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Review

Structure, physicochemical properties, and uses of millet starch

Fan Zhu

School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

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ABSTRACT

There has been increased interest in millet utilization due to the various "rediscovered" health benefits and also critical role in food security in semiarid areas of Africa and Asia. The major component of millets is starch, which may amount up to 70% of the seed and determines the quality of millet products. This review summarizes the current knowledge of the isolation, chemical composition, structure, physicochemical properties, enzyme susceptibility, modifications, and uses of millet starch. Lack of systematic knowledge of millet starch seriously hinders further development of millets as sustainable crops. Needed research to diversify the variations in the quality and to improve the utilization of this starch is suggested.

Contents

1. Introduction

Millet is a generic term describing a range of small-seeded grains in two tribes Paniceae and Chlorideae of the family Poaceae (true grass). It became a staple food for humans 10,000 years ago already before the rise of wheat and rice (Lu et al., 2009). Nowadays, the most cultivated species include pearl (*Pennisetum glaucum*, with synonyms of *Pennisetum americanum*, *Pennisetum typhoides*, *Pennisetum typhoideum*), proso (*Panicum miliaceum*), and foxtail (*Setaria italica*) millet. Less grown millet species but with meaningful local production include finger (*Eleusine coracana*), browntop (*Brachiaria ramosum*), barnyard

E-mail address: fzhu5@yahoo.com.

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(Japanese) (*Echinocloa frumentacea*), shama (*Echinocloa colona*), white fonio (*Digitaria exilis*), and black fonio (*Digitaria iburua*) (Baltensperger & Cai, 2004). The taxonomy and common names of diverse millet species have been well documented previously (Baltensperger & Cai, 2004; Shahidi & Chandrasekara, 2013). Millets in general have good productivity on marginal lands, short growing cycle, and excellent adaptability to a wide range of climate including high temperature and dry conditions. This makes millets favorable crops for food security in semi-arid areas of Asia and Africa where the other major crops tend to fail (Baltensperger & Cai, 2004; Taylor, 2004). The total world production of millet seeds was estimated as 704,239 tonnes in 2012 with India being the top producer (273,000 tonnes) followed by Niger (106,427 tonnes) and Nigeria (60,800 tonnes) (FAO, 2014).

The nutrient composition and potential health benefits of millets have been summarized previously (Saleh, Zhang, Chen, & Shen, 2013). In brief, millets can be rich in B vitamins, minerals (calcium and iron), phosphorus (in phytic acid form), lipids, dietary fiber, and polyphenols, depending on the specific type (Abdalla, El Tinay, Mohamed, & Abdalla, 1998; Saleh et al., 2013; Shahidi & Chandrasekara, 2013; Taylor, 2004). Because millets lack gluten, they can be an aid for people with celiac disease (Taylor & Emmambux, 2008). Millets also possess hypoglycemic properties though the underlying reasons are still to be better studied (Annor, Marcone, Bertoft, & Seetharaman, 2013). The above-mentioned nutritional factors and bioactive properties make millets potential candidates for diverse functional foods that could prevent and delay the occurrence of non-communicable diseases (Dixit, Azar, Gardner, & Palaniappan, 2011; Saleh et al., 2013; Shahidi & Chandrasekara, 2013). Apart from the novel promising applications, traditionally, millets have already been used to produce various food and beverage products including porridge, fermented and non-fermented flatbreads, popping meals, composite flour ingredients, beer, distilled spirit, non-alcoholic drinks and so on (Baltensperger & Cai, 2004; Taylor, 2004). The production and quality of these millet products are, to a great extent, linked to the properties, structures, and interactions of the major component starch.

Compared with other major cereals, millets remain much understudied and under-utilized, though there has been increased interest in their utilization in recent years. Understanding the properties, structure, and potential uses of millet starch greatly contributes to the further development of millets as alternative functional crops. This review aims to summarize the present knowledge on the isolation methods, composition, structure, physicochemical and nutritional properties, modifications, and uses of starches from diverse millet species. Numerous research opportunities to improve the utilization of millet starch in food and non-food industries are suggested.

2. Starch isolation, yield, and chemical composition

Starch from millets has been mostly isolated using wet-milling based methods. In brief, whole millet kernels (or flour) are steeped in aqueous solution for several hours to facilitate the separation of starch from other components before the kernels are milled. Then the slurry is repeatedly washed with water and sifted to remove protein and fibrous components. The separated starch is recovered by centrifugation before drying (Kumari & Thayumanavan, 1998; Yanez & Walker, 1986). Procedures of acidic and alkaline methods for extraction of proso millet starch on the laboratory scale are detailed in Table 1 (Yanez & Walker, 1986), and another study showed the wet-milling flow chart of isolation of black and white fonio millets from raw grain to dried starch (not adapted here) (Jideani & Akingbala, 1993).

The starch isolation methods from various studies differ greatly, especially in the steeping condition which is neutral/near neutral, alkaline, or acidic (e.g., Table 1). Solution neutral or at pH 6.5 with the addition of small amount of sodium azide (e.g., 0.01%)/mercury(II) chloride (e.g., 0.01 M) to inhibit bacteria growth/amylase activity was used for starch extraction from pearl, proso, foxtail, barnyard, kodo, and little millets (Beleia, Varriano-Marston, & Hoseney, 1980; Fujita, Morita, & Fujiyama, 1993; Kumari & Thayumanavan, 1998). However, these methods involved the uses of sodium azide and mercury(II) chloride, and may raise safety issues. Acidic solution with small amounts of lactic acid (e.g., 15 g/L) and/or sulfur dioxide (e.g., 0.5 g/L or 0.15%) addition was used to isolate starch from proso (Yanez & Walker, 1986) and black and white fonio (Jideani & Akingbala, 1993) millets. Alkaline solution with low concentration of sodium hydroxide (e.g., 0.1%) or sodium borate buffer (pH = 10, 12.5 mM) containing SDS (0.5%) and $Na_2S_2O_5$ (0.5%) was employed to extract starch from proso (Yanez & Walker, 1986), kodo (Annor et al., 2013), and fonio millets (Carcea & Acquistucci, 1997). The isolation solution can have a profound influence on the chemical composition and the properties of the isolated starch. For example, the acidic steeping gave a higher content of residual protein (4.3%) in the granules compared with the alkaline one (0.7%), and starch isolated from these two different methods had notable difference in the pasting profiles (Yanez & Walker, 1986). Thus the starch isolation method should be carefully noted when comparing data from different studies. It should also be noted that alkaline, neutral, or acidic solution may either cause starch degradation or give low recovery of total starch from the flour. Extraction techniques based on dimethyl sulfoxide (DMSO) dissolution (Carpita & Kanabus, 1987) and ethanol/methanol precipitation (Klucinec & Thompson, 1998) for laboratory analysis may be developed to overcome these issues.

The yield percentage and chemical composition of millet starch vary greatly among different reports (Table 2). The yield ranges from 52 to 68.2%, amylose content 6–38.6%, lipid 0.16–2.9%, protein 0.2–4.3%, and ash 0.02–1.4%. The amino acids in starch granules of finger millet were mostly glycine, glutamine, and aspartic acid (Wankhede et al., 1979). Neutral lipids (NL) and phospholipids (PL) were the major lipid class in the free and bound lipid extracts of pearl millet, respectively. The major fatty acid in the NL fraction was linolenic acid, whereas palmitic acid was the major one in PL and glycolipid fractions (Hoover et al., 1996). It should be noted that the exact lipid composition differed greatly among diverse species and also among different genotypes of the same species (Madhusudhan & Tharanathan, 1995; Wankhede et al., 1979). The variation in chemical composition of starch could not only be attributed to the natural factors of the millets (genetics and environments), but also to a good extent, the isolation method used in the specific studies as discussed above.

Amylose content is a major player in the properties and potential uses of starch (Srichuwong & Jane, 2007). The method of measurement can be influential to the amylose content value (Gaffa et al., 2004; Hoover et al., 1996; Zhu, Yang, Cai, Bertoft, & Corke, 2011). The defatting of starch greatly tended to give higher amylose content as lipids could form inclusion complex with amylose in the form of helix (Hoover et al., 1996). The iodine could also complex with the longer chain segments of amylopectin, interfering the color development of amylose–iodine interaction (Zhu et al., 2011). Thus the amylose content from various studies should be carefully compared in the context of specific method used. Nevertheless, using the same experimental setting, genetic diversity in amylose content (nil, 11–27%) was observed (Fujita et al., 1996), representing useful genetic resource for improvement of desired composition of starch. Genotypes with greater variation in amylose content, especially the waxy and high amylose (amylose content N40%) genotypes remain to be developed for improving the utilization of millets.

3. Morphology and crystallinity of granules

The size and shape description of starch granules are summarized (Table 3). The granules are mostly simple ("simple" as opposed to "compound") with spherical and polygonal shapes. Some compound granules from finger millet were observed (McDonough, Rooney, & Earp, 1986). It was observed that granules in the flinty endosperm tended to be angular and polygonal and spherical in the mealy endosperm of both foxtail and proso millet kernels (Lorenz, 1977). A comparative observation noted that finger millet had little spherical starch granules