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A COMPREHENSIVE REVIEW ON THE NUTRITIONAL SIGNIFICANCE AND ANTIOXIDANT ACTIVITY OF MILLETS

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Abstract

Various endogenous systems in our body produce free radicals, which are reactive oxygen species. It is formed when our body is exposed to different physical and chemical conditions. A balance between free radicals and antioxidants is necessary for normal physiological function. Plant foods are important for their antioxidant activity, which is attributed to the phenols, which are known to protect against the harmful effects of oxygen radicals. Millet contains an abundance of bioactive compounds with antioxidant activity. The intake of antioxidants through the diet is essential for improving human health. The review is aimed at evaluating the antioxidant compounds in millets and the factors that influence their antioxidant activity. The millet contains naturally occurring phenolic compounds, which include phenolic acids, flavonoids, and tannins. In addition to xylo-oligosaccharides, insoluble fibers, peptides, and certain lipophilic antioxidants, including vitamin E and carotenoids, were extensively distributed among varieties.

Key words: Antioxidant activity, Reactive oxygen species, bioactive compounds, millets

1. Introduction

Millet is a drought-resistant grain and the sixth most economically significant global agricultural crop. Millets belong to the family Poaceae (earlier called Graminaeae) and consist of several varieties. Pearl millet (Bajra–Pennisetum glaucum), Foxtail millet (Kauni–Setaria italica), Proso millet (cheena–Panicum mililaccum), Finger millet (Ragi–Eleusive coracana), Kodo millet (Arikalu–Paspalum setaceum), little millet (milliare or kutkl–Panicum sumaahense), Barnyard millet (Sanwa–Echinoclos utilis).

Millet proteins are excellent sources of essential amino acids (except for lysine and threonine), and grains are also rich sources of phytochemicals and micronutrients (Ashwak Ahmed Sabuz et al., 2023). Millets are recognized for their numerous health benefits, which include the enhancement of wound healing, the prevention of cardiovascular diseases, and decreasing blood glucose and cholesterol levels (Saleh, et al., 2013). A previous study postulated that oxidative stress might cause various chronic conditions, including cardiovascular diseases, cancer, neurodegenerative disorders, arthritis, and diabetes. Hence, the review is aimed at evaluating the antioxidant compounds in millets and the factors that influence their antioxidant activity.

1.1. Nutritional composition of millets

Millets as food are rich sources of micronutrients and phytochemicals (Hasan et al., 2021). Millets possess high nutritional value (Parameswara and Sadasivan 1994). Millets possess proteins ranging from 7–12%, carbohydrates from 65-75%, fat from 2–5%, and dietary fiber from 15-20%. Pearl millet is the richest in both protein (12–16%) and lipid (4-6%). Millet proteins contain greater amounts of healthy, rich essential amino acids (Bhat et al., 2018; Shah et al., 2021). Finger millet contains a distinctive amount of sulfur-containing amino acids and is a better source of calcium, several micronutrients, and pyridoxine. Millets are rich in vitamin B complex. The major portion of dietary fiber is made up of non-starch polysaccharides, which are present in seed bran as well as endosperm. The dietary fiber of the food offers several physiological benefits, including the health of the GIT (Nithyananthan, et al., 2019). Millets could be effectively utilized as functional and healthy foods for the target population.

Micronutrient deficiency and its imbalance cause age-related diseases in humans like obesity, diabetes, osteoporosis, etc. (Rao et al., 2017). In millets, the mineral content ranges from 1.7 to 4.3 g/100 g, which is comparatively higher than rice and wheat. Minerals play a chief role in structure and rigidity, muscular contractions, the formation of strong bones and teeth, oocyte activation, blood clotting, oxygen transport, regulation of the heartbeat, maintenance of fluid balance, nerve signal transmission, etc. The calcium content of finger millet (Ca 340 mg/100 g) is almost 8 times higher than major cereals like wheat and rice.

The consumption of pearl millet and barnyard millet helps with protection from anemia because they have been found to be the richest sources of iron. The highest content of zinc (4.1 mg/100 g) in Foxtail Millet makes it a special source of iron (2.7 mg/100 g). The immune system is bolstered by the intake of iron and zinc. The Foxtail millet has the richest source of thiamine (0.6 mg/100 g), while the Barnyard millet has the highest content of riboflavin (4.2 mg/100 g) (Diksha Bhatt, et al., 2022).

Millets	Carbohydrates	Protein	Fat	Minerals	Fibre
Pearl millet	67.0	11.8	4.8	2.2	2.3
Finger	72.05	7.3	1.3	2.7	11.5
millet					
Foxtail	63.2	11.2	4.0	3.3	6.7
millet					
Kodo millet	66.6	9.8	3.6	3.3	5.2
Proso millet	70.4	12.5	3.1	1.9	14.2
Little millet	65.55	8.92	2.55	1.72	6
Barnyard	68.8	10.5	3.6	2.0	12.6
millet					

Table 1: Nutritional composition of Millets (mg/100 g)

Table 2: Mineral nutritional composition of Millets (mg/100 g)

Millets	Ca	Р	Fe	Mg	K	Na	Mn	Cu	Zn
Pearl	46	37 <mark>9</mark>	8	137	442	12	1.8	1.06	3.1
millet									
Finger	137.33	15 <mark>8.43</mark>	1.46	6.38	35.19	3.70	2.85	0.06	0.48
millet									
Foxtail	23	310	3.2	130	27 <mark>0</mark>	10	2.2	0.9	2.1
millet									
Kodo	32.33	30 <mark>0</mark>	3.17	110	141	4.8	1.10	1.60	32.7
millet							-		
Proso	10	200	2.2	120	210	10	1. <mark>8</mark>	0.8	1.7
millet									
Little	30	260	20	133	37 <mark>0</mark>	8.1	20	4	11
millet									
Barnyard	22	280	18.6	82	-	- /	0.96	0.60	3
millet	23.						6	<u>NO</u>	

(Courtesy: ICAR – IIMR)

1.2. Antioxidants

Antioxidants are thought to be reducing oxidative damage. Phytochemicals profiling of millets indicated the presence of significant amounts of antioxidants such as carotenoids, phenolics and tocopherols. The presence of all the required nutrients in millets make them superior to rice and wheat. Antioxidants provide stable radical intermediates which prevent the oxidation–induced damage of fatty acids and oils (Lobo, et al., 2010). Antioxidant compounds act as defense mechanisms in all living organisms to prevent the oxidation reaction. Antioxidants plays an important role in Physiological process. The common function of antioxidant is to decrease the DNA damage and lipid peroxidation. It maintains the immune system and inhibit the malignant transformation of cells (Prashanth, et al., 2021).

Antioxidant components like Polyphenols, Phenolic acid and Flavonoids can scavenge free radicals such as peroxide and hydroperoxide and inhibit the oxidative mechanism that leads to degenerative diseases. The millets contain phytochemicals components such as dietary fibers, soluble and insoluble fractions (Sreeramulu, et al., 2009). Regulation of oxidative stress, through antioxidant administration, is also capable

of controlling different health related issues such as diabetes, cancer, neurodegenerative disorders, cardiovascular problems.

There are two basic categories of antioxidant compounds, namely Synthetic and Natural. Synthetic antioxidants compounds are compounds with Phenolic structures of various degrees of alkyl substitution. 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. Antioxidants are thought to be important in reducing oxidative damage. Phytochemical profiling of millet indicated that it contained significant amounts of antioxidants such as carotenoids, phenolics and tocopherols.

Several methods have been developed to measure "antioxidant activity". Commonly used assays are reducing power assay (RPA), ferric reducing antioxidant power (FRAP) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical scavenging activity.

1.3. Antioxidant activity of millets

The polyphenols (taxifolin and catechin) of finger millet and kodo-millet have shown antioxidant and hypoglycemic potential. The study revealed that the polyphenol-rich extracts of millets were found to have a profound effect on mitigating lipopolysaccharide-induced inflammation in murine macrophage cells and reducing HFD-induced metabolic complications in male Swiss albino mice.

The extensive antioxidant effect of Foxtail millet may be critically important in protecting against the development of acute gastric mucosal injury. They promote a protective role by decreasing TBARS values and the ulcer index (Yallanki sireesha et al., 2023). Foxtail millet plays a role in increasing NPSH concentrations (Hui-Ching Lin, et al., 2020). The antioxidants of Finger millet and Kodo millet shown hypoglycaemic effect. The study suggested that diet supplementation with millets restored diet the levels of enzymatic and non-enzymatic antioxidants and lipid peroxide in alloxan-induced diabetic rats.

Antioxidant properties derived from pearl millet were isolated using trypsin (Agarwal et al., 2016). The antioxidant properties of the hydrolysates from foxtail millet were like alpha-tocopherol (Mohamed et al., 2012). Histidine, leucine, glycine, and proline amino acids play a crucial role in radical scavenging activity (Tessier et al., 2005). Peptide fractions obtained via the PR-HPLC purification of fermented Tyr/Leu-rich Foxtail millet were reported to exhibit significant radical scavenging activity (Amadou et al., 2016).

Naturally occurring vitamin E consists of eight vitamins, namely alpha, beta, gamma, and delta tocopherols, including four corresponding unsaturated tocotrienols. The total tocopherol content in millet varieties ranges from 1.3 to 4.0 mg/100g (Asha Rani et al., 2010; Panfili et al., 2003).

1.4. Mechanism of action of antioxidants

Phenolic acids (Kodo, Finger, Foxtail, Proso, Little, and Pearl millets): Phenolic acids can donate hydrogen atoms via hydroxyl groups on benzene rings to electron-deficient free radicals and in turn form a resonance-stabilized and less reactive phenoxy radical (Chandrasekhara, et al., 2011; Seema Sharma, et al., 2016).

Flavonoids (Kodo, Finger, Foxtail, Proso, Little, and Pearl Millet): Multiple hydroxyl groups confer upon the molecule substantial antioxidant activity. A double bond and carbonyl function in the heterocycle or polymerization of the nuclear structure increase its activity by affording a more stable flavonoid radical through conjugation and electron delocalization (Suma, et al., 2012).

Tannins (Finger Millet): Procyanidin o-quinone can produce oligomeric compounds through various coupling reactions that retain the number of hydroxyl groups and that can act as pro-oxidants by forming reactive oxygen species (ROS) through futile redox cycling (Siwela, et al., 2007); (Xiang, et al., 2018)

Xylo-oligoosaccharides (finger millet): And most oligosaccharides consist of ester-linked phenolic acids. Apart from phenolic acids, the presence of sugars with >C=O (uronyl and acetyl groups) and the degree or nature of polymerization impart strong antioxidant activity to the polysaccharides (Brunthadevi, et al., 2014; Veenashri, et al., 2011)

Insoluble fibers (Foxtail millet): The antioxidant properties of insoluble fibers could be attributed in part to their unique phytochemical composition. The insoluble fibers in Foxtail millet also exhibited antioxidant activity, with the yellow kind displaying higher amounts of antioxidants compared to the white variety (Bongoura, et al., 2013).

Proteins and Peptides (Pearl and Foxtail Millet): The antioxidant activity of proteins and peptides (Pearl Millet and Foxtail Millet) is due to complex interactions between their ability to inactivate ROS, scavenge free radicals, chelate prooxidative transition metals, reduce hydroperoxides, enzymatically eliminate specific oxidants, and alter the physical properties of food systems in a way that separates reactive species.

Carotenoid (Finger, Little, Foxtail, Proso millets): Carotenoids act as antioxidants by quenching single oxygen and free radicals.

Vitamin E (Finger, Little, Foxtail, and Proso millets): The biological activities of tocopherols (Finger, Little, Foxtail, and Proso millets) are generally believed to be due to their antioxidant action by inhibiting lipid peroxidation in biological membranes.

1.5. Factors affecting antioxidant activity

Raw kodo millet and finger millet have higher DPPH radical scavenging activities. However, cooking these millets by roasting or boiling reduced their antioxidant activity (Hegde et al., 2005). The Bran Rich Fraction showed high antioxidant activity in terms of RPA, which was due to the tannin, phytic acid, and flavonoid levels. The millet subjected to various heat treatments exhibited higher antioxidant activity (DPPH scavenging activity and RPA), mainly due to its flavonoid content (Florence Suma Pushparaj et al., 2014). Plants produce phenolic compounds in response to stress conditions such as infections, wounding, and UV radiation, among others. Environmental factors such as sun exposure, soil type, and rainfall influence the phenolic content of plants. In addition to environmental factors, cultivated location, growing season, and cultivar have also influenced the phenolic and flavonoid contents of buckwheat seeds (Oomah et al., 1996).

Finger Italian millet and barnyard millet extracts exhibited high antioxidant capacities. The soluble phenolics of these millet varieties, predominantly flavonoids, demonstrated potent inhibition of α -glucosidase and α -amylase activities as compared with the commonly used drug, acarbose, indicating their potential to reduce postprandial hyperglycemia by retarding carbohydrate digestion (Fred Kwame Ofosu et al., 2020). The antioxidant activity of roasted millet was higher compared to the steamed grain sample, which could be attributed to an increase in the extractability of bound phenolics by the thermal degradation of the cellular constituents (Pradeep et al., 2010). Pearl millet, when subjected to heat treatment, showed higher antioxidant capacity due to flavonoids.

Fermentation increased the levels of soluble phenolic compounds, condensed tannins, and individual phenolic compounds while decreasing the levels of the bound compounds (Gaza et al., 2016). The fermentation process increases the total polyphenolics and anthocyanins of finger millet. The study suggested that with increased concentrations of polyphenols, flavonoids, and antioxidant activity, TAC decreased. The extrusion process increases antioxidant activity due to shear, resulting in the breakdown of cellular components of Proso millet. Fermentation of Foxtail Millet produces bioactive peptides, which can also increase the antioxidant content. Phenolics in Foxtail millet are most bioavailable in gastrointestinal digestion, and protein hydrolysate had the highest antioxidant activity in hydrophobic form.

The results of the study showed that soluble as well as bound fractions of millet grains are rich sources of phenolic compounds with antioxidant, metal chelating, and reducing power. The potential of whole millets as natural sources of antioxidants depends on the variety used. The importance of the insoluble bound fraction of millet as a source of ferulic acid and p-coumaric acid was established, and their contribution to the total phenolic content must be considered in the assessment of the antioxidant activity of millets (Chandrasekhara and Sahidi et al., 2011). Optimized germinated millet flour contains higher antioxidant activity, dietary fiber, proteins, magnesium, calcium, iron, and sodium. With germinated millet as a raw material, the antioxidant activity was the highest (91.34%) after a soaking period of 13.81 h and

germination at 38.75°C for 35.82 h, which were the optimal conditions for flour production (Sharma et al., 2017).

Hejazi et al., (2016) found that germination slightly decreased the phenol content, DPPH, and ABTS activity of finger millet by as much as 25%. Malting induced dynamic alterations in the phenolic acid content of finger millet and affected its antioxidant activity (Rao et al., 2002; Rao et al., 2006).

2. Discussion

Oxidative stress is one of the causes of diseases and aging. The risk of chronic diseases could be alleviated by the intake of antioxidants. Millets not only provide high-quality nutrients but also possess antioxidant properties such as phenolic acids, flavonoids, tannins, and carbohydrates. (ex. XOs and insoluble fibers, specific proteins and peptides, as well as certain micronutrients such as vitamin E and carotenoids). Millets could be enriched with antioxidants (i.e., phenolics and flavonoids) through germination and fermentation. Dry thermal treatment increases the antioxidant activity of millet due to the release of phenolic components.

3. Conclusion:

From the literature reviewed above, it was evident that millet possesses' various substances with antioxidant properties that can be increased by processing techniques such as germination, malting, and fermentation. It is necessary for future research to establish additional scientific methods to evaluate the nutritional value of millet, especially the potential health benefits of antioxidants for animal and human IJCR models.

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