



Processing induced changes on coarse cereals (majorly millets) derived antioxidant compounds - a review

Dipesh Aggarwal¹, Aastha Bhardwaj², Anupreet Kaur Sobti³, Sana Fatma⁴, Nitya Sharma⁵, Vasudha Bansal³

¹ Department of Food Technology, Lady Irwin College, University of Delhi, New Delhi-110001, India; ² Department of Food Technology, School of Interdisciplinary Sciences and Technology, Jamia Hamdard, New Delhi-110062, India; ³ Department of Foods and Nutrition, Government Home Science College, Chandigarh-160011, (Affiliated to Panjab University, Chandigarh, India); ⁴ DDU Kaushal Kendra, Rajiv Gandhi South Campus, Banaras Hindu University, Barkachha, Mirzapur, Uttar Pradesh- 231001, India; ⁵ Centre for Rural Development and Technology, Indian Institute of Technology Delhi, New Delhi, 110016, India

(Both 1 and 2 contributed equally)

***Corresponding author:** Vasudha Bansal, Department of Foods and Nutrition, Government Home Science College, Chandigarh-160011, Affiliated to Panjab University, Chandigarh, India

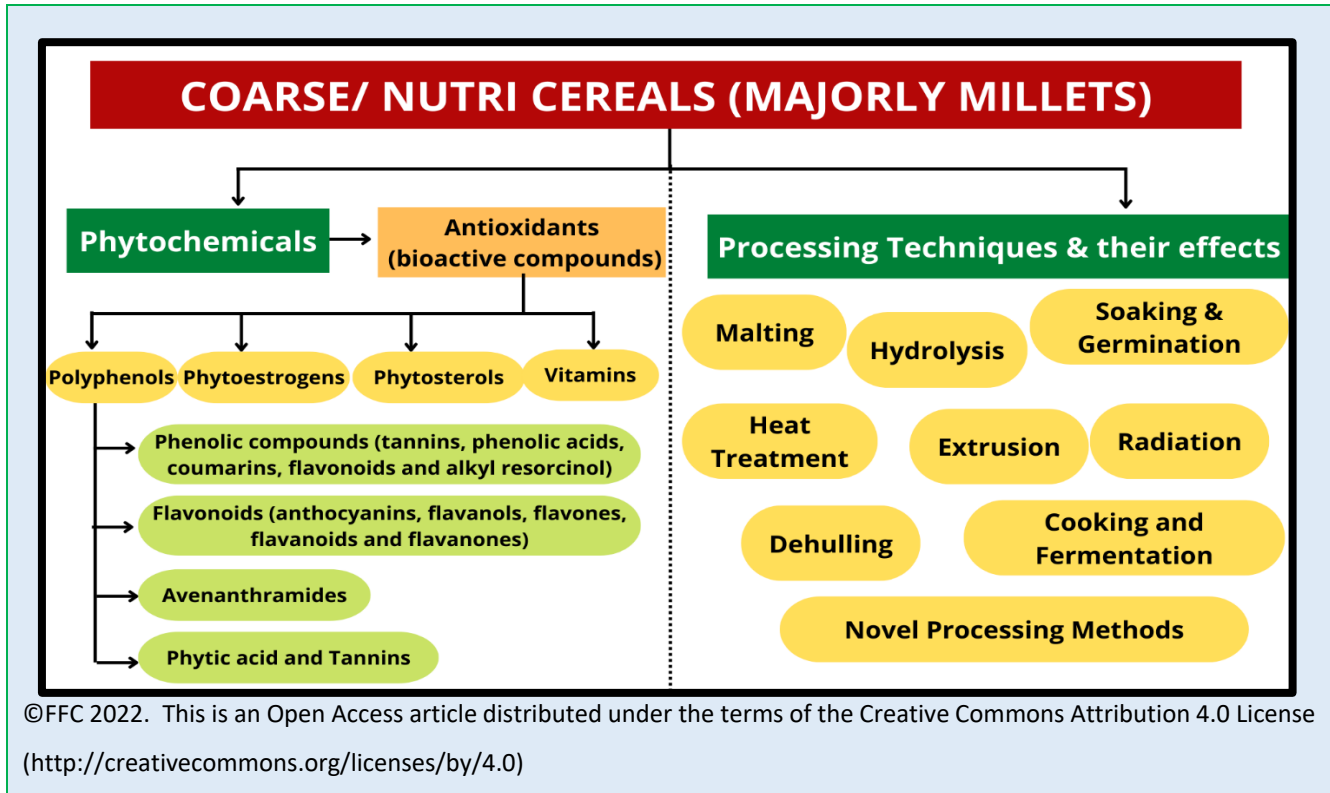
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ABSTRACT

Coarse cereals also known as nutriceals contain several bioactive components that provide many health-promoting and disease-preventing properties. This paper presents a review of the effect of processing on the various antioxidant compounds present in coarse cereals. Polyphenols, phenolic compounds, flavonoids, tannins, avenanthramides, vitamins, and phytoestrogens are the major categories that contribute to the antioxidant properties of coarse cereals. As per the literature, processing technologies like fermentation, boiling, malting, hydrolysis, soaking and germination, heat treatment, microwaving and extrusion, etc, have a significant effect on these antioxidant compounds present in coarse cereals. Coarse cereals and their processed products could be of potential benefit to human health, but extensive research is required to optimize the dietary recommendation for realizing these health benefits.

Keywords: Millets; flavonoids; polyphenols, processing techniques



INTRODUCTION

Plants are the sources of many bioactive food constituents called phytochemicals. A major part of these phytochemicals has antioxidant properties because of their redox-active molecules. Antioxidant compounds, work against the action of free radicals and other reactive oxygen. Even in low concentrations, these are capable of counteracting the damaging effect of oxidation on animal tissues [1] and are responsible for promoting anti-aging effects and playing a dynamic role in the prevention of most chronic diseases such as cardiovascular, diabetes, cancer, etc [2]. It has been found that the bioactive compounds in foods can substantially impart *in vivo* antioxidant activity, thus contributing to the beneficial health effects related to antioxidant defense [3], longevity [4], and maintenance of cell and DNA repair [5]. Apart from this, antioxidant compounds are also frequently used for maintaining the quality and enhancing the shelf life of food products in the food industry.

It is well explained that an antioxidant inhibits or delays the oxidation of other molecules by inhibiting the

initiation or propagation of oxidizing chain reactions. There are two basic categories of antioxidant compounds, namely synthetic and natural. In general, synthetic antioxidant compounds are compounds with phenolic structures of various degrees of alkyl substitution, whereas natural antioxidant compounds can be phenolic compounds (tocopherols, flavonoids, and phenolic acids), nitrogen compounds (alkaloids, chlorophyll derivatives, amino acids, and amines), or carotenoids as well as ascorbic acid. Figure 1 shows the classification of antioxidant compounds in coarse cereals. Out of all quantifying analytical methods available for antioxidant activity, some measure by detecting inhibition of peroxidation (malonaldehyde, carotene bleaching, conjugated diene), and a few detect electron or free radical scavenging activity (2, 2-diphenyl-1-picrylhydrazyl or DPPH; 2, 2'-azinobis 3-ethylbenzothiazoline-6-sulfonic acid or ABTS assay), and other detect ferric reducing antioxidant potential (FRAP) [6]. Therefore, the mode of action of these compounds to neutralize free radicals will depend on their relative concentrations in the sample matrix. Bijalwan et al., also

found that the antioxidant potential of millets is related to the structural characteristics of arabinoxylans (hemicellulose present in its cell wall)[7]. They concluded that the in vitro antioxidant capacity of hydroxycinnamic acid-bound arabinoxylans of millets was influenced by the phenolic acid content and composition, uronic acid content, and degree of substitution of xylan backbone.

Coarse cereals refer to the class of cereal grains excluding staple food like wheat and rice. They are commonly used as animal feed or for brewing or biofuel production. Nowadays, these are also substituted as nutriceals as they are rich in macro- and micro-nutrients like essential amino acids, minerals, and vitamins [8]. Phytochemicals with antioxidant properties are of special concern among the nutrients present in such coarse cereals [9]. Their cultivation is mostly centered in the semi-arid tropical regions of Asia and Africa, where farming is rain-dependent [10]. The coarse cereal crops can give higher grain yields in regions of less rainfall or drought, elevated temperature, and lower soil fertility. In other words, they perform well under poor soil and growing conditions. The class of coarse cereals includes maize (*Zea mays*), oats (jai; *Avena sativa*), sorghum (jowar; *Sorghum vulgare*), barley (jow; *Hordeum vulgare*), millets including pearl millet (bajra; *Pennisetum glaucum*) and other minor millets such as finger millet (ragi; *Eleusine coracana*), kodo millet (Arikalu; *Paspalum sorobiculatum*), proso millet (Cheena; *Penicum miliaceum*), foxtail millet (Kauni; *Sestaria italia*), little millet (Kutki; *Panicum miliare*) and barnyard millet (Sanwa; *Echinochola colona*). The presence of all the required nutrients in millets makes them superior to rice and wheat and suitable for commercial manufacture of value-added food products like baby foods, fortified snack foods, and dietary food [11].

Protective effects of coarse cereals against diabetes, obesity, cardiovascular diseases, etc. are well documented [12,13]. Table 1 also summarizes the intended effects of components derived from coarse cereal grains on human health as demonstrated by *in-vivo* studies. From the perspective of a healthy human diet, coarse cereals should be regarded as a source of various active phytochemicals having antioxidant capacities, which in combination may act synergistically in the human system. In an alternative view, coarse cereals are considered to be a potential source of specific compounds that can be extracted, purified, and marketed as food supplements or incorporated into other food products. For the above applications and also to make these coarse cereals edible in the whole form, it needs to undergo various processes. Such processes in isolation and/or combination form the basis of the processing of coarse cereals. These may cause certain changes in their phytochemicals, thereby altering the antioxidative properties of processed food made out of them.

Coarse cereals even after being nutritious have always been neglected in a common man's diet as these are regarded as crops for the poor. Owing to this they lack the status of commercial crops and also lag behind in various research and development prospects. However, with the increasing population and elevated demands for nutritious food, these crops are getting serious concern from communities to achieve health and better living. Correspondingly an increasing trend has also been observed in the utilization of these cereals in various food products. Therefore, in this review, an attempt has been made to provide a consolidate overview on the changes that occur with the different processing techniques in coarse cereals.

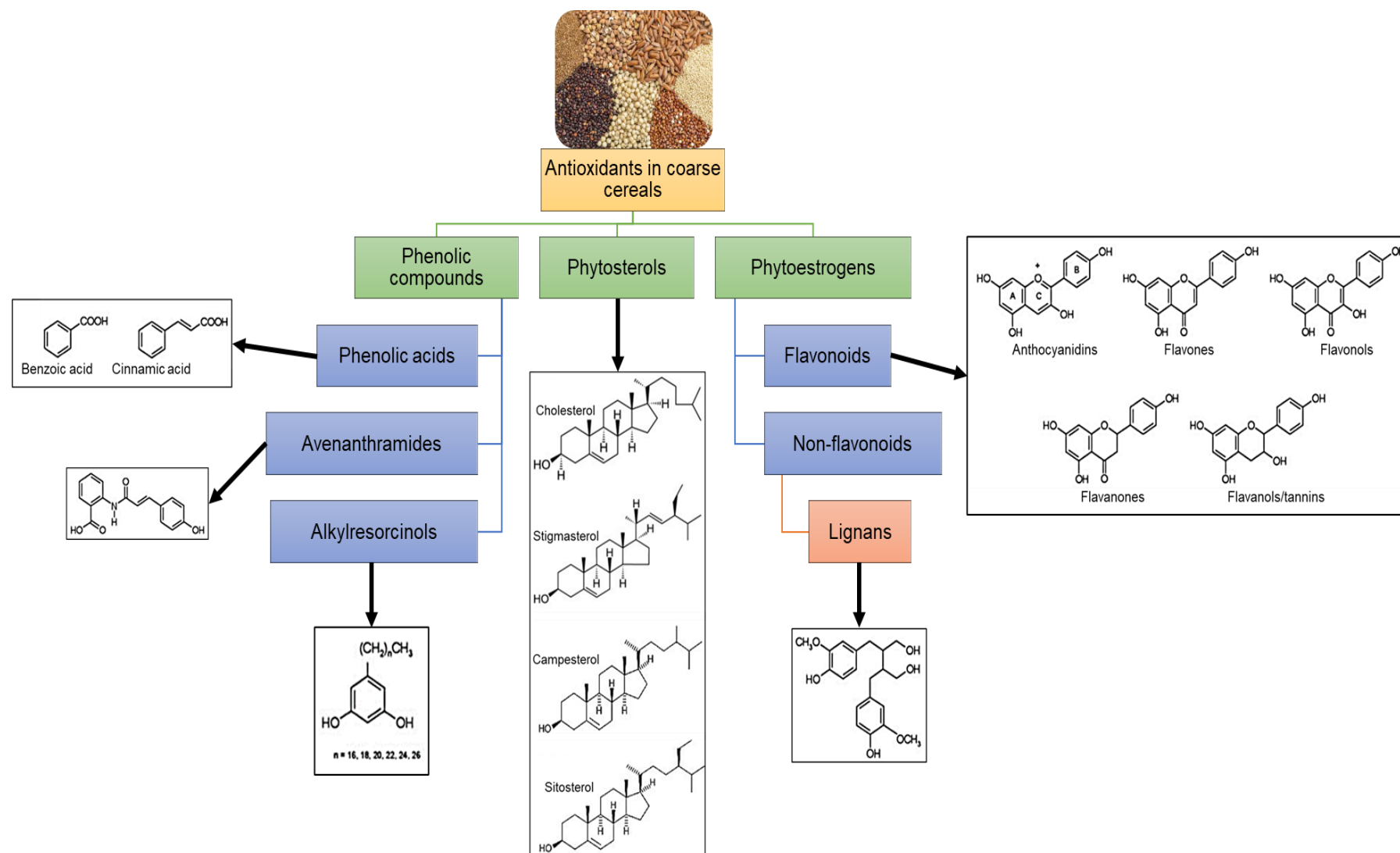


Figure 1 Classification of antioxidants in coarse cereal

Table 1. Crucial finding(s) of *in vivo* studies of some bioactive components found in coarse cereals

Bioactive Compound	Source	Suggestive property	Summarized study	References
β -glucan, dietary fiber, resistant starch, and polyphenols	Millet, maize, oat, soybean, and purple potato	Anti-hyperlipidemic; Gut modulation	This study dealt with supplementation of extruded puffed coarse cereals mixture to mice over a period of time that resulted in decreased body weight gain and lesser fat accumulation, improved blood glucose tolerance and serum lipids levels, reduction in systemic inflammation, and down-regulation of the expression of hepatic lipogenic genes, thus preventing high-fat diet (HFD)-induced obesity. Also, the stimulated release of short-chain fatty acids was indicative of modulation of gut microbiota in mice.	[14]
Flavonoids	Whole-grain oat	Regulate lipid metabolism	The research was suggestive of a positive regulatory effect of flavanoids from whole grain oat on bile acid metabolism in hyperlipidemic mice. This was attributed to the upregulation of genes (PPAR α , CPT-1, CYP7A1, FXR, TGR5, NTCP, and BSTP) and down-regulation of genes (SREBP-1c, FAS, and ASBT) that are involved in bile acid metabolism, thereby regulating lipogenesis, lipolysis, and bile acid synthesis. The results showed improved serum lipid profiles and decreased body weight and lipid deposition in HFD-fed mice.	[15]
Procyanidin B1 and p-coumaric acid	Barley	Regulate glucose metabolism	A dosage of 300mg/kg body weight was found to be effective for modulating glucose metabolism in glucose tolerant mice. This was ascribed to the active compounds found in highland barley grain that demonstrated improved glucose uptake and glycogen synthesis by up-regulation of expression of glucose transporter genes and down-regulation of glycogen synthase kinase-3 β gene. The research was suggestive of the consumption of barley grains to restore impaired glucose metabolism.	[16]
Polyphenols and phenolic acids	Foxtail millet	Gastro-protective property	The study suggests millet and adlay diets possess gastro-protective and anti-ulcerative effects against gastric mucosal lesions in rats. This was attributed to the antioxidants present in the grains that promoted ulcer protection by decreasing ulcer index, TBARS values, and increasing non-protein sulfhydryl (NPSH) concentrations.	[17]
Polyphenols (taxifolin and catechin)	Finger millet and Kodo millet	Antioxidant and hypoglycaemic potential	The polyphenol-rich extracts of millets were found to have a profound effect on mitigating lipopolysaccharide-induced inflammation in murine macrophage cells and reduced HFD-induced metabolic complications in male Swiss albino mice.	[18]
Phytochemicals (Oat- β -glucan; buckwheat- vitexin, hyperin and rutin; flavonoids)	Oats, buckwheat, barley, and foxtail millet	Anti-hyperglycemic	The research dealt with studying the supplementation of various varieties of oats, buckwheat, barley, and foxtail millet as a whole food, against streptozotocin-induced hyperglycemia in rats. Nutrients and phytochemicals collectively seemed to exert a positive synergistic effect against hyperglycemia <i>in vivo</i> .	[19]
Bio-active peptides	Sorghum (kafirin and flour)	Anti-hyperlipidemic and antioxidant property	The study involved feeding of sorghum kafirin extract as diet for 28 days to rats and assesses its effect on their serum lipid profile. Results showed improved lipid metabolism and increased serum antioxidant potential (upto 67%) The study suggested the prevention of atherosclerosis and other chronic diseases through sorghum supplementation.	[20]

Plant Sterols and Policosanols	Hexane extractable lipid fraction of whole sorghum		In this study, male hamsters were fed diets supplemented with the source. After 4 weeks of diet administration, a significant reduction was observed in plasma non-HDL cholesterol concentration in a dose-dependent manner, compared with controls. According to the study, plant sterols (0.35 g/100 g lipid extract) reduce cholesterol absorption, and policosanols (8 g/100 g lipid extract) may inhibit endogenous cholesterol synthesis.	[21]
β - Glucan	Oats		Wistar rats (ten per group) were fed on a dietary fiber-rich oat-based diet containing 30–92 g/kg β -glucan and 122–304 g/kg total dietary fiber. The result after six weeks demonstrated a significant reduction in serum total cholesterol, a higher count of bifidobacteria, a lower count of coliforms, and more bile acids in the faeces.	[22]
Xylanase inhibitor-like protein (XILP)	Sorghum		Sorghum XILP was found to be thermostable and pH stable. The study also revealed the ability of XILP as a potent antifungal, antiproliferative, and HIV-1 reverse transcriptase inhibitory agent.	[23]
Polyphenols	Pasta made from white and red wholegrain sorghum flour		The study concluded the presence of higher polyphenolic content and different polyphenolic species in red whole-sorghum flour as compared to white whole-sorghum flour. They also demonstrated that pasta from red whole-sorghum flour improved antioxidant status in healthy subjects (n=20) than control and white sorghum pasta.	[24]
β - Glucan	Barley		Ileorectomised rats were given diets with different content of β - Glucan. Higher dietary levels of β -glucan (2.6% and 4.3%) were found to lower feed intake but final body weight was only lowered by the 4.3% β -glucan diet. Protein, lipid, and starch digestibility were unrelated to the dietary β -glucan content. β -glucan had shown a non-significant effect on intestinal fermentation and macronutrient digestibility.	[25]
Antioxidants	Malt extract from barley		The antioxidant activity of malt extract was evaluated in male Kunming mice. The extract exhibited high antioxidant activities in vivo which was evident by its ability to scavenge hydroxyl- and superoxide-radicals, high reducing power, protection against macromolecular oxidation damage and improved total antioxidant capacity in D-galactose treated mice.	[26, 27]
Antioxidants	Finger millet and kodo millet		Diet supplemented with millets restored diet the levels of enzymatic and non-enzymatic antioxidants and lipid peroxide in alloxan-induced diabetic rats. Inhibition of glycation of rat-tail tendon collagen and an overall reduction in blood sugar and total cholesterol were also observed in rats given millet supplemented diet.	[27,28]
Avenanthramides	Oats		The effect of avenanthramides against Cu ²⁺ induced oxidation was observed in BioF1B hamsters only when the diet is supplemented with ascorbic acid.	[27,29]
Avenanthramides	Oats		Better bioavailability and increased antioxidant capacity of avenanthramides were observed in six healthy adults when taken along with skimmed milk	[27,30]
Antioxidant	Rye bread		A clinical trial of rye bread in healthy humans revealed increased resistance of LDL against oxidation.	[27, 31]

Processing of coarse cereals: Processing may increase or decrease the bioavailability of bio-active compounds in grains [32,33]. Some processing methods include soaking, decortication, flaking, grinding, malting, and heat treatment. The summary of the effects of processing techniques on the bioactive compounds of coarse cereals is shown in Figure 2. Such processes can also include hydrolysis of food components by alkali, acid, or enzyme which release the bound phenolics prior to extraction. The effects of different processing techniques on the bioactive components of coarse cereals are presented in Table 2.

Malting: Malting of grains involves three stages namely steeping i.e., soaking of grains at an optimum temperature that facilitates efficient germination, and finally kilning to halt the metabolic processes and

ascertain the stability of the dried grains. Malting is also associated with the development of desired flavor and aroma as well as shows a pronounced effect on the phenolic and antioxidant activity of grains. Several studies have indicated the effect of malting on the activity of antioxidant compounds and TPC in coarse cereal grains [34,35,36,37,38]. For instance, malting showed a steep increase (3.6 times higher) in total phenolics and total flavonoid content in malted quinoa seeds. The observed increase was attributed to the action of endogenous esterase which is synthesized during germination and results in the liberation of phenolic compounds originally restricted to the seed matrix [34]. Likewise, higher antioxidant activity and total phenolic content as compared to their corresponding unmalted barleys, thus indicating the scope for use of barley flour and a whole-grain meal in baked and extruded nutritionally superior food products.

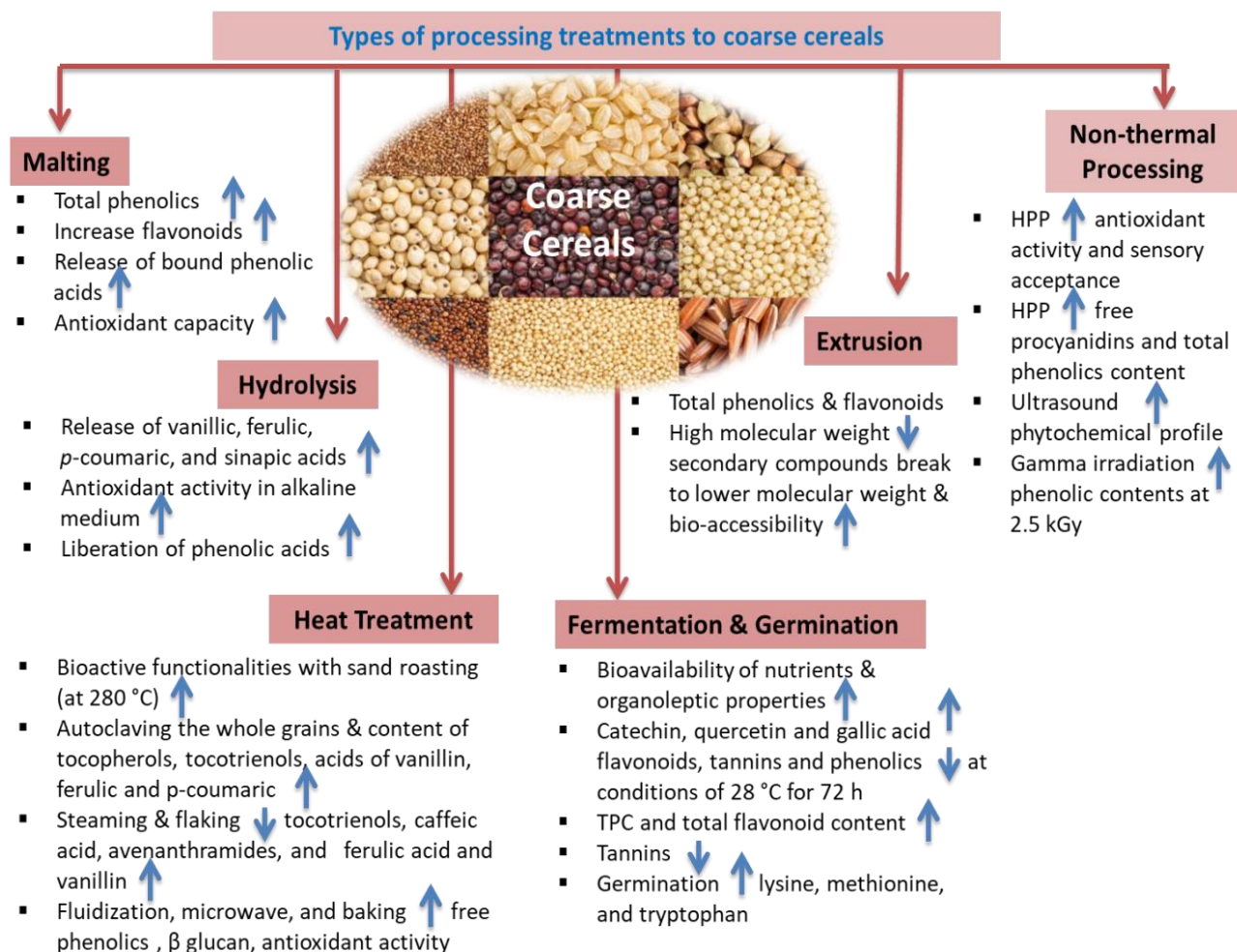


Figure 2. Effects of different processing techniques on bioactive compounds profile of coarse cereals

Table 2. Effects of different processing techniques on the bioactive components of coarse cereals

Coarse cereal	Type of bio-active	Processing method	Process conditions	Findings (amount retained/lost)	References
Finger millet	Total polyphenolics, anthocyanins	Fermentation	Fermentation; 96 h	Increased concentration of polyphenols, flavonoids, and antioxidant activity; TAC decreased	[39]
Sorghum	Polyphenolics (syringic acid, veratric acid, p-hydroxybenzoic acid, caffeic acid etc.)	Microwave boiling	400–300 W for 5-15 s	Bound phenolics content decreased in microwave boiling than in HP processing. HP processing retained anti-oxidant activity to a great extent.	[40]
		High pressure (HP) processing	100 kPa for 10-30 min		
Broomcorn millet	Phenolic compounds (syringic acid, gallic acid, 4-hydroxy benzoic acid, ferulic acid, sinapic acid)	Roasting	10 min at 110 °C.	Roasting significantly increased the content of secondary compounds and the antioxidant properties in comparison to other treatments	[41]
		Steaming	10 min at 110 °C.		
		Puffing	110 °C and 1.0MPa		
		Extrusion	110 °C, pressure: 80–100 bar		
Sorghum	Total polyphenolics	Boiling	Open vessel boiling (35 min)	Antioxidant activity (based on DPPH radical scavenging) decreased by 52 %, w.r.t control due to degradation at a higher temperature.	[42]
		Fermentation	Inoculation in tofu whey-based media with LAB (12 h)	Antioxidant activity (based on DPPH radical scavenging) increased by 41 %, w.r.t control.	
		Fermentation and steaming	Inoculation in tofu whey-based media with LAB (12 h) followed by open steaming (30 min)	TPC decreased by 36% w.r.t. control.	
Barley	Antioxidants, Polyphenols	Malting and Brewing	Steeping (16° C, 8h) Germination (18-22° C, 4 days) Kilning (40-83° C, 32 h) Mashing (at 52-73° C) followed by wort separation, hop boiling, filtration, fermentation	Enhanced antioxidant activity during mashing.	[43]
Foxtail millet	Coumaric acid, p-hydroxy benzoic acid, Vanillic acid, Caffeic acid, Cinnamic acid, Ferulic acid.	De-hulling	Dehuller (power: 2kW)	TPC of dehulled millet decreased and TFC of dehulled millet increased. Compared with dehulled millet, the TPC and TFC of cooked and steamed millet decreased.	[44]
		Cooking	100° C for 30 min		
		Steaming	100° C for 10 min		
Proso millet	Antioxidants	Extrusion	Moisture (17–25%), screw speed (170–250 r.p.m.) and temperature (90–150 °C)	Increase in antioxidant activity due to shear resulting in breakdown of cellular components	[45]
Pearl Millet	Phenolic acids such as p-coumaric acid and vanillic acid	Milling	Plate mill; sieve: 44 mesh	Milled millets showed reduced TFC. Millets subjected to heat treatment showed higher antioxidant capacity due to flavonoids. germination showed a negligible effect.	[46]
		Boiling	100° C for 30 min		
		Pressure cooking	9.8 × 104 Pa		
		Roasting	10–15 min at 200 °C.		
		Germination	Overnight soaking; sprouting for 72 h.		

The improvement in the anti-oxidative profiles of grains was ascribed to release of bound phenolic acids that impart enhanced antioxidant property to the grains. Two antioxidant compounds, ferulic and sinapic acid, were shown to withstand malting and subsequent brewing step. Efficient release and/or extraction of phenolic compounds during the malting process depicted increased TPC and antioxidant capacity at this stage. In apparent contrast, grains have shown contradictory results regarding the malting effects. The steeping process decreased the total phenolic content by 15% and germination further reduced total phenolics by 73% [47]. Similarly, a 1-2-fold decline was found in the levels of bound forms of ferulic, caffeic, and coumaric acids in finger millet upon malting for 96 hr; while the level of bound protocatechuic acid decreased from 45 to 16 mg/100g with the same treatment. The total phenolic compounds, flavonoids, and antioxidant activity increased initially however, observed plodding decrease during germination (post 48 h) in malted barley [48]. TFC of malted sorghum grains decreased by 12 % in comparison to unmalted sorghum, possibly due to their sensitivity to thermal processing or to conversion to other phenolic compounds during germination [49]. Thus, it is evident that malting has a significant effect on the antioxidant and polyphenolic potential of coarse cereal grains.

Hydrolysis: Alkaline cooking is a process of soaking coarse grains in an alkaline medium at a suitable temperature and is usually employed for traditional as well as industrial production of products such as tortillas, chips, etc. It is a chemical reaction in which cleavage of a compound occurs by adding a molecule of water in acidic or alkaline conditions. A large number of phenolic compounds like vanillic, ferulic, *p*-coumaric, and sinapic acids present in oats are found to be released upon

alkaline hydrolysis of the residue from 80% ethanol extract of groats [50]. DPPH radical scavenging property of the millets also reduced on alkaline cooking, which could be ascribed to the loss of heat-labile components responsible for antioxidant activity. Antioxidant activity of highland hull-less barley after extraction/hydrolysis and *in-vitro* simulated digestion in the presence of alkaline solutions enhanced upon respective treatments; however, the activities were significantly higher in *in-vitro* simulated digestion than extraction [51].

Microfluidization followed by solvent extraction treatment also facilitated an increase in alkaline and acid hydrolyzable phenolic contents of wheat bran through the liberation of phenolic compounds [52]. Two novel antioxidant peptides were isolated from finger millet protein hydrolysate by trypsin enzyme using ultrafiltration, gel filtration and chromatography; the activities increased significantly upon digestion and purification processes. The presence of aromatic and hydrophobic amino acids in their sequences and low molecular weights were the probable reasons for their high radical scavenging activity [53]. A recent intervention involving the use of nixtamalization with calcium salts (NCS) for the development of foods with better nutraceutical characteristics has been prevalent lately [54]. NCS in blue tortilla observed a higher antioxidant capacity than traditional tortilla as measured by FRAP assay indicating that retention of phenolics presents in blue maize during cooking [55]. However, there have been studies that report conversely that alkaline cooking drastically reduced the phytochemical content of nixtamalized foods but released phenolics and ferulic acid [56]. Likewise, nixtamalization reduced tannins content (up to 74.3%) in sorghum grains however, improved the antioxidative properties [57].

Soaking and Germination: The cereal germination

process has been practiced for ages to improve certain properties of grains such as softening the kernel, reducing its anti-nutritional components, and improving the nutritional value. Several studies have revealed enhanced functional attributes of coarse cereal grains through germination [21,58,59,60] and also confirmed an exceptional increase in the *in vitro* antioxidant activities in germinated Kodo millet, along with other rheological changes (e.g. thinning behavior of flour leading to decreased pasting properties).

Tannins and phytic acid levels varied to a great extent where variations were found to be a function of the sprouting period. During germination, the major reason for the decrease of tannins in the leaching process might be the hydrophobic linkage of tannins with seed enzymes (phytase activity) and protein [61]. Studies on sprouting of coarse cereals have demonstrated a reduction in anti-nutritional components of the grain and derived products where soaking and sprouting carried out for 24 h and 96 h caused about 33% and 61% decrease in tannins. This was attributed to the synergistic effect of soaking and fermentation, as observed during this period. Further, it was brought into concern that quantitative reduction in anti-nutritional components (tannins, polyphenols, and phytic acid) as well as other macromolecules of the grains, particularly carbohydrates had positive correlation with protein content of pearl millet upon germination of the grains. During germination major reason for decrease of tannins in leaching process might be the hydrophobic linkage of tannins with seed enzymes (phytase activity) and protein [61].

During germination, certain enzymes get activated that break down complexes to release free tannins which then leach out in the soaking medium. Sangma et al. attributed the increase in total phenolic content of germinated foxtail millets to the degradation of cell walls by enzymes [62]. The free and bound phenolic contents

of both waxy and nonwaxy, germinated pro so millet-based flours were significantly higher than the ungerminated ones, which was again associated with softening of tissues and leaching of phenolics into water [63]. In another study, germinated millets showed the highest phenolic content as well as superior antioxidant and enzyme inhibitory activities. It also indicated the potential use of germinated millet grains as a source of phenolic antioxidant compounds and strong natural inhibitors for α -amylase and α -glucosidase [64].

Conversely, Pal et al., reported lesser DPPH radical scavenging activity in germinated horsegram than in raw samples [65]. This could be due to the leaching of its antioxidant compounds into soaked water. The lower level of total phenols and total flavonoids after soaking may be due to the release of these phenolic compounds into soaking water, especially during longer soaking durations [66]. Likewise, Abioye, et al., studied the effect of germination on antioxidant activity, total phenols, and flavonoid content of finger millet-based flour [67]. The total phenolic and tannin content decreased while flavonoid and antioxidant activity increased significantly along with a significant reduction in the concentration of anti-nutritional factors. Subastri et al., assessed the nutritional and phytochemical content of porridges prepared from finger millet, germinated (fermented and non-fermented), and non-germinated (fermented and non-fermented) flour (FMF) [68]. The highest protein, carbohydrate, and glycoprotein contents were found in porridge prepared from germinated and non-fermented FMF. The observations lead to the conclusion that porridge prepared from germinated and non-fermented FMF contained a higher level of carbohydrate, protein, and glycoprotein, while germinated and fermented porridge had increased amino acids, phytochemicals, and free radical scavenging activity. Hence it was suggested that the consumption of porridge made from germinated

and fermented FMF may provide easily digestible and energetic nutrients for a healthier life.

Heat Treatment: Thermal treatment of coarse cereals such as roasting, baking, puffing etc., are often associated with numerous physico-chemical changes related to gelatinization, protein denaturation and maillard browning. These changes in turn bring about alterations to the nutritive, functional and organoleptic. Some antioxidant compounds in coarse cereals are likely to be altered by heat application and are likely to have a significant effect on the phenolic activity. For example, sand-roasted barley observed higher antioxidant potential, metal chelating behavior, and reducing power and showed better retention of total phenolic and flavonoids in comparison to microwave-cooked barley [69]. Likewise, Gujral et al. reported an increase in reducing power and antioxidant activity of sand roasted (280 °C for 15 s) hulled oats [70]. Kora., suggested the use of sand-roasted legumes, millets, and cereals as alternatives to polished grains with enhanced functionalities [71].

Autoclaving whole grains increase the content of tocopherols, tocotrienols, and acids of vanillin, ferulic and p-coumaric, but degrades avenanthramides content [72]. Significant reductions in all tocopherols and phenolic compounds were observed during the drum drying of a whole meal or rolled oats but no change was observed in avenanthramides content [73]. Steam treatment resulted in a significant decrease in all other individual phenolic acids except for chlorogenic acid of barnyard and gallic acid of foxtail millet [63].

Thermal processing of millets brings about relevant changes in phenolic indices. Although both steam and microwave treatments decreased the TPC of barnyard millet, however, it increased in the case of foxtail and proso millets [63]. In addition, it was found that browning during thermal processing caused an increase in TPC and

free radical scavenging capacity. This increase could be due to the dissociation of conjugated phenolic moiety during thermal processing and further polymerization and/or oxidation reaction which formed phenolics other than those endogenous in the grains [74]. The antioxidant activity of highland barley subjected to three heat treatments namely, heat fluidization, microwave, and baking showed positive correlations with free phenolics and β -glucan extractability that pointed to the functional attributes of processed barley [75]. Out of the three treatments, heat fluidization demonstrated the highest antioxidant activity, and this was attributed to the release of bound antioxidant substances upon disruption of the cell structure. According to Shobana & Malleshi, and Towo et al., hydrothermal treatment of finger millets reduced polyphenolic content by 14% and 1.7 times the initial value, respectively [76,77]. Significant reduction in polyphenols (28%) and phytic acids (38%) of coarse cereals was also reported in blanching. Malting however caused higher losses in polyphenols (38–48%) and phytic acid (46–50%) content as compared to blanching. Seventy-two hours of germination was thus found optimum to decrease the level of these anti-nutritional components [78].

Extrusion: Extrusion is one of the severe heat treatments that involve starch gelatinization and protein degradation. Heat treatment via extrusion cooking is carried out at a temperature of up to 200 °C and can have both positive as well as negative impacts on the bioavailability of phenolic compounds in coarse cereals [79]. Extrusion is accompanied by degradation of heat-labile phenolic compounds and may also cause their polymerization at high temperature and pressure conditions. Ample studies have reported decreased phenolic and antioxidant activity of coarse grains, depending on the type of coarse grain, the severity of heat treatment, and time of exposure [80]. Conversely, extrudates made from a composite blend of sorghum, barley, and horse-gram processed at high temperature

and low moisture conditions (120 °C and 14%) have shown to possess higher free phenolics and antioxidant activity by 25-40% and 16-52% compared to un-extruded snacks [81]. The total phenolic content (TPC), total flavonoid content (TFC), and antioxidant activity of extruded finger millet and sorghum flours at high temperatures reduced significantly; while TPC, TFC, and antioxidant levels were retained up to 54 %, 78 %, and 57 % in finger millet respectively and 87%, 89% and 86% in sorghum, respectively at lower temperatures [82], suggesting that these parameters are also dependant on feed moisture, die head temperature and screw speed. Likewise, whole broomcorn millet flour was observed to possess exceptional TPC and TFC upon extrusion as compared to other heat treatments like roasting and puffing. This was because of the breakdown of the high molecular weight secondary compounds into their lower molecular weight constituents that have higher bioaccessibility [41]. Salazar Lopez et al., also established that the extrusion process (180°C with 20% feed moisture) improved total phenolic content in sorghum bran in comparison with non-extruded counterparts [83]. Natural phenolic compounds could be used as antioxidant compounds in extruded foods. The addition of antioxidant compounds to foods prior to extrusion could result in more stable products. The addition of benzoin, catechin, chlorogenic acid, ferulic acid, and quercetin together at levels of 1.0 g/kg or higher generally results in delayed onset of oxidation. Benzoin was not expected to be an effective free radical scavenger because it lacked hydroxyl groups in its aromatic rings. However, extrusion might have modified its structure to enhance its efficacy [84].

Radiation: Gamma irradiation and microwave treatments have been observed to have a significant effect on the antioxidant and phenolic content of cereal grains. These non-thermal processing methods preserve the nutritional and functional properties of grains, unlike

heat treatments that negatively influence these properties. Gamma irradiated (2, 5, 10, and 15 kGy) finger millets showed a considerable increase in free radical scavenging potential as compared to untreated millet samples, as measured by DPPH radical scavenging activity (DPPH-RSA) test. The increased level of DPPH RSA was attributed to the presence of polyphenols and tannins [85]. Similarly, gamma irradiated pearl, proso, finger, and kodo millets (exposed at 2.5 kGy) demonstrated a significant increase in their total phenolic contents as reported by (Wani et al., 2021) [86]. Likewise, microwave radiation affects the phenolic content in the grain possibly by liberating β -ether-bound phenolic compounds from cell walls [87]. In a study, it was found that grain extracts when microwaved at 50° or 100°C did not show any major differences in phenolic content regardless of the solvent used and it was also insignificant when compared to heat treatment at 100°C [88]. While with elevated microwave temperature, the greater antioxidant activity of oat bran concentrate (OBC) extracts was observed irrespective of the solvent used [88]. Microwave roasted sorghum grains observed an enhanced total phenolic content, total flavonoid content, and antioxidant properties [89]. Microwave cooked proso and little millets also showed similar behavior in terms of functional and rheological properties [90].

Dehulling: The dehulling process reportedly reduces the polyphenol content and subsequently the antioxidant components of the grains. In a study conducted, dehulled oats were separated into bran (>420 μ m) and starch-rich (<420 μ m) fraction by sieving, among which the bran was reported to have a higher antioxidant capacity [91]. The concentration of avenanthramide, a phenolic compound in oats, was found to be higher in steeped and germinated oat groats than in milled [73]. According to a study by Chandrasekara and Shahidi, dehulling has been shown to decrease the TPC of whole grain millets, owing

to the removal of outer layers of the grain containing phenolic acids [92]. Hulled grains of kodo, foxtail, proso, pearl, little, and finger millets showed higher TPC than dehulled grains. Kodo and pearl millet hulls had 34- and 4-folds content of ferulic acid, respectively, and about 7-fold content of p-coumaric acid compared to their dehulled counterparts. Chandrasekara et al. also reported no significant difference in TPC of dehulled and cooked grains of millet except for finger millets [92]. While Shobana and Malleshi, reported a reduction in polyphenolic content in finger millet by 14% and 74% following hydrothermal treatment and decortication, respectively [76].

Cooking and fermentation: Fermentation is a biochemical process that modifies the primary food matrix under the influence of microorganisms and their respective enzymes and brings about considerable changes to the bioavailability of nutrients and improves food's organoleptic properties. Fermentation has shown beneficial as well as adverse effects on the phytochemical and antioxidant potential of cereal grains. For instance, higher concentrations of catechin, quercetin, and gallic acid and lower amounts of flavonoids, tannins, and phenolics were observed in fermented (28 °C for 72 h) whole grain sorghum-based products [93]. This was ascribed to the hydrolysis of phenolic constituents and release of bioactive by fermenting microflora, respectively. Likewise, Chandrasekara and Shahidi, reported that simulated gastrointestinal digestion and colonic fermentation *in vitro* released millet grain phenolics which showed antioxidant activity through different mechanisms such as free radical scavenging, and ferrous ion chelation, and reducing activity [94]. In the process of digestion, both TPC and total flavonoid content increased for all millet grains employed [94].

Fermentation and dehulling of pearl millet reduced the TPC as determined by Folin–Denis method. The TPC of the standard cultivar of pearl millet decreased from 304 to 122 mg/100 g upon fermentation for 14 h [95].

Both soaking and fermentation were found to decrease the tannins content in coarse grains. The decrease was found much greater for fermented seeds than for the control and soaked seeds. The lowest value of tannins for the 96 h fermented seeds was because of the synergistic effect of sprouting and fermentation. These processes produced enzymes that break down the product's nutritional quality. HPP products reportedly exhibit higher antioxidant activity and sensory acceptance, than those in other processing treatments. Bread prepared from high-pressure processed hydrated oat, finger millet and sorghum flour revealed exceptional sensory scores along with high anti-radical activity and retained a maximum amount of phenolics, as compared to other conventionally prepared bread [97]. Luo et al., also demonstrated increased free procyanidins and total phenolic content of high-pressure processed sorghum hull [40]. Ultrasound processing of sprouted sorghum seeds observed a superior phytochemical profile (in terms of radical scavenging activity) that would serve as a raw material for developing high-protein functional foods [61]. Irradiation is another novel processing technique that shows significant effects on the functional properties of food products. For instance, Pearl, Proso, Finger, and kodo millets at 12% moisture content showed a significant increase in phenolic contents at 2.5 kGy level of gamma irradiation treatments compared to native grains [86].

Conclusion and prospects: Coarse cereal grains are laden with abundant phytochemicals such as phenolic acids,

phytosterols, anthocyanins, antioxidant compounds, and other bio-actives that portray innumerable beneficial effects on the health of the host. Processing treatments of these cereals (e.g., thermal processing, soaking, germination, extrusion, etc.) may enhance or reduce their respective amounts. Thermal processing techniques like extrusion and cooking eventually decrease the phenolic contents of the grains while irradiation and hydrostatic pressures are known to enhance the phenolic activities of treated grains. The changes in turn have implications with respect to the health benefitting effects as well as the bioactive characteristics of coarse grains. Coarse cereal utilization and its processing convey a wide scope of applications and future perspectives in relation to enhanced bioavailability and nutritional quality along with added health benefits.

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Contribution: DA documented the idea and original draft of the manuscript; AB, AK, and SF did data collection and interpretation; NS and VB validated, interpreted, and set up the original draft.

Abbreviations: FRAP: ferric reducing antioxidant potential; DPPH: 2, 2-diphenyl-1-picrylhydrazyl; ABTS: 2, 2'-azinobis 3-ethylbenzothiazoline-6-sulfonic acid; HFD: High-fat diet; NPSH: non-protein sulfhydryl; TPC: Total phenolic content; TFC: Total flavonoid content

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