Phenolic Compounds in Cereal Grains and Their Health Benefits

- Whole grain cereals are a good source of phenolics.
- Black sorghums contain high levels of the unique 3-deoxyanthocyanidins.
- Oats are the only source of avenanthramides.
- Among cereal grains, tannin sorghum and black rice contain the highest antioxidant activity in vitro.

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Research has shown that whole grain consumption helps lower the risk of cardiovascular disease, ischemic stroke, type II diabetes, metabolic syndrome, and gastrointestinal cancers (36,37). In addition to dietary fiber, whole grains contain many health-promoting components such as vitamins, minerals, and phytochemicals, which include phenolic compounds. Phenolic compounds have antioxidant properties and can protect against degenerative diseases (i.e., heart disease and cancer) in which reactive oxygen species (i.e., superoxide anion, hydroxyl radicals, and peroxy radicals) are involved (32,57).

The general definition of a phenolic compound is any compound containing a benzene ring with one or more hydroxyl groups. Phenolic acids, flavonoids, condensed tannins, coumarins, and alkylresorcinols are examples. All plant-based foods have phenols, which affect their appearance, taste, odor, and oxidative stability (45). In cereal grains, these compounds are located mainly in the pericarp, and they can be concentrated by decorticating the grain to produce bran, which can be incorporated into a food product (i.e., breads, cookies, and tortillas) with increased dietary fiber levels and nutraceutical properties.

Most of the literature on plant phenolics focuses mainly on those in fruits, vegetables, wines, and teas (33,50,53,58,74). However, many phenolic compounds in fruits and vegetables (i.e., phenolic acids and flavonoids) are also reported in cereals. The different species of grains have a great deal of diversity in their germplasm resources, which can be exploited. Some phenols are unique to one plant species, such as the oat avenanthramides (12). Different methods of analysis for phenols and antioxidant activity are reported in the literature. Unfortunately, it is difficult to make comparisons of phenol and antioxidant activity levels in cereals since different methods have been used. The purpose of this article is to give an overview of phenolic compounds reported in whole grain cereals and to compare their phenol and antioxidant activity levels.

Phenolic Acids

Phenolic acids are derivatives of benzoic and cinnamic acids (Fig. 1) and are present in all cereals (Table I). There are two classes of phenolic acids: hydroxybenzoic acids and hydroxycinnamic acids. Hydroxybenzoic acids include gallic, *p*-hydroxybenzoic, vanillic, syringic, and protocatechuic acids. The hydroxycinnamic acids have a C6-C3 structure and include coumaric, caffeic, ferulic, and sinapic acids. The phenolic acids reported in cereals occur in both free and bound forms. Sorghum and millet have the widest variety of phenolic acids. Free phenolic acids are located in the outer layer of the

Table I. Phenolic acids reported in cereal grains

Phenolic Acid	Grain	References
Hydroxybenzoic acids:		
Gallic	Millet[a], rice, sorghum	29, 67, 75
Protocatechuic	Barley, maize, millet[b], oat, rice, rye, sorghum, wheat	29, 41, 43, 44, 66, 67, 69
p-Hydroxybenzoic	Barley, maize, millet[c], oat, rice, rye, sorghum, wheat	29, 39, 41, 43, 44, 66, 69
Gentisic	Millet[d], sorghum	44, 70
Salicylic	Barley, sorghum, wheat	39, 43, 70
Vanillic	Barley, maize, millet[d], oat, rice, rye, sorghum, wheat	29, 39, 41, 43, 44, 66, 67, 69, 75
Syringic	Barley, maize, millet[d], oat, rice, rye, sorghum, wheat	39, 41, 43, 44, 66, 69, 70, 75
Hydroxycinnamic acids:		
Ferulic	Barley, maize, millet[d], oat, rice, rye, sorghum, wheat	3, 29, 39, 41, 43, 44, 66, 67, 69, 75
Caffeic	Maize, millet[d], oat, rice, rye, sorghum, wheat	29, 39, 41, 44, 66, 67, 75
o-Coumaric	Barley	43
m-Coumaric	Barley	43
p-Coumaric	Barley, maize, millet[d], oat, rice, rye, sorghum	3, 29, 39, 41, 43, 44, 66, 67, 69, 75
Cinnamic	Millet[d], sorghum, wheat	29, 44
Sinapic	Barley, millet[e], oat, rice, rye, sorghum	3, 41, 43, 44, 66, 69, 70

[a] Detected in finger millet.
[b] Detected in finger, pearl, and teff millets.
[c] Detected in finger, pearl, and foxtail millets.
[d] Detected in finger, pearl, teff, and foxtail millets.
[e] Detected in finger and pearl millets.

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pericarp and are extracted using organic solvents (29,30,41,66,67). Bound phenolic acids are esterified to cell walls; acid or base hydrolysis is required to release these bound compounds from the cell matrix (29,30,39,41,59,66,67). The major phenolic acids in cereals are ferulic and *p*-coumaric acids (29,34,41,44,66,75). Phenolic acid levels vary among cereals; their brans concentrate these compounds threefold (Table II).

Flavonoids

Flavonoids are compounds with a C6-C3-C6 skeleton that consists of two aromatic rings joined by a three-carbon link; they include anthocyanins, flavanols, flavones, flavanones, and flavonols (Fig. 1). More than 5,000 flavonoids have been identified in nature (74). Flavonoids are located in the pericarp of all cereals. Thus far, sorghum has the widest variety of flavonoids reported (Table III).

Table II. Phenolic acid content in cereal grains

Sample	Amount (µg/g)	References
Whole grains:		
Barley	450–1346	34, 41
Finger millet	612	44
Foxtail millet	3907	44
Maize	601	41
Oat	472	41
Pearl millet	1478	44
Rice	197–376	41
Rye	1362–1366	41
Sorghum	385–746	29
Wheat	1342	41
Brans:		
Oat	651	41
Rye	4190	41
Wheat	4527	41

Anthocyanins are water-soluble pigments that contribute the blues, purples, and reds in plant foods (i.e., blueberries, blackberries, and strawberries) and are the major flavonoids studied in cereals. The six common anthocyanidins in nature are cyanidin, delphinidin, malvinidin, pelargonidin, petunidin, and peonidin. These compounds have been reported in the pericarp of pigmented varieties of barley, maize, rice, rye, and wheat (Table III); the amounts are reported in Table IV. Milling these cereals into bran concentrates the anthocyanins. For example, blue and purple whole wheat and bran have anthocyanin levels of 93–152 and 236–453 µg/g, respectively (1).

Sorghums contain unique anthocyanins called 3-deoxyanthocyanins, which lack the hydroxyl group in the 3 position of the C-ring (Fig. 2). This feature is believed to increase their stability at high pH compared to common anthocyanins (6,22), which could make them good natural food colorants. The two main sorghum 3-deoxyanthocyanidins are the yellow apigeninidin and the orange luteolinidin (18). Sorghums with a black pericarp have higher levels of 3-deoxyanthocyanins than red sorghums (19). Decortication of black sorghum grain to produce bran concentrates anthocyanin levels almost sevenfold. For example, in our laboratory, the grain and bran of Tx430 black have anthocyanin levels of 944 (Table IV) and 6,695 µg/g, respectively (unpublished data).

Other flavonoids found in fruits and vegetables are also reported in cereals. For example, the flavone apigenin, a compound found in parsley and celery (58,74), is also reported in millet, oat, and sorghum (Table III). Flavanones, which are compounds mainly reported in citrus (58,74), are also reported in cereals such as sorghum and oat (Table III). Flavonoids are reported to have antioxidant, anticancer, anti-allergic, anti-inflammatory, anticarcinogenic, and gastroprotective properties (13,32,58,74).

Condensed Tannins

Condensed tannins, which are also called proanthocyanidins or procyanidins, consist of polymerized flavanol units (Fig. 1), and they contribute to astringency in foods. These compounds are found in sorghum with a pigmented testa layer, red finger millets, and barley (18,21).

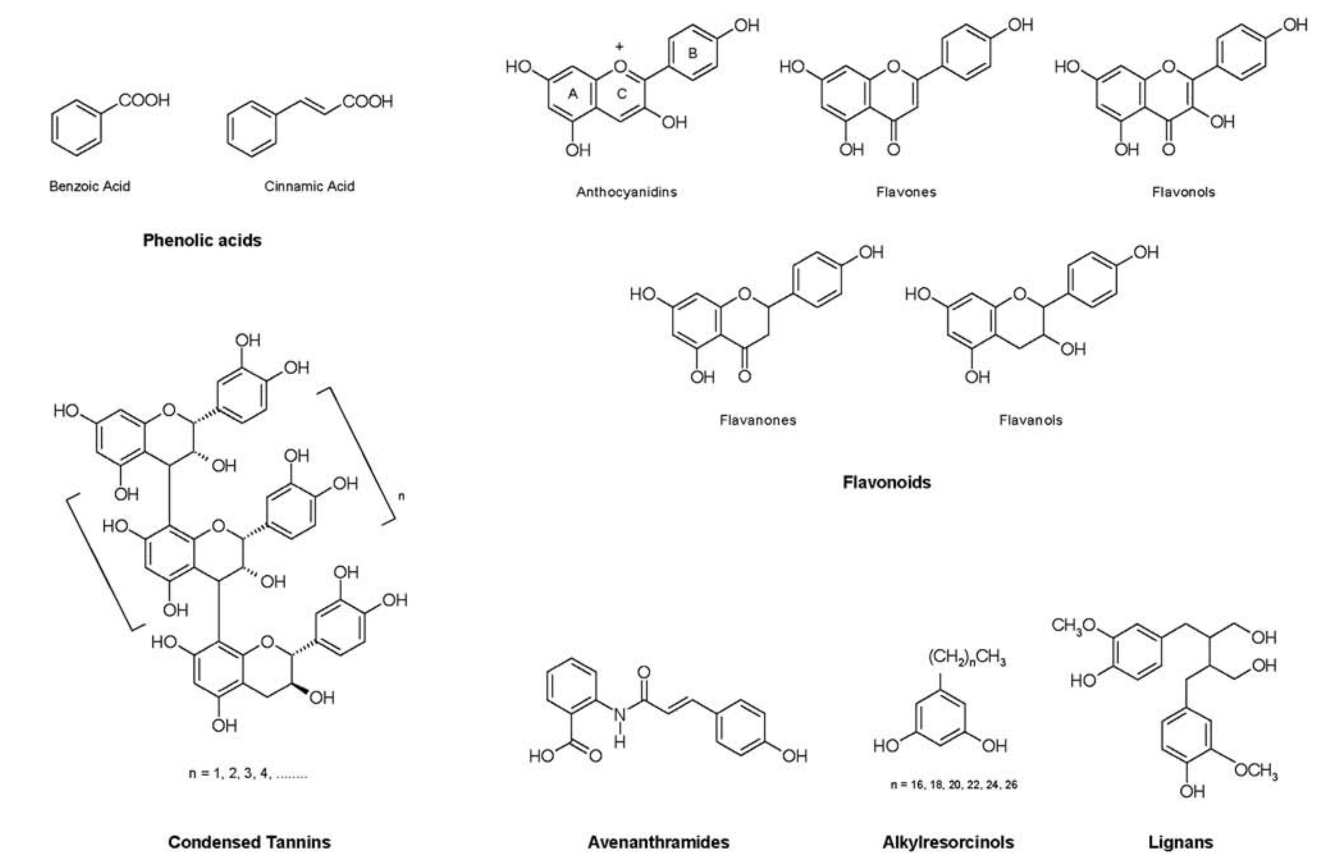

Fig. 1. Chemical structure of classes of phenolic compounds in cereal grains.

Over the years, it has been difficult to determine tannins in foods due to the lack of appropriate standards. For many years, colorimetric methods (i.e., the vanillin/HCl, butanol/HCl, or the 4-dimethylamino–cinnamaldehyde [DMACA] assays) have been used to measure condensed tannins (18). However, these methods can over-estimate or yield false-positive results since monomeric phenols react with the reagents (18).

Table III. Flavonoids reported in cereal grains

Compound	Grains	References
Anthocyanins:		
Apigeninidin	Sorghum	6, 47
Apigeninidin 5-glucoside	Sorghum	46, 47, 73
Cyanidin	Barley	43
Cyanidin 3-galactoside	Maize, wheat	1, 43
Cyanidin 3-glucoside	Barley, maize, rice, rye, wheat	1, 2, 43
Cyanidin 3-rutinoside	Maize, rice, wheat	2
Delphinidin	Barley	43
Delphinidin 3-glucoside	Wheat	2
Delphinidin 3-rutinoside	Rye, wheat	2
Luteolinidin	Sorghum	6, 47
Luteolinidin 5-glucoside	Sorghum	47, 73
5-Methoxyapigeninidin	Sorghum	64
7-Methoxyapigeninidin	Sorghum	48, 64, 73
7-Methoxyapigeninidin 5-glucoside	Sorghum	73
5-Methoxyluteolinidin	Sorghum	64, 73
5-Methoxyluteolinidin 7-glucoside	Sorghum	73
7-Methoxyluteolinidin	Sorghum	64
Pelargonidin	Barley	43
Pelargonidin 3-glucoside	Maize	43
Pelargonidin glycosides	Barley, maize	43
Peonidin-3-glucoside	Maize, rice, rye, wheat	1, 2, 43
Petunidin 3-glucoside	Barley, wheat	2
Petunidin 3-rutinoside	Wheat	2
Flavones:		
Apigenin	Millet[a], oat, sorghum	26, 51, 63, 64
Apigenin glycosides	Wheat	65
Glucosylorientin	Millet[b]	56
Glucosylvitexin	Millet[b]	56
Luteolin	Millet[c], oat, sorghum	63, 64, 51, 71
Isovitexin	Oat	43
Tricin	Millet[d], oat, wheat	51, 65, 71
Vitexin	Millet[b], oat	43, 56
Flavanones:		
Eriodictyol	Sorghum	38
Eriodictyol 5-glucoside	Sorghum	26
Homoeriodictyol	Oat	43
Naringenin	Sorghum	26
Flavonols:		
Chrysoeriol	Barley	43
Kaempferol	Maize, oat	51, 65
Kaempferol 3-rutinoside	Oat	51
Kaempferol 3-rutinoside-7-glucuronide	Sorghum	46
Quercetin	Maize, oat	51, 65
Quercetin 3-rutinoside	Oat	51
Dihydroflavonols:		
Taxifolin	Sorghum	26
Taxifolin 7-glucoside	Sorghum	26
Flavan-4-ols:		
Apiforol	Sorghum	72
Luteoforol	Sorghum	7
Flavanols (monomers/dimers):		
Catechin	Barley, sorghum	27, 34, 43
Leucocyanidin	Barley, maize	43, 65
Leucodelphinidin	Barley	43
Leucopelargonidin	Maize	65
Procyanidin B-1	Sorghum	26, 27
Procyanidin B-3	Barley	21, 34, 43
Prodelphinidin B-3	Barley	21, 34

[a] Detected in fonio millet.
[b] Detected in pearl millet.
[c] Detected in fonio and Japanese barnyard millets.
[d] Detected in Japanese barnyard millet.

Normal-phase HPLC with fluorescence detection separates and quantifies condensed tannin according to the degree of polymerization (23,31). For instance, tannin levels in barley and in tannin sorghum are 0.74 mg/g and 7.88–21.97 mg/g, respectively (4,24). The tannins in barley are monomers, dimers, and trimers, whereas those found in tannin sorghums are polymers (4,23,24,34).

Tannins bind to proteins, carbohydrates, and minerals, which decrease digestibility of these nutrients and reduce feed efficiency of ruminants and monogastrics during feeding (18). Plants containing high tannin levels are not preferred by birds and insects. However, humans have acquired a taste for moderately astringent foodstuff (i.e., dark chocolate and cranberries) or beverages (i.e., red wine and tea) (49). Condensed tannins have high antioxidant activity in vitro compared to monomeric phenolic compounds (28). In addition, these compounds may have anticarcinogenic, cardiovascular, gastroprotective, anti-ulcerogenic, and cholesterol-lowering properties, and they also promote urinary tract health (18,54).

Avenanthramides

Avenanthramides consist of an anthranilic acid derivative linked to a hydroxycinnamic acid derivative (Fig. 1). The three major avenanthramides reported in oat are avenanthramides 1, 3, and 4, which are also known as avenanthramides B, C, and A, respectively (12,16,51). Levels of avenanthramide 1 range from 40–132 µg/g in the grain; they are heat stable during processing (17). Oat flakes have more avenanthramides (26–27 µg/g) than oat bran (13 µg/g) (41). These compounds are bioavailable, and they have anti-inflammatory, anti-atherogenic, and antioxidant properties (8,10,20,40,52).

Table IV. Anthocyanin content of pigmented cereal grains

Sample	Amount (µg/g)
Blue barley[a]	4
Maize:[a]	
Pink	93
Red	558
Blue	225
Purple	965
Black rice[a]	2,283
Black sorghum[b]	944
Wheat:[a]	
Blue	106–153
Purple	13–139

[a] Data obtained from Abdel-Aal and coworkers (2).
[b] Rooney and coworkers (Cereal Quality Lab, Texas A&M University, College Station, TX, unpublished data).

Lignans

Lignans (Fig. 1) are a class of phytoestrogens that are predominant in flaxseed, but they are also found in cool season cereal grains (i.e., barley, oat, rye, triticale, and wheat). The amount of lignans in these cereals ranges from 8–299 µg/100 g (9,42). The two plant lignans identified are secoisolariciresinol and matairesinol. When ingested, secoisolariciresinol and matairesinol are converted into the mammalian lignans enterodiol and enterolactone, respectively, by microbial enzymes in the colon (35,68). These compounds are bioavailable and are believed to reduce the risk of hormone-dependent cancers (i.e., breast and prostate), colon cancer, and heart disease, and they also have antioxidant properties (9,14, 35,55,68).

Alkylresorcinols

Alkylresorcinols are 1,3-dihydroxybenze derivatives with an odd-numbered *n*-alkyl side-chain at C-5 on the benzene ring (Fig. 1). These compounds are found in the bran of wheat, rye, triticale, and barley (62). Wheat, rye, and barley contain 339–759 µg/g, 575–1,008 µg/g, and 8 µg/g of alkylresorcinols, respectively (11,41,61). Wheat and rye brans contain 2,211–3,225 µg/g and 2,758–4,108 µg/g of alkylresorcinols, respectively (11,41). Alkylresorcinols have antibacterial and antifungal properties and antioxidant activity in vitro (60). These compounds are of interest as biomarkers of whole grain cereal intake, which would help us understand the link between whole grain cereal consumption and health (60).

Phenol and Antioxidant Activity Levels in Cereal Grains

Figures 3 and 4 compare phenol and in vitro antioxidant activity levels of a wide array of cereal grains. The Folin-Ciocalteu and the 2,2'-azinobis (3-ethyl-benzothiazoline-6-sulfonic acid (ABTS) assays were used, respectively using 1% HCl in methanol as the solvent (25). In general, tannin-containing grains (i.e., sorghum) and pigmented cereal grains had the highest levels of phenols and antioxidant activity in each grain category (Figs. 3 and 4). Tannin sorghums and black rice had the highest levels of phenols and antioxidant activity whereas nonpigmented cereals (i.e., white rice, wheat, and waxy

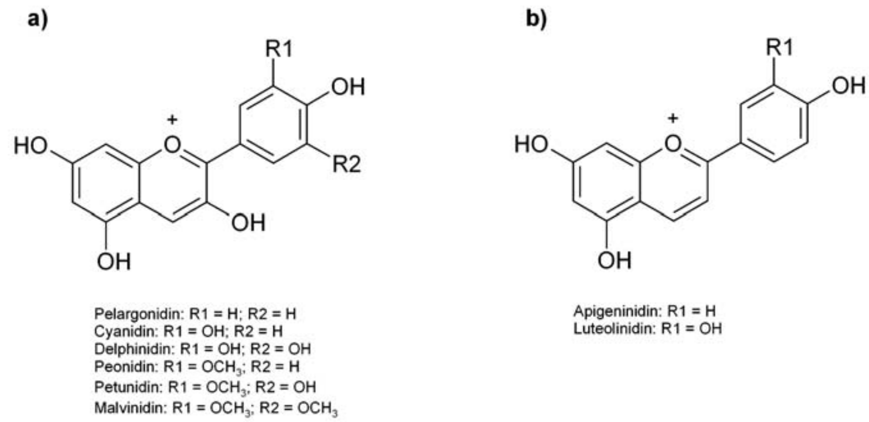

Fig. 2. Chemical structure of A, the six common anthocyanidins, and B, the 3-deoxyanthocyanidins.

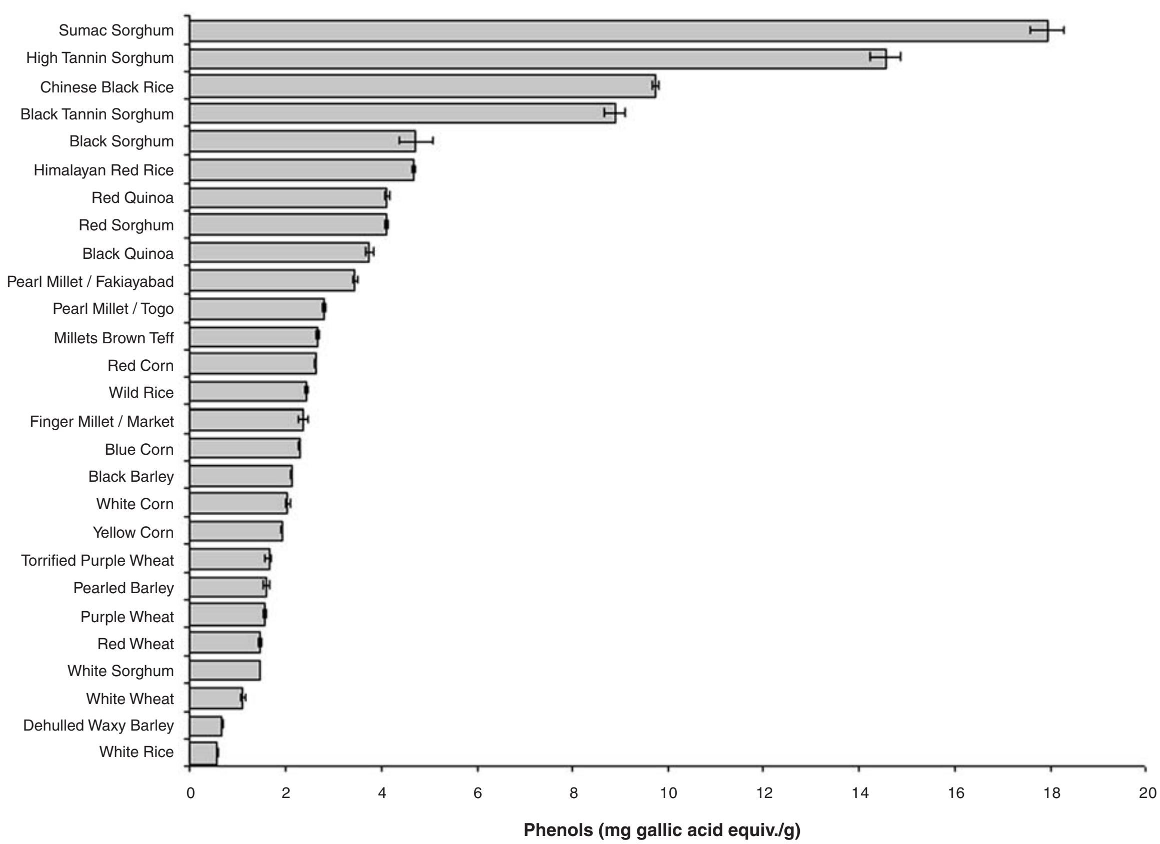

Fig. 3. Total phenol levels of cereal grains. (Adapted from Guajardo-Flores and coworkers [25]).

barley) had the lowest levels. These results suggest that condensed tannins and pigment-contributing compounds such as the anthocyanins increase phenols and antioxidant activity. There is a high correlation between total phenols and antioxidant activity (R^2 = 0.96), which suggests that the antioxidant activity is contributed by the phenolic compounds. In vitro methods used to measure antioxidant activity (i.e., ABTS, DPPH, and ORAC) do not give information about the bioavailability or metabolism of these compounds in biological systems. However, these methods are useful to screen and compare antioxidant activity levels among a wide variety of samples. To date, reports on human health benefits of cereal phenols are limited, and, therefore, more research is needed in this area.

Sorghums containing condensed tannins have consistently shown the highest antioxidant activity in vitro, and they approach or exceed the antioxidant levels of fruits and vegetables (Table V). Sorghums containing condensed tannins dominate production of grains in hot, humid regions of Africa because they have significantly improved resistance to grain molds and birds, which allow for their successful production. Tannin sorghums contain a pigmented testa, which contributes astringency during grain maturation and causes birds to utilize other food sources. When other grains are unavailable, birds consume the tannin sorghums (18). These tannin sorghums are grown extensively in east and southern Africa.

The condensed tannins cause depressed feed efficiency because they slow down and decrease digestion of the grain components. Thus, the tannin sorghums are discriminated against in sorghum markets. Very little tannin sorghums are grown in the United States since they are discounted in the grain markets. In Africa, the tannin sorghums are used in a wide variety of traditional foods including beer, porridges, unleavened breads, and other products. Special tannin sorghums are consumed when farmers are doing field work. The tannin sorghum porridges stay with the person longer and are said to be more satisfying, probably because of the reduced rate of digestion (5,18). The estimated glycemic index of ground whole sorghums with tannins is significantly lower than sorghums without tannins (15).

Future Perspectives

This article gives an overview of phenolic compounds in cereals. Many phenolics found in fruits and vegetables are also detected in cereal grains. However, many of these compounds are unidentified. Therefore, further research is needed to isolate and characterize phenolic components that contribute to health, which is challenging. Many of these compounds are bound to the matrix of the grain, making their extraction difficult. Also, the lack of appropriate standards increases the difficulty of identifying these phenols. The combination of mass spectrometry coupled with liquid chromatography is effective in the isolation, characterization, and identification of those compounds.

Identifying and quantifying cereal phenols will help us select grains with increased levels of these health-promoting compounds. Research is also needed to determine their bioavailability, metabolism, and health contribution in humans. Within cereals, great variation in colors and phenol components occur among genetic materials. Special grains are available and can provide large quantities of potentially health-promoting substances. Often, the cereal varieties commonly grown have been selected for absence of color and bland taste, which means the phenol content is reduced.

Since phenol profile and quantities depend on the sample's genetics, this

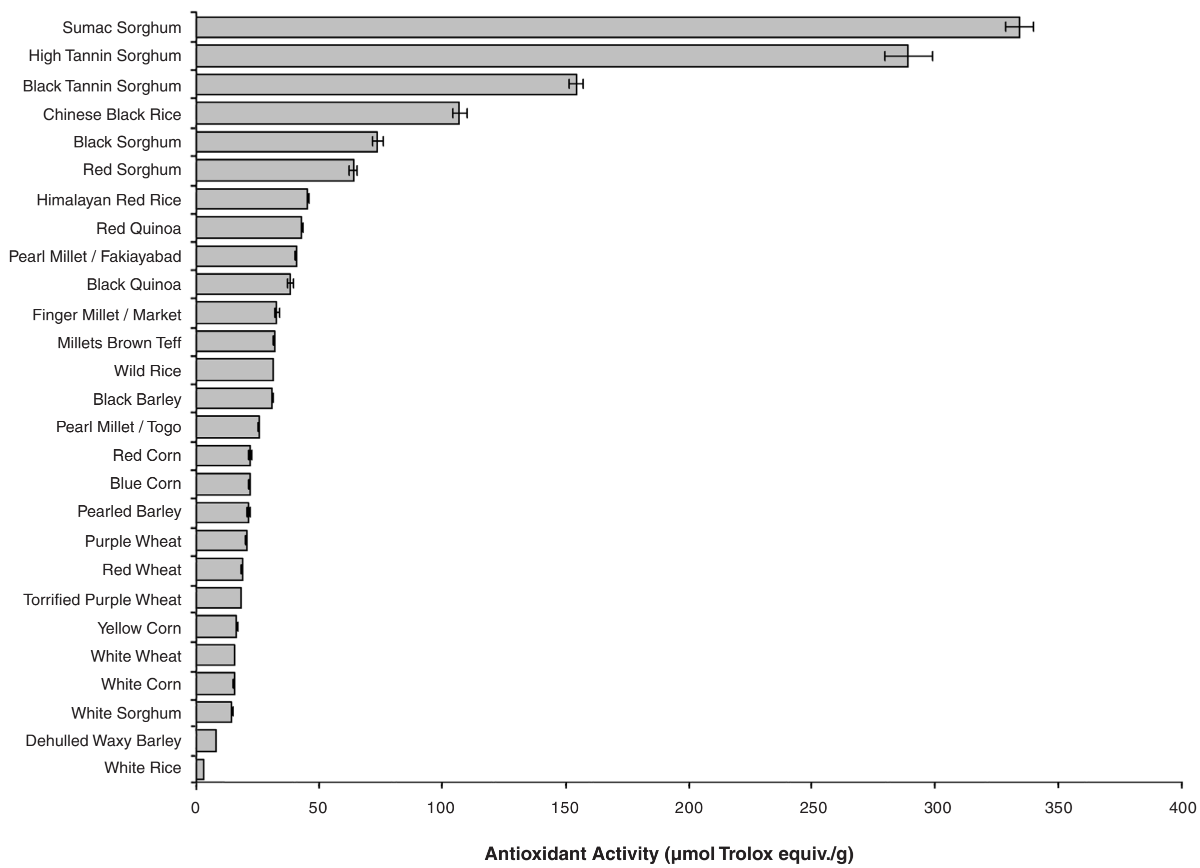

Fig. 4. Antioxidant activity (ABTS) levels of cereal grains. (Adapted from Guajardo-Flores and coworkers [25]).

information will also help plant breeders produce cereals with high levels of the desired compounds. Developing special varieties of cereals high in phenolics is possible and has been done for sorghum. For example, we know enough about the genetics affecting sorghum phenolics to develop cultivars with high levels of condensed tannins and special anthocyanins. Milling to produce bran concentrates these compounds, which can be used for potential nutraceutical application or as food colorants.

Obtaining phenolic compounds from cereals has several attractive advantages. Compared to fruits and vegetables, cereal grains are (1) dry, (2) easy to store for long periods of time, and (3) possibly easier to process into shelf-stable concentrates. Cereals can provide viable alternatives to diversify sources of healthy components in foods. Obviously, the benefits are highest for whole grain cereal consumption.

Table V. Antioxidant activity (ORAC) of sorghum grains and brans compared to common fruits and vegetables[a]

Commodity	ORAC (µmol TE/g, dry wt.)
Tannin sorghum (grain)[b]	868
Tannin sorghum (bran)[b]	3124
Black sorghum (grain)	219
Black sorghum (bran)	1008
Red sorghum (grain)	140
Red sorghum (bran)	710
White sorghum (grain)	22
White sorghum (bran)	64
Blueberry, lowbush	842
Strawberry	402
Plum	495
Watermelon	18
Apple, red delicious	295
Orange, navel	137
Broccoli	173
Carrot	108
Onion, red	93
Sweet pepper, green	105
Radishes	217
Potatoes, russet	63

[a] Adapted from Dykes and Rooney [18].
[b] Sumac.

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