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Review

Increasing the utilisation of sorghum, millets and pseudocereals: Developments in the science of their phenolic phytochemicals, biofortification and protein functionality

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ABSTRACT

There is considerable interest in sorghum, millets and pseudocereals for their phytochemical content, their nutritional potential and their use in gluten-free products. They are generally rich in a several phenolic phytochemicals. Research has indicated that the phenolics in these grains may have several important health-promoting properties: prevention and reduction of oxidative stress, anti-cancer, anti-diabetic, anti-inflammatory, anti-hypertensive and cardiovascular disease prevention. However, increased research on the actual health-promoting properties of foods made from these grains is required. Biofortified (macro and micronutrient enhanced) sorghum and millets are being developed through conventional breeding and recombinant DNA technology to combat malnutrition in developing countries. Enhanced nutritional traits include: high amylopectin, high lysine, improved protein digestibility, provitamin A rich, high iron and zinc, and improved mineral bioavailability through phytate reduction. Some of these biofortified cereals also have good agronomic characteristics and useful commercial end-use attributes, which will be important to their adoption by farmers. Knowledge of the structure of their storage proteins is increasing. Drawing on research concerning maize zein, which shows that it can produce a visco-elastic wheat-like dough, it appears that the storage proteins of these minor grains also have this potential. Manipulation of protein β-sheet structure seems critical in this regard.

1. Introduction

Many, so-called minor grains, sorghum, the millets (major species – pearl millet, foxtail millet, proso millet, finger millet, teff and fonio) and the pseudocereals (major species – amaranth, buckwheat and quinoa) continue to be important for food security and health in at-risk communities in Africa, South America and Asia. This is because of their adaptation to the harsh environmental conditions of their centres of origin and similar agro-ecological zones. However, over the past 30 years their relative, and even actual production, has declined. For example, the average annual production of sorghum in Africa over the 5-year periods 1979–1983 and 2007–2011 was 12.2 and 23.9 M tons, an increase of 93%, whereas maize production increased 119% (FAOSTAT, 2011). More starkly, annual millet production in India increased by only 22% from 9.7 to 11.8 M tons, whereas wheat production increased by 119%, from 36.8 to 80.5 M tons. World production of buckwheat actually declined by 40% over the period, from 3.5 to 2.1 M tons.

Notwithstanding this, these minor grains have some most useful quality characteristics. Notably, they are characterised by being rich in many "health-promoting" phytochemicals, which exhibit antioxidant and free-radical scavenging activity (Przbylski et al., 1998; reviewed by Dykes and Rooney, 2006). This is perhaps because in the regions where these grains are traditionally cultivated, breeding has selected those varieties rich in phytochemicals such as phenolics, as they confer resistance to biotic stresses (Waniska et al., 1989). Sorghum and millets belong to the Andropogoneae, Eragrostideae and Paniceae tribes of the cereal grass family

Abbreviations: ABC, ATP-binding cassette; ABS, Africa biofortified sorghum; ACE, angiotensin-1 converting enzyme; DDGS, distillers dried grain and solubles; FAN, free amino nitrogen; GM, genetically modified; GBSS, granule-bound starch synthase; HDL, high density lipoprotein; ICRISAT, International Crops Research Institute for the Semi-Arid Tropics; LDL, low density lipoprotein; LKR, lysine ketoreductase; MIK, myo-inositol kinase; MRP, Multidrug resistance-associated protein; QTL, quantitative trait locus; RNAi, RNA interference technology; TBARS, thiobarbituric acid reactive substances; TNF, tumour necrosis factor.

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(Morrison and Wrigley, 2004) and thus are distantly related to the Triticeae tribe cereals (wheat, barley and rye) and the pseudocereals are dicotyledonous plants. As such, all these minor grains are considered as "gluten-free" and suitable for persons suffering from coeliac disease and wheat-induced enteropathy, sensitivities and allergies (Arendt and Dal Bello, 2008). For these reasons, there is great interest among the public and scientists in their use for food. For example, in June 2013 Google yielded 329,000 hits for "teff recipes" and more than 28 million for "quinoa recipes". Also, this year the FAO (2013) has designated 2013 as the International Year of Quinoa.

In the early 2000s, two multi-author monographs were published on the minor grains (Belton and Taylor, 2002; Abdel-Aal and Wood, 2005). These books dealt primarily with their grain structure, chemical and nutrient composition and traditional food and beverage use. Since then, there has been huge progress in our knowledge of these grains across the spectrum of cereal science and technology (Gallagher, 2009; Arendt and Dal Bello, 2009; Zannini and Arendt, 2013). This paper will review the "state-of-the-art" in the science of three topics concerning sorghum, the millets and the major pseudocereals, which have become of great interest: 1. Their phenolic phytochemicals and the available scientific evidence for their health-promoting and disease-prevention action; 2. The science of biofortification to enhance their content and bioavailability of macro and micronutrients, and 3. The potential protein functionality of such grains to enable the production of high quality bread and related dough-based products.

The objective is to promote a deeper understanding of the unique properties and potential of these minor grains to improve human health and well-being, with the aim of increasing their cultivation productivity and utilisation, particularly in developing countries. This is crucially important as a "Nutrition Transition" from traditional grains to a "Western" high fat and high sugar diet in developing regions (Popkin, 2003), such as sub-Saharan Africa, is already leading to dramatic increases in cardiovascular disease (Mbewu, 2009) and Type 2 diabetes (Mbanya et al., 2010).

2. Phytochemicals

2.1. Phenolic composition of sorghum, millets and pseudocereals

Phenolic compounds form a very large group of compounds containing the phenol functional group as a fundamental component. Conveniently, they may be classified based on increasing molecular weight into phenolic acids, flavonoid-type compounds and tannins. In reality, there are various classes of phenolic compounds as follows: flavonoids, phenolic acids, lignans, coumarins, phenols, phenylpropanoids, quinines, stilbenoids, and xanthones. Flavonoids, which make up the largest group among phenolics, are further subdivided into anthocyanins, flavanols including proanthocyanidins, flavonols, dihydroflavonols, flavones, isoflavonoids, flavonones, chalcones, and dihydrochalcones. Phenolic acids are further subclassified as hydroxybenzoic acids, hydroxycinnamic acids, hydroxyphenylacetic acids and hydroxyphenylpropanoic acids. Other phenolics include alkylmethoxyphenols, alkylphenols, curcuminoids, furacoumarins, hydroxybenzaldehydes, hydroxybenzoketones, hydroxycinnamaldehydes, hydroxycoumarins, hydroxyphenylpropenes, methoxyphenols, naphthoquinones, phenolic terpenes, and tyrosols. A brief discussion of the phenolic composition of sorghum, millets and pseudocereals follows.

2.1.1. Total phenolic content and total flavonoid content

Spectrophotometric assays such as the determination of total phenolic content using the Folin–Ciocalteu reagent and total flavonoid content using the $AlCl_3$ assay are used extensively to quantify phenolics in grains. Although these assays generally provide good information regarding trends in certain parameters, they suffer from their non-specificity. It is also difficult to make direct comparisons of values in literature as different solvents have been used to prepare extracts for analysis and also different standards have been used. Nevertheless, they offer a useful way of characterising the grain material regarding content of phenolics.

Sorghum has a total phenolic content ranging from 3 to 43 mg/100 g (Dykes and Rooney, 2006; Ragaee et al., 2006; Sikwese and Duodu, 2007). Total phenolic and total flavonoid contents of some of the major millets have been reported by Chandrasekara and Shahidi (2010) for soluble (free and soluble esterified) and bound phenolic fractions. Typical total phenolic contents reported are 411–610 mg/100 g (finger millet), 168 mg/100 g (pearl millet) and 140 mg/100 g (proso millet) ferulic acid equivalents in the soluble phenolic fraction. For the bound phenolic fraction, total phenolic contents range from 62–74 mg/100 g (finger millet) to 178 mg/100 g (pearl millet) and 43 mg/100 g (proso millet) ferulic acid equivalents. Total flavonoid contents have been reported as 203–228 mg/100 g (finger millet), 49 mg/100 g (pearl millet) and 140 mg/100 g (proso millet) catechin equivalents in the soluble phenolic fraction. For the bound phenolic fraction, total flavonoid contents range from 10–30 mg/100 g (finger millet) to 8 mg/100 g (pearl millet) and 13 mg/100 g (proso millet) catechin equivalents.

Buckwheat has a total phenolic content ranging from 29 to 1371 mg/100 g, depending on the method of extraction, and which standard (gallic acid or ferulic acid) was used for calibration (Holasova et al., 2002; Alvarez-Jubete et al., 2010b; Gorinstein et al., 2007; Velioglu et al., 1998; Oomah et al., 1996; Cao et al., 2008; Zielinski et al., 2009). Amaranth has a total phenolic content ranging from 2 to 24 mg/100 g (Alvarez-Jubete et al., 2010b) while the total polyphenols ranges from 2 to 300 mg/100 g both on as is and dry weight basis (Pasko et al., 2009; Khandaker et al., 2008). Anthocyanin contents of 90 and 103 mg cyanidin 3-glucoside equivalents/100 g were reported (Pasko et al., 2009).

2.1.2. Phenolic acids and flavonoids

Various phenolic acids and flavonoids have been identified in these minor grains. The phenolic acids are mainly derivatives of benzoic acid and cinnamic acid and occur largely in bound form (especially the cinnamic acid derivatives). The flavonoids may be classified into various groups such as flavanols, flavanones, flavones, flavonones and anthocyanins. With regard to anthocyanins, the presence of 3-deoxyanthocyanins in pigmented sorghums is of considerable interest due to their potential health benefits. Table 1 gives a summary of various phenolic acids and flavonoids identified in sorghum, millets and pseudocereals.

2.2. Health-promoting properties of these minor grains

The potential health-promoting properties of grains resulting from their phytochemicals can be classified into reduction and/or prevention of oxidative stress, anti-cancer, anti-diabetic, anti-inflammatory, and cardiovascular disease prevention and anti-hypertensive.

2.2.1. Reduction and/or prevention of oxidative stress

Free radicals, generally in the form of reactive oxygen species or reactive nitrogen species are usual by-products of cellular redox processes in the body. It is postulated that at low concentrations, these have beneficial effects on cellular responses and immune function (Pham-Huy et al., 2008). However, at high concentrations they cause the condition known as oxidative stress which is harmful to cell structures. In simple terms, oxidative stress has been defined as the condition whereby the balance between formation and

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