] that buckwheat constitutes high amount of total phenolics, with the highest DPPH radical scavenging activity and capacity for Fe\(^{3+}\) reduction. Phenolic acids from breakfast cereals exhibit strong antioxidant activity in vitro at concentrations that can be obtained from a normal serving of whole wheat cereal [20]. Available data
from the literature also reveals that sorghum is a significant source of phytosterols (tocopherols, tocotrienols) and policosanol, while rice has been shown to be rich in oryzanols [22].

Cereals naturally contain a wide variety of polyphenols such as the hydroxycinnamic, ferulic, vanillic, and ε-coumaric acids [20], which show a strong antioxidant power and may help to protect oxidative stress thus decreasing the risk of contracting several diseases [23,24]. Whole grains including wheat, contains several essential compounds that impact on the oxidative stability of cells. These compounds include selenium, β-carotene, vitamins C and E, phytate, proteins, polysaccharides, phenolics, lignans and tocopherols [20]. Phytic acid can protect
tissues against oxidative reactions through its ability to sequester and inactivate pro-oxidative transition metals [25,20]. In addition, acid conditions and enzymic hydrolysis has been reported to increase the solubility and activity of wheat phenolics, suggesting that the digestive process could be important in altering the antioxidant potential of wheat-based foods [20]. Simulated gastrointestinal pH treatment and enzymatic hydrolysis also increase the antioxidant activity of wheat and wheat-based breakfast cereal extracts, suggesting that the digestive process could be important in further enhancing the antioxidant potential of wheat-based foods [20]. However, it is still unclear if the consumption of cereal causes better health or whether it is a case of health status influencing food choice [26,27,23].

Processed products from cereals contain different antioxidant contents at varying amounts (Table 2). The cereals containing most antioxidants include barley, millet, maize and oats. Notably, polished rice and refined wheat, which are the main cereals eaten by humans globally are among the cereals with the lowest content of antioxidants [28]. In contrast, common millet and sorghum, which are important in particular regions in sub-Saharan Africa, South America and Asia, contains medium to high concentrations of antioxidants. The predominant types of antioxidants in corn are ferulic acid, anthocyanins, catechin and ⁶-caomaric acid. Wheat is high in β-glucan, β-cryptoxanthin, catechins, lutein, zeaxanthin and phytosterols. Barley is rich in tocopherols, tocotrienols and ferulic acids. Millet is high in tricin, luteolin and serotonin, whilst buckwheat contains rutin and catechins. Oats and rice are rich in avertramidin, catechins, proanthocyanidins and anthocyanins [3].

In the case of whole grains, corn, wheat, rice and oats are regarded as grains with high antioxidant activities. Corn has the highest total antioxidant activity compared to the other three grain types, followed by wheat and then oats. Rice has the lowest antioxidant activity compared to corn, wheat and oats [29]. Corn shows the highest total phenolic content at 1560 ± 60 μmol gallic acid equivalents/100 g, followed by wheat at 800 ± 40 μmol gallic acid equivalents/100 g, oats at 650 ± 20 μmol gallic acid equivalents/100 g and rice at 560 ± 20 μmol gallic acid equivalents/100 g. A study designed to investigate the complete phytochemical profiles in free, soluble conjugated, and insoluble bound forms, as well as their antioxidant activities in uncooked whole grains [30] showed that corn had the highest total antioxidant activity (181.42 ± 0.86 μmol of vitamin C equivalent/g of grain), followed by wheat (76.70 ± 1.38 μmol of vitamin C equivalent/g of grain), oats (74.67 ± 1.49 μmol of vitamin C equivalent/g of grain), and rice (55.77 ± 1.62 μmol of vitamin C equivalent/g of grain). Bound phytochemicals were the major contributors to the total antioxidant activity; 90% in wheat, 87% in corn, 71% in rice and 58% in oats. Bound phytochemicals can survive stomach and intestinal digestion to reach the colon. This may partly explain the mechanism of grain consumption in the prevention of colon cancer, other digestive cancers, breast cancer and prostate cancer as supported by epidemiological studies. Antioxidant activity of methanolic extracts from some grains consumed in Korea [31] revealed that the methanolic extracts prepared from red sorghum and black rice showed significantly higher antioxidant activities and contained higher polyphenolic contents than other grains such as white rice, brown rice, mungbean, foxtail millet, prosomillet, barley and adlay. Polyphenolic compounds were found to be the major naturally occurring antioxidants in grains. Antioxidant activity of small grain cereals
caused by phenolics and lipid soluble antioxidants as investigated in [32] showed a general considerable variation in antioxidant activities and phytochemical contents between cereals. A higher DPPH radical scavenging ability and reducing power were detected in hull-less barley, followed by rye and hull-less oat and durum and bread wheat, indicating that small grain species have different major antioxidants with different properties. Hull-less barley was found to have the highest content of total free phenols, flavonoids, PVPP bound phenolics and contained flavan-3-ols, not found in other species. Hull-less oat had the highest content of tocopherols, very high content of yellow pigments and PVPP bound phenolics. Ferulic acid was the major free phenolic acid in small grain cereals tested. A study designed to determine the composition in hydroxycinnamic acids and the antioxidant properties of soluble extracts from wheat, rye and buckwheat [33] revealed that the highest levels of total hydroxycinnamic acids and derivatives were found in the wheat bran and rye bran fractions whereas the buckwheat flours had only trace quantities of these compounds. The most abundant com-

<table>
<thead>
<tr>
<th>Cereals</th>
<th>Botanical name</th>
<th>Family</th>
<th>Amount present in cereals mmol/100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barley, whole meal flour</td>
<td>Hordeum vulgare</td>
<td>Poaceae</td>
<td>1.09</td>
</tr>
<tr>
<td>Common millet, wholemeal flour</td>
<td>Pennisetum glaucum</td>
<td>Poaceae</td>
<td>0.82</td>
</tr>
<tr>
<td>Maize, white flour</td>
<td>Zea mays</td>
<td>Poaceae</td>
<td>0.62</td>
</tr>
<tr>
<td>Oats, rough oatmeal</td>
<td>Avena sativa</td>
<td>Poaceae</td>
<td>0.59</td>
</tr>
<tr>
<td>Barley, white flour</td>
<td>Hordeum vulgare</td>
<td>Poaceae</td>
<td>0.58</td>
</tr>
<tr>
<td>Rye, wholemeal flour</td>
<td>Secale cereal</td>
<td>Poaceae</td>
<td>0.47</td>
</tr>
<tr>
<td>Wheat, wholemeal flour</td>
<td>Triticum aestivum</td>
<td>Poaceae</td>
<td>0.33</td>
</tr>
<tr>
<td>Oats, white flour</td>
<td>Avena sativa</td>
<td>Poaceae</td>
<td>0.32</td>
</tr>
<tr>
<td>Bulgur wheat, wholemeal flour</td>
<td>Triticum aestivum</td>
<td>Poaceae</td>
<td>0.31</td>
</tr>
<tr>
<td>Sorghum, wholemeal flour</td>
<td>Sorgum bicolor</td>
<td>Poaceae</td>
<td>0.30</td>
</tr>
<tr>
<td>Common millet, white flour</td>
<td>Pennisetum glaucum</td>
<td>Poaceae</td>
<td>0.25</td>
</tr>
<tr>
<td>Rye, white flour</td>
<td>Secale cereal</td>
<td>Poaceae</td>
<td>0.23</td>
</tr>
<tr>
<td>Rice, grains</td>
<td>Oryza sativa</td>
<td>Poaceae</td>
<td>0.17</td>
</tr>
<tr>
<td>Wheat, white flour</td>
<td>Triticum aestivum</td>
<td>Poaceae</td>
<td>0.13</td>
</tr>
<tr>
<td>Durum wheat, white flour</td>
<td>Triticum durum</td>
<td>Poaceae</td>
<td>0.05</td>
</tr>
<tr>
<td>Rice, white flour</td>
<td>Oryza sativa</td>
<td>Poaceae</td>
<td>0.04</td>
</tr>
<tr>
<td>Pseudo-cereals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buckwheat, wholemeal flour</td>
<td>Fagopyrum esculentum</td>
<td>Polygonaceae</td>
<td>1.99</td>
</tr>
<tr>
<td>Buckwheat, white flour</td>
<td>Fagopyrum esculentum</td>
<td>Polygonaceae</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Adapted from [28].

Table 2. Total antioxidant concentration of cereals.
pound present in the wheat and rye fractions was ferulic acid but small quantities of diferulic acids, sinapic acid, ρ-coumaric acid and benzoic acid derivatives were also present. The largest proportions of these phenolic compounds were found as covalently bound (esters) in the insoluble pellet but between 10% and 30% of the total compounds were solubilized, mostly in water. Most of the antioxidant capacity was found in the water extracts from all the cereal fractions. Overall, buckwheat and wheat germ products exhibited the highest antioxidant capacity whereas the rye products had the lowest antioxidant values, an indication that the consumption of buckwheat and wheat germ could be an important source of antioxidants required for healthy living.

The phytochemical content and antioxidant activity of six diverse varieties of whole wheat as reported in [34] showed free phenolic content ranging from 255 (KanQueen) to 499 (Roane) 1mol gallic acid equivalents/100 g DW. The bound phenolic content ranged from 582 (Roane) to 662 (Cham1) 1mol gallic acid equivalents/100 g DW. The bound fraction contributed 53.8 - 69.7% of the total phenolic content of the wheat varieties analysed. Ferulic acid was the predominant phenolic acid found in whole wheat. Total ferulic acid content ranged from 310.8 (Caledonia) to 496.1 (KanQueen) 1mol ferulic acid/100 g DW. The percentage of ferulic acid found in the insoluble-bound fraction ranged from 87.4% (Caledonia) to 97.2% (KanQueen). Other phenolic acids, ρ-coumaric acid, syringic acid, vanillic acid, and caffeic acid were also detected. Lutein was the predominant carotenoid found in the whole wheat varieties analysed. Zeaxanthin, β-carotene, and β-cryptoxanthin were also detected. Mainly α- and β-tocopherols and α- and β-tocotrienols were found in all varieties of whole wheat though δ-tocopherol was detected in all but two varieties. β-tocotrienol was the predominant form of vitamin E found in all varieties of whole wheat (Table 3). The antioxidant activity was assessed using the oxygen radical absorbance capacity (ORAC) assay. The ORAC of the free fraction ranged from 1958 to 3749 1mol Trolox equivalents/100 g DW. The ORAC of the bound fraction ranged from 3190 to 5945 1mol Trolox equivalents/100 g DW. Total phenolic content correlated with oxygen radical absorbance capacity ($R^2 = 0.810; p < 0.001$). They concluded that phytochemicals found in whole grains may be responsible for the health benefit derived from whole grain consumption.

<table>
<thead>
<tr>
<th>Grains</th>
<th>Tocopherols</th>
<th>Tocotrienols</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α</td>
<td>β</td>
</tr>
<tr>
<td>Wheat</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Rye</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>Barley</td>
<td>8.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Oats</td>
<td>14.9</td>
<td>3.0</td>
</tr>
<tr>
<td>Maize</td>
<td>3.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Rice</td>
<td>14.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

NA = not available. Source: [35-37].

Table 3. Vitamin E content of whole grains flour mg/kg dry matter.
Rice is rich in phytochemicals that are present in lipophilic, hydrophilic and insoluble forms. In reference [38], it was indicated that tocopherols, tocotrienols (Figure 4) and γ-oryzanol, are major lipophilic fractions of whole grain rice and are beneficial to human health. It also contains tricin, ferulic acid, caffeic acid and methoxycinnamic acid which are hydrophilic phenolic compounds reported to have cancer protective potential. Barley grains contain DFs, β-glucans, arabinoxylans and polyphenols [39,40]. β-glucans and arabinoxylans present in barley are critical nutrients that determine wort viscosity, foam stability and beer filtration rates, thus playing a significant role in beer brewing process [41,42]. Barley β-glucans also plays health beneficial roles in the reduction of blood cholesterol level, glucose level and helps in weight loss by increasing satiety, thereby reducing susceptibility to heart disease and type-2 diabetes [40]. Oats and psyllium husk which contains fibres have also been implicated in the reduction of homocysteine, cholesterol and risk of CVD [43]. Millets are rich source of DF, phytochemicals, micronutrients, nutraceuticals, and could be rightly termed as nutricereals.

Figure 4. Tocopherols and tocotrienols in grains
3. Grains and human health

Dietary antioxidants are food compounds that impede the deleterious effects of reactive oxygen species, reactive nitrogen species, or both, on the normal physiological function in humans [44,27]. Dietary antioxidants include ascorbate, tocopherols, carotenoids and bioactive plant phenols. ROS; oxygen ions, free radicals, and peroxides and reactive nitrogen species (RNS); nitrous anhydride, peroxynitrite, and nitrogen dioxide radicals, causes oxidation, nitrination, halogenation and deamination of biomolecules of all types, including lipids, proteins, carbohydrates, and nucleic acids, with the resultant formation of toxic and mutagenic products [45,46]. Biological systems control these oxidative factors by a variety of antioxidative mechanisms that restrict the reactivity of ROS and RNS and oxidation catalysts [20]. In human cells, de novo antioxidant production is much more limited and oxidative damage resulting from excess production of free radicals has been reported to initiate the pathogenesis of most chronic degenerative diseases such as brain stroke, diabetes mellitus, rheumatoid arthritis, Parkinson’s disease, Alzheimer’s disease, and cancer [27,28]. The production of ROS and RNS are speedily formed in cells as a consequence of disease processes (e.g. inflammation), tobacco smoke, environmental pollutants, ingestion of oxidized foods, ischemia, drugs, ethanol and radiations. If unchecked, such cellular event can promote a chain of chemical reactions that form free radicals, peroxides and secondary oxidation breakdown products which in turn reacts with and cause damage to cellular membranes, proteins and nucleic acids [20,23].

Phenolic compounds present in whole grains are known to be effective in protecting against CVDs and some cancer (Table 4). This protective effect is thought to be mediated through their action as antioxidants to prevent oxidative damage induced by ROS to some biomolecules (DNA, lipids and proteins) under pathological conditions [47]. In reference [48], it was reported that phenolic compounds could be responsible for chelating metals as well as inhibiting the free radicals capitation by limiting the action of the lipoxygenase enzyme. Phytate compounds on the other hand may exert antioxidant activity by complexing with iron, reducing the formation of free radicals and peroxidation of membranes, which could provide anticarcinogenic power. Lignans on their part are a group of dietary phytoestrogen found in a variety of plant foods like corn, oats, rye, wheat, flaxseeds, legumes, fruits and vegetables. These plant lignans when consumed are converted to the mammalian lignans, enterodiol and enterolactone which have strong antioxidant activity. β-glucan is mostly found in cell walls of oats, barley and wheat. Its major biological effects include lowering of blood cholesterol level, controlling blood sugar, promotion of weight management, encouraging the growth of beneficial gut microflora and enhancing the immune system. This is probably due to its high viscosity property as a soluble fibre to bind cholesterol and bile acids and facilitate their elimination from the body. It has been [93] indicated that β-glucan had an effect in controlling blood sugar in diabetes subjects, and was helpful in reducing the elevation in blood sugar levels after a meal. The authors further indicated that this is probably as a result of delaying gastric emptying, allowing dietary sugar to be absorbed more gradually, as well as by possibly increasing the tissue sensitivity to insulin. The United States Food and Drug Administration (FDA) is allowing whole grain barley products that can supply β-glucan at levels of 0.75 g per serving or 3 g per day to carry a claim that they reduce the risk of coronary heart disease [49].
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Cereals/Parts Found</th>
<th>Method of Determination</th>
<th>Effects on Humans</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitamins (Tocopherols and tocotrienols)</td>
<td>Germ of all cereal grains</td>
<td>HPLC</td>
<td>Induction of immune responses; lowering of cholesterol levels; defence against oxidative stress; antimutagenic and anticancer</td>
<td>[50,51,52]</td>
</tr>
<tr>
<td>Phytosterols (Sitosterol, campesterol, stigmasterol, brassicasterol)</td>
<td>Aleurone, pericap and germ of rice, wheat, rye, oat and barley.</td>
<td>Gas chromatography analysis</td>
<td>Prevent CVDs.</td>
<td>[53,54,55]</td>
</tr>
<tr>
<td>Phenolics (Lignans, phenolic acids, alkylresorcinols, avenathramide, coumarins)</td>
<td>Bran layer of most cereals e.g. barley, sorghum, rice, rye, wheat, millet and oat.</td>
<td>HPLC, GC-MS</td>
<td>Believed to have anticancer activity; prevent oxidative stress, cholesterolemia, atherosclerosis and aging; anti-inflammatory and anti-irritant.</td>
<td>[56,57,52,58]</td>
</tr>
<tr>
<td>Carotenoids</td>
<td>Yellow endosperm of durum wheat.</td>
<td>UV/Vis spectrometry, HPLC and MS spectrometry</td>
<td>Prevent cataracts, age-related muscular degeneration, cancer and cardiovascular disease.</td>
<td>[59,52,60]</td>
</tr>
<tr>
<td>Flavonoids (anthocyanidins, flavonols, flavanones)</td>
<td>Yellow lemon sorghum, aleurone of blue and red coloured maize.</td>
<td>UV/Vis spectrometry, HPLC, mass spectrometry</td>
<td>Inhibitory effects on cancer, anti-inflammatory properties, reduce glycemia, combats complications of diabetes.</td>
<td>[61,52,62,63]</td>
</tr>
<tr>
<td>Phytate (Inositol hexaphosphate)</td>
<td>Aleurone layer and scutellum cells of germ of most cereals.</td>
<td>HPLC, HPIC</td>
<td>Gene regulation, anti-inflammatory, prevents complications of diabetes, antineoplastic in breast, colon and liver.</td>
<td>[64,65,66]</td>
</tr>
</tbody>
</table>

Table 4. Antioxidant compounds in cereals, human effects and methods of determination

According to [67], these antioxidant compounds may offer protection against heart disease, hormone-related breast and prostate cancers. Enterodiol and enterolactone inhibited colon cancer cell growth, induced cell cycle and apoptosis in vitro [68]. In a study conducted among post-menopausal women diagnosed with heart conditions, whole grains was associated with a slower build-up of artery-narrowing plaque among the post-menopausal women and in lowering the overall risk of mortality associated to CVDs [69,70]. Whole grains were also implicated in a 66% reduction in cancer in a study conducted in over 2000 people fed with a...
high-fibre whole grain diet [71]. Available epidemiological evidence suggests that sorghum consumption reduces the risk of certain types of cancer in humans compared to other cereals [19]. Positive effects of sorghum and/or millet consumption on cancer have been documented. Sorghum consumption consistently correlated with low incidence of oesophageal cancer [72] in various parts of the world (including several parts of Africa, Russia, India, China and Iran) whereas wheat and corn consumption correlated with elevated incidence [19]. Sorghum containing tannins are widely reported to reduce caloric availability and hence weight gain in animals. However, with obesity as a major and ever-increasing problem in the developed world (with more than 60% of Americans reported to be overweight), this attribute of sorghum tannins has the potential of mitigating the problem [19]. Although information on how sorghum phytochemicals affect human health is limited, overall epidemiological studies suggest that sorghum possesses anti-carcinogenic properties when consumed regularly in the diet.

Whole grains, oilseeds, nuts and legumes are rich in sterols and stanols. In humans, high intake of sterols or stanols is associated with lowering of serum and LDL cholesterol concentrations. Phytosterols compete with cholesterol for micelle formation in the intestinal lumen and inhibit cholesterol absorption [73]. Whole grains are good sources of health beneficial phytochemicals. These phytochemicals are in free soluble-conjugated and bound forms [74]. Most of them are bound to the cell wall materials and insoluble. This makes it difficult for these phytochemicals to be released during the upper gastrointestinal tract digestion. As a result of this, colonic digestion of such materials by microflora results in the release of the bulk of bound phytochemicals to exert their health benefits. Hence, the reduced risk of colon cancer associated with increased consumption of whole grain products. Higher beans consumption apart from being associated with reduced risk of diabetes and obesity, is inversely associated with prostate, breast and colon cancers [10]. This is due to the presence of elements which are able to retard the glycemic response, slowing the release of glucose into the blood [75]. This antioxidant and anticarcinogenic effect of beans has been attributed to the presence of phenolic and phytate acids, which were previously regarded as unwanted compounds with antinutritional factors.

Consuming whole grains and their products regularly is associated with risk reduction of developing chronic diseases such as CVDs, type 2 diabetes and some cancers. Therefore, dietary modification by increasing the consumption of wide variety of fruits, vegetables and whole grains daily is a practical strategy for consumers to optimize their health and reduce the risk of chronic diseases [76].

4. Fortified antioxidant grain-based products

Cereal extruded products are mainly composed of starches, and or vegetable proteins. The role of these constituents is mainly to impart structure, texture, bulk, mouth feel and other desired characteristics for finished products [77]. Infant cereals are one of the most common weaning foods. However, these foods in their natural form may lack some vital infant nutritional requirements for proper growth. The nutritional quality of raw cereal based infant
products is low, hence they have to be processed (fortified) to improve their overall nutritional quality [78].

5. Novel antioxidant grain-based products

A novel way of consuming grain products is the consumption of functional foods. Functional here refers to foods that provide other health benefits to the body apart from those derived from its nutrients. Eating whole grain meals and functional food products will therefore enhance the nutritional intake derived from whole grain related diets [79].

6. Global policies affecting antioxidant-rich grain production

Recent dramatic increases in food prices are having severe consequences for poor countries and their populace. The Food and Agriculture Organization (FAO) of the United Nations, reports that food prices rose by nearly 40% in 2007 and made further large jumps in early 2008. Nearly all agricultural commodities including rice, maize, wheat, meat, dairy products, soybeans, palm oil, and cassava are affected. In response to the price hikes, food riots have occurred in many developing countries, including Burkina Faso, Cameroon, Côte d’Ivoire, Egypt, Haiti, Indonesia, Senegal, and Somalia. According to the FAO, 37 countries are now facing food crises [80].

7. Future research on natural antioxidant-rich grains

Many investigations continue to establish the protective cancer-preventive and healthful compounds in cereal grains [81-83,12]. In [84], it was reported that many epidemiological studies suggested that consumption of whole grain cereal is highly correlated to reduced incidences of chronic diseases. Experimental and epidemiological studies have shown that consumption of grains, lower the incidence of aging diseases, as well as other non-communicable diseases such as colorectal cancer, hypertension, stroke and heart diseases [85-87]. There is strong epidemiological evidence that whole-grain cereals protect the body against age-related diseases such as diabetes, CVDs and some cancers. This may be due to the fibre and micronutrients in the outer layer and germ fractions of the grain acting together to combat oxidative stress, inflammation, hyperglycaemia and carcinogenesis. It has been shown that the whole wheat flours of different wheat varieties contain significant amounts of phenolic antioxidants and dietary fibres. Cereal bran fibres, good for colon health, show good potential for high incorporation into extruded foods [88]. Sorghum phytochemicals have been shown to have potential impact on human [19]. There is now evidence that the consumption of whole grains and whole-grain products is implicated in the prevention of cancer and other chronic diseases [83]. Studies have shown that plant food material with polyphenolic constituents have more potent antioxidant
and anti-inflammatory activities. In many epidemiologic studies, an inverse association between high cereal intake and low cancer incidence has been observed [83,11].

Future research in antioxidant rich grains may address regional health issues. In Africa, future research on antioxidant-rich foods can also be directed to address nutritional issues. It was suggested that while corn starch provides all the features for production of highly acceptable extruded snack foods its nutritional value is far from satisfying the needs of health conscience consumers [78]. In the US, future prospective studies may address the question of whether whole grain intake is directly related to body weight and obesity and whether the associations are primarily driven by fiber, other dietary component of whole-grain foods, or some other related aspect of the diet [89].

Epidemiological studies have shown that the consumption of whole grain cereal foods reduces the risk of chronic diseases linked with metabolic syndrome, such as CVD and diabetes. Aggressive and consistent consumer education needs to be put in place by the government or relevant agencies to educate consumers on the health benefits of cereal foods especially in the developing countries where the level of ignorance is high and literacy is low. Furthermore, food scientists and engineers, nutritionists and consumer scientists should look into developing more varieties of appealing cereal based products from the already identified cereal grains rich in antioxidants and bioactive components. More clinical trials are required to strengthen the proposed link between the phenolic compounds found in rice and chronic disease prevention. Research is needed to evaluate the effects of both hydrophilic and lipophilic antioxidants on their antioxidant capacity. Clinical trials that ascertain the phytochemicals found in whole grains may be responsible for the health benefit derived from whole grain consumption.

8. Conclusion

The beneficial effects associated with whole grain consumption are in part due to the existence of the unique phytochemicals of whole grains [9]. Based on the epidemiological data, consumption of whole wheat grain has been recommended to improve insulin sensitivity and to lower serum insulin concentration [90,91].

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