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Nutraceutical Properties of Polyphenols and Dietary Fibers from Finger Millet

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Abstract: Finger millet (*Eleusine coracana*) is a cereal grain grown in several Asian and African nations. It possesses numerous nutraceutical and health-promoting qualities, including hypoglycemic, hypocholesterolemic, nephroprotective, antidiabetic, decreased cardiovascular disease, antiulcerative, antioxidant, antibacterial, and wound healing capabilities. These qualities of finger millet are due to its high nutritional content, which includes protein (6%-13%), dietary fibre (18%), carbs (65%-75%), minerals (2.5%-3.5%), phytates (0.48%), tannins (0.61%), phenolic compounds (0.3-3%), and trypsin inhibitory factors. It has the most calcium (344 mg%) and potassium (408 mg%) of any cereal or millet. This review focuses on the existence and possible benefits of polyphenols and dietary fibres found in finger millet.

Keywords: Finger millet • Nutraceutical properties • Polyphenols • Dietary fibers • Bioaccessibility

Introduction

Finger Millet (*Eleusine coracana*, commonly known as ragi in India) is a nutritionally rich crop belonging to the family Poaceae. It is grown in varied agroclimatic conditions in India and ranks sixth in production after wheat, rice, maize, sorghum and bajra (Devi et al., 2014). Finger millet is considered to be one of the most nutritious, digestible and least allergenic grains (Singh & Raghuvanshi, 2012). Being gluten-free it is a very good option for those people who are suffering from celiac disease. Many of the health benefits associated with finger millet can be attributed to the presence of phenolic compounds and dietary fibers in it. The millet kernel has a seed coat, an embryo (germ), and an endosperm. As compared to other millets such as sorghum, pearl millet, proso millet, and foxtail millet, the seed coat or the testa in finger millet is multilayered (five layered), which is unique (FAO, 1995). This might be one of the possible reasons for the higher dietary fiber content in finger millet. The seed coat of the millet is a rich source of dietary fiber and polyphenols (0.2–3.0%) (Devi et al., 2014).

Phenolic Compounds of Finger Millet

Phenolic compounds of finger millet grain are present in free, soluble and insoluble bound forms. More than 50 phenolic compounds belonging to several classes are reported in finger millet (Saleh et al., 2013). Polyphenols of finger millet are mainly present in the seed coat and endosperm cell wall of the grain (Shobana et al., 2013). The total phenolic content of finger millet varies from 265-373 mg/100g as free and bound phenolics (Shahidi & Chandrasekara, 2013). Chethan et al. (2008) reported that 85% of the total phenolics in finger millet are derivates of benzoic acid.

The hydroxybenzoic acids are the major free phenolic fraction (70–71%) of finger millet and include p-hydroxybenzoic, gallic acid, protocatechuic, vanillic, gentisic acids etc. (**Table 1**) (Rao & Muralikrishna 2002; Chandrasekara et al., 2012; Hithamani & Srinivasan, 2014).

Table 1: Different classes of polyphenols in finger millet. Modified from Review Czech J. Food Sci. (Okwudili et al., 2017)

Classes of Phenolic Compounds	Basic skeleton	Compounds/ Quantity (μg/g)	References
Hydroxybenzoic acid derivatives	C6–C1	Gentisic acid / 4.5 Vanillic acid/ 20.0 Gallic acid/ 3.91-30.0 Syringic acid / 10.0-60.0 Salicylic acid / 5.12-413.0 Protocatechuic acid / 119.8-405.0 p-Hydroxybenzoic acid / 6.3-370.0	Rao & Muralikrishna (2002) Chethan & Malleshi (2007) Dykes & Rooney (2006) Hithamani & Srinivasan (2014)
Hydroxycinnamic acid derivatives	C6–C3	Caffeic acid/ 5.9-10.4 Sinapic acid/ 11.0-24.8 p- Coumaric acid / 1.81-41.1, trans-Cinnamic acid / 35-100.0 trans-Ferulic acid / 41-405.0	Chethan et al. (2008) Shobana et al. (2013) Dykes & Rooney (2006) Shahidi & Chandrasekara (2013) Hithamani& Srinivasan (2014)
Flavonoids	C6-C3–C6	Quercetin / 3 catechin gallocatechin, epicatechin, epigallocatechin, taxifolin, vitexin, tricin, luteolin, myricetin, apigenin, kempherol, narigenin, diadzein, Proanthocyanidins (Condensed tannins) procyanidin B1, orientin, isoorientin, isovitexin, saponarin, violanthin, lucenin-1, saponarin, violanthin	Rao & Muralikrishna (2002) Chethan et al. (2008) Dykes and Rooney (2006) Shahidi & Chandrasekara (2013)

Hydroxycinnamic acids are bound phenolic acids that include caffeic, chlorogenic, sinapic, trans-cinnamic, p-coumaric, and trans-ferulic acids (Rao &Muralikrishna 2002; Chethan & Malleshi, 2007; Dykes & Rooney, 2007; Chandrasekara et al., 2012; Shahidi & Chandrasekara, 2013; Hithamani & Srivivasan, 2014).

Protocatechuic acid is the major free phenolic acid (45.0 mg/100 g) of the millet and Ferulic acid is the major bound phenolic acid (18.60 mg/100 g) followed by caffeic and coumaric acids (Rao & Muralikrishna, 2002; Dykes & Rooney, 2006).

Finger millet flavonoids (quercetin, catechin, gallocatechin, epicatechin, and epigallocatechin etc.) are mostly present in the soluble form and their content is highest (2100 μg/g) in finger millets among other millets (Chandrasekara et al. 2012; Shahidi & Chandrasekara 2013).

Proanthocyanidins or condensed tannins are also present in different varieties of finger millet (Dykes and Rooney 2006). Procyanidins (procyanidin B1 and B2) are high-molecular weight polymerized flavan-3-ol and/or flavan-3,4-diol containing polyphenols.

Polyphenol contents vary in different varieties of millets. Studies by Ramachandra et al. (1977) on different Indian finger millet varieties indicated that brown varieties contained (1.2–2.3% as catechin equivalents) higher polyphenol content than white (0.3–0.5%) varieties, which was due to high anthocyanin content. Wadikar et al. (2006) reported less tannin content in hilly region varieties as compared to plain region varieties.

Polyphenols demonstrate a wide range of activities such as antioxidant, anti-inflammatory, antibacterial, antifungal and antiviral properties. Tannins present in the outer layers of the finger millet serve as a physical barrier and resist fungal invasion (Seetharam and Ravikumar, 1994). Polyphenols form free radicals that bring about the oxidation of membranes and cell components of microorganisms. Polyphenols also form irreversible complex with nucleophilic amino acids that inhibit microbial enzymes. Further interaction of tannins with carbohydrates, proteins, metals, ions etc. makes these biomolecules unavailable for microorganisms (Cowan 1999).

Polyphenols are good reducing agents, metal chelators, and singlet oxygen quenchers. They exhibit excellent antioxidant properties against super oxide, hydroxyl and nitric oxide free radicals. The antioxidant activity of phenolics depends on the position and extent of hydroxylation of the benzene rings. Antioxidant property is contributed by their ability to donate hydrogen atoms through their hydroxyl groups on benzene rings to electron deficient free radicals which in turn form a resonance stabilized phenoxyl radical (Miyake and Shibamoto, 1997). As per studies conducted by Rao and Muralikrishna (2002), the free phenolic acid fraction exhibited higher antioxidant activity as compared to the bound phenolic acid fraction. Other natural antioxidants including carotenoids and tocopherols are also present in finger millet. The total tocopherol content in finger millet is quite high (3.6–4.0 mg/100 g). The total carotenoids in different varieties of millet range from 78–366 mg/100 g. Asharani et al. (2010) have shown that the millet contains 199 μg/100 g carotenoids and 4 mg% Vitamin E. HPLC analysis of carotenoids and vitamin E showed a higher proportion of γ-and α-tocopherols, low levels of tocotrienols and the absence of β-carotene. Ferulic acid is also reported to exhibit very good anti-inflammatory, antioxidant and free radical scavenging properties (Devi et al., 2014).

Health Benefits of Dietary Fibers Present in Finger Millets

Dietary fibers are complex carbohydrate polymers with 10 or more monomeric units that are somewhat resistant to digestion by the endogenous enzymes in the small intestine of humans. Dietary fibers are categorized as water soluble or insoluble. Each category has different therapeutic effects. Water-soluble fiber (SDF) consists of non-starchy polysaccharides (NSP), mainly β-glucan and arabinoxylan. Water-insoluble fiber (IDF) contains lignin, cellulose and hemicelluloses (Dhingra et al., 2012), and NSP such as water-unextractable arabinoxylan.

Dietary fibers must be present in foods to ensure good health. An inverse relationship between intake of dietary fiber and diseases like obesity, cancer, type 2 diabetes, and cardiovascular disease is reported. Insufficient dietary fiber intake may result in constipation, an increased risk of coronary heart disease, and a fluctuation of blood glucose levels (American Association of Cereal Chemists [AACC], 2001). The beneficial effect of dietary fiber on health can be explained by its fate in the gastrointestinal tract (GIT) in terms of delayed nutrient absorption, lowering of blood lipids, barrier to digestion, high mobility, increased faecal bulk and faecal transit time and fermentability characteristics (Tharanathan and Mahadevamma, 2003).

The metabolism of soluble polysaccharides through bacterial enzymes in the small and large intestine results in products that are taken up by colonic microflora, which is beneficial to digestion (Weisburger et al., 1993; Devi et al., 2011; Okwudili et al., 2017).

Finger millet carbohydrates (72%) comprise starch as the main constituent and 15–20% of NSP in the seed matter as an unavailable carbohydrate. Finger millet grain has the highest content of total dietary fiber 22.0% compared to most other cereal grains, e.g., 13.4% maize, 12.8% sorghum, 12.6% wheat, and 4.6% rice. Chethan and Malleshi (2007) reported that finger millet grain contains 15.7% insoluble dietary fiber and 1.4% soluble dietary fiber, whereas another report by Shobana and Malleshi (2007), states 19.7% insoluble dietary fiber, and 2.5% soluble dietary fiber in finger millet. According to Thomas et al. (1990), the neutral detergent fiber in millet viz. hemicellulose, lignin, cellulose and silica are 34.41±0.99, 29.98±0.99, 27.58±0.85, 9.02±0.28 g/100g respectively, whereas Navita and Sumathi (1992) reported total dietary fiber (TDF), IDF, SDF, neutral detergent fiber (NDF), acid detergent fiber, crude fiber, hemicellulose, lignin content in finger millet as 17.6, 15.7, 1.8, 15.6, 5.2, 4.0, 10.4, and 1.3% respectively.

As per most diabetic and nutritional associations, high dietary fiber (DF) intake is highly recommended because of its physiological advantages in terms of hypoglycemic and hypocholesterolemic characteristics (Shobana and Malleshi, 2007). Several mechanisms are proposed, including altered lipid absorption, altered bile acid metabolism in the cecum, and reduced bile acid absorption in the cecum. Viscous and gel-forming properties of soluble DF inhibit macronutrient absorption, reduce postprandial glucose response, influence certain blood lipids and promote colonic fermentation by microflora, bringing about many desired metabolic effects of fiber (Lopez et al. 1999). Shobana et al. (2018) reported that Millet-based preparations with dietary fiber (DF) content between 5.8-15.6 g % are believed to elicit lower glycemic responses and are therefore recommended for diabetic individuals.

Soluble dietary fibers have arabinoxylans as the major components. These help in reducing the cholesterol, the disease symptoms of constipation and colorectal cancer (Devi et al., 2014). These fibers also have wound dressing potential. The backbone of arabinoxylan molecule is 1,4-β-D-xylan, with major residues substituted at C-3. A bound phenolic acid known as Ferulic acid, is mainly responsible for the physicochemical properties of arabinoxylans. It prevents tissue damage and stimulates the wound healing process (Sarita & Singh 2016).

Resistant starch (RS), a functional fiber fraction is also present in finger millet and provides better appearance, texture, and mouth feel than conventional fibers (Devi et al., 2014). RS escapes enzymatic digestion and is highly susceptible to fermentation in the large intestine into short chain fatty acids (SCFAs) by commensal microflora present in the colon and cecum. They also provide fermentable carbohydrates for colonic bacteria, thereby preventing several intestinal disorders and promoting large bowel function (Tharanathan and Mahadevamma, 2003).

Insoluble fibers like cellulose and hemicellulose can aid in waste and toxin removal through several mechanisms (Weisburger et al., 1993). They speed up intestinal transit and increase faecal bulk through the water-holding capacity of unfermented fiber. This reduces the contact time for faecal mutagens to interact with the intestinal epithelium. Some fibers can adsorb or bind some carcinogens that are ultimately eliminated in the faeces (Devi et al., 2014).

The hypocholesterolemic action of fibers was demonstrated in finger millet-fed rats. These rats showed lower concentrations of cholesterol and triglycerides in their serum and tissues. In vitro binding of NDF with bile acids was found to be low (Thomas et al., 1990). These immense health benefits of dietary fiber make these kinds of polysaccharides a part of dietary plans to treat cardiovascular diseases and Type 2 diabetes.

Bioaccessibility of Finger Millet Nutrients

Bioaccessibility of cereal grains is the fraction or amount of food substance from the food matrix that is soluble in the gastrointestinal environment and is available for absorption. Complex formation of bioactive compounds with dietary fiber, polyphenols, and other antinutritional factors such as phytates and tannins and causes their slow release in the gastrointestinal tract.

Few studies have reported the bioaccessibility potential of finger millet bioactive compounds, especially minerals and phenolic compounds (Tatala et al., 2007; Platel et al., 2010; Hithamani & Srinivasan, 2014; Okwudili et al., 2017). The effect of malting on the availability and bioaccessibility of iron, calcium, zinc, copper, and manganese in finger millet was evaluated, and the report indicated a decrease in the mineral contents but an increase in bioaccessible iron and calcium in millet after malting. The reason for the decrease in mineral content was explained in terms of the complexes that phytates and other antinutritional factors form with the minerals. In another report by Tatala et al. (2007), a nearly 60% increase in bioaccessible/bioavailable iron (0.75 ± 18 to 1.25 ± 0.5 mg/100 g) was observed after the germination of finger millet grain. The increase in bioaccessible iron could result from the activation of esterases and phytases (endogenous enzymes) that act on phytate-mineral complexes to release the mineral (Platel et al., 2010; Okwudili et al., 2017).

Processing methods for grains such as milling, sprouting, roasting, enzymatic digestion, and fermentation also play an important role in the bioaccessibility of cereal bioactive compounds. Sprouting increases the bioaccessibility of phenolic compounds in the grain by 67%. These methods help to release bioactive compounds by increasing their surface area ratio, which in turn induces the activity of endogenous enzymes and initiates bioconversion of the bioactive compounds into more active forms (Hithamani & Srinivasan 2014). Mutshinyani et al. (2020) suggested that spontaneous fermentation of finger millet flours can improve its bioactive compounds and antioxidant activity.

In vitro protein digestibility (IVPD) of finger millet is in the range of 50 to 65% (Singh & Raghuvanshi, 2012). Utilisation of proteins is affected by tannins as they bind to both exogenous and endogenous proteins, including enzymes of the digestive tract (Singh & Raghuvanshi, 2012). Finger millets are reported to contain high amounts of tannins ranging from 0.04 to 3.74% of catechin equivalents (Rao, 1994; Singh & Raghuvanshi, 2012). Rao and Prabhavati (1982) reported 360 mg/100g tannins in brown finger millet and also observed that 50% of the iron present in the diet might be bound to tannins.

Processes like soaking, germination, boiling, roasting, and fermentation help reduce tannin content (Rao & Prabhavathi, 1982; Singh & Raghuvanshi, 2012). As per reports by Rao (1994), malting decreases the tannin content by 54% in brown finger millet.

Rao (1994) reported the phytate content to be 150 mg/100g in finger millet grains. The dietary phytic acid binds with other endogenous minerals in the digestive tract along with the seed-derived minerals (Raboy, 2000). Malting of the grain decreases the phytin phosphorus content of finger millet by 58 to 65% (Rao and Deosthale, 1988; Rao, 1994). Agte & Joshi (1997) reported that soaking cereal flour prior to heating can activate phytases and favor zinc availability. Mamiro et al. (2001) found that phytic acid decreased by 49.2 and 66.5% after germination and fermentation, respectively. Phytic acid content can be decreased by 84% using different combinations of processing methods (Singh & Raghuvanshi, 2012).

Conclusion

Finger millet is a promising source of nutraceuticals that can meet the growing need for more nutritious and healthy foods. The inclusion of a variety of polyphenols and dietary fibres adds to finger millets' antioxidative, antidiabetic, hypocholesterolemic, hypoglycemic, and many other health benefits. Soaking, germination, roasting, and other treatments improve the bioavailability of the rich mineral content of Finger millet grains. The nutritional content and bioaccessibility of millet crops can be studied to aid in the development of nutritionally balanced blends for food products.

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