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Isolation, characterization and functionalities of bio-fiber gums isolated from grain processing by-products, agricultural residues and energy crops☆

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ABSTRACT

Potentially valuable water soluble bio-fiber gums (hemicellulose B) were prepared from low-valued grain processing by-products, agricultural residues and energy crops by an alkaline extraction followed by ethanol precipitation. The bio-fiber gum (BFGs) from all these sources are very rich in soluble dietary fiber (87.2–93.6%) except from wheat bran and sugarcane bagasse (only 60.3 and 55.5% respectively) and they are predicted to be non-caloric in human diets qualifying as non-caloric food ingredient in many products. The sugar composition of these BFGs showed that they were typical arabinoxylans containing high molar ratio of arabinose to xylose with some other sugars such as galactose, glucose, galacturonic acid and glucuronic acid in the side chains. The yield of pure BFG from these plant materials varied from 2.33 (rice fiber) to 25.13% (corn bran) and they all, except BFG from wheat bran, are very good emulsifiers for stabilizing oil in water emulsions. Their ORAC values ranged from about 7000 to 29,000 μmole Trolox/100 g sample showing that they have the ability to provide antioxidant activity in foods, as well as offering the other functionalities and health-promoting benefits of dietary fiber. The ORAC values of BFGs are higher than their respective original plant materials indicating that the antioxidant-rich portions of the various plant materials can be solubilized and fractionated by the present alkaline extraction process.
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1. Introduction

The grain processing by-products (corn bran/fiber, wheat bran, rice fiber etc.), agricultural residues (corn stover, wheat straw, sugarcane bagasse etc.) and lignocellulosic energy crops (switchgrass, miscanthus etc.) are abundant and often low-valued agricultural materials produced in USA and other parts of the world. They are natural composites of three major polymeric components: cellulose, hemicelluloses and lignin, which are linked together via covalent and hydrogen bonds. Along with the three major polymeric components, namely cellulose, hemicellulose, and lignin, they may also contain other minor components, such as extractives (phenolics, lipids, etc.), starch, pectins and proteins (Parajó, Garrote, Cruz, & Dominguez, 2004; Monlau et al., 2012). Corn fiber/bran, a renewable resource available in a large quantity, can be a good source of valuable consumer products, as for an example corn fiber gum (Yadav, Johnston, Hotchkiss, & Hicks, 2007a, 2016a, b). These agricultural materials are the source of many bio-based products, which can be used in many food and non-food industries. The fibrous materials from lignocellulosic sources have various applications, such as building materials, particle board, human food, animal feed, cosmetics, medicines and many others (Reddy & Yang, 2005; Reddy et al., 1989). They are also a very good source of dietary fiber. Dietary fibers are complex carbohydrates resistant to digestion by human digestive enzymes. They can be classified into an insoluble group and a soluble group. The soluble dietary fiber (SDF) helps to suppress blood cholesterol levels, especially LDL-cholesterol, by binding to bile acids, which are made from cholesterol, in the gastrointestinal tract and carrying them out of the body as waste (Woo & Kim, 2005). It also inhibits lipid absorption in the digestive tract. In addition, fermentation of SDF in the colon generates short chain fatty acids (SCFA) which can suppress the synthesis of cholesterol and maintain a healthy bacterial population. Diets high in fiber-rich carbohydrates can improve glucose and

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insulin level and also contribute to a decrease in blood lipids for people with Type II diabetes (Chandalia et al., 2000). However, the levels of fiber required to induce these beneficial effects are high (up to 35 g/day) (Franz et al., 2002), which may be difficult for people accustomed to Western diets to achieve. For this reason, the development of SDF has gained increasing interests (Groop, Aro, Stenman, & Groop, 1993; Vuksan et al., 1999; Wursch & Pi-Sunyer, 1997). Arabinoxylan-rich fiber (hemicellulose B) has drawn special attention because of its unique acceptability and palatability (Lu, Walker, Muir, Mascara, & O'Dea, 2000a; Lu, Gibson, Muir, Fielding, O'Dea, 2000b, 2004). Arabinoxylan has a beta-1,4-linkage that cannot be hydrolyzed by human digestive enzymes, and thus is a good dietary fiber.

In addition to above uses, lately lignocellulosic materials are also being used for making cellulosic ethanol. Cellulosic biomass contains about one third hemicelluloses A and B (Höije, Gröndahl, Tommeraas, & Gatenholm, 2005), in which Hemicellulose B (Hemi. B) contains mainly carbohydrate biopolymer "arabinoxylan" with some other minor components. Arabinoxylan has a linear 1,4 linked xylan backbone with α-L-arabinose, galactose, glucuronic acid and some other sugars in the side chains. Hemi. B from corn fiber has been isolated and its structure function relationship is well studied (Doner & Hicks, 1997 and 1998 and Doner & Hicks, 1997; Yadav et al., 2007a, b, c, d; 2008). Hemi. B from corn fiber (also called corn fiber gum, CFG) is found to be a very good emulsifier for the oil-in-water emulsion system. It contains minor, but functionally significant amounts of protein, phenolic acids and lipids, which contribute towards it emulsifying properties and may also provide nutraceutical value (Yadav et al., 2007a, b, d and 2008). The insoluble cellulosic residue remaining after hemicellulose solubilization of corn fiber gum has also been processed and isolated in 25% yield (Doner & Johnston, 2001; Yadav, Kale, Hicks, & Hanah, 2017). The functional hemicellulose B from barley hulls, several varieties of barley straws and several sorghum materials has been isolated, characterized and studied (Yadav & Hicks, 2015, Qiu, Yadav, & Yin, 2017). The effects of CFG on the pasting, thermal and gelatinization behaviors of starch have also been well studied (Qiu et al., 2015; Qiu et al., 2016).

In recent years, bioethanol production from lignocellulosic biomass is hoped to be a very important alternative to gasoline for transportation as it can reduce greenhouse CO_2 emissions. Another big advantage using lignocellulosic biomass for biofuel production is that it does not complete with food supplies. The commercially available biofuel of today is still mostly produced from edible feedstocks, such as corn starch and sugarcane juice, which can sometimes compete for their food and feed uses. Since lignocellulosic materials are non-food biomass they may have less impact on food and/or feed markets. These biomasses may have a considerable amount of alkali soluble, non-cellulosic carbohydrate polymers. Such alkali soluble carbohydrates are usually polymers of pentoses such as xylose and arabinose which are not easily fermented to biofuel in high yield as are sugars such as glucose, found in the insoluble cellulose-rich fibers. Removal of these alkali soluble polymers from the cellulosic biomass would yield a cellulose-rich (and glucose-rich) feedstock that could be easily hydrolyzed and easily fermented by well-known microorganisms such as brewer's yeast, *Saccharomyces cerevisiae*. Thus our current studies are focused on developing valuable uses for these alkali soluble polysaccharides, so they can become valuable coproducts of the cellulosic ethanol process, improving the overall economics for cellulosic biofuel production. In this work, we focus on food grade hemicellulose B, also called bio-fiber gum (BFG) from grain processing by-products, agricultural residues and energy crops by treating them with alkali, characterizing them and study their emulsifying and antioxidant properties.

Note: This manuscript has been written to honor and celebrate Prof. Glyn O. Phillips's 90th Birthday for his excellence and invaluable contribution in the field of hydrocolloids.

2. Materials and methods

2.1. Materials

The plant materials were obtained from various sources as follows: Corn bran (Bunge Milling, Inc., St. Louis, MO), Corn stover (Lawrence Shrawder, a Private Farm, Kempton, PA), Rice fiber (SunOpta Ingredients, Cedar Rapids, IA), Wheat bran (Deibel Laboratories, Bethlehem, PA), Wheat straw (Hougar Farms LLC, Coatesville, PA), Switchgrass (ARS lab at University Park, PA), Miscanthus (University of Illinois at Urbana-Champaign, Champaign, IL) and Sugarcane bagasse (Southern Regional Research Center, ARS, USDA, New Orleans, LA). They were oven dried and ground to a 20-mesh particle size using a Wiley mill. Termamyl α-amylase was a gift from Novozymes, Davis, CA. Medium Chain Triglyceride (MCT) oil was purchased from Nestle Nutrition, Minneapolis, MN. Sodium hydroxide and hydrochloric acid were obtained from Sigma-Aldrich (St. Louis, MO). All chemicals were reagent grade.

2.2. Standard proximate analyses

Protein (N × 6.25), ash and moisture contents of all samples were determined using AACC Approved Methods 46-30, 08-01 and 44-19 respectively (AACC International, 1995). Crude fat content was determined using the ANKOM XT10 Extractor with hexane as the extracting solvent. Starch content was determined using a total starch assay kit (Megazyme, Inc., Wicklow, Ireland) based on the use of thermostable α-amylase and amyloglucosidase (McCleary, Gibson, & Mugford, 1997).

2.3. Dietary fiber determination

Insoluble dietary fiber (IDF), soluble dietary fiber (SDF), total dietary fiber (TDF) and neutral detergent fiber (NDF) in CAF were determined following the standard A2000 automated fiber analyzer procedure (ANKOM Technology, 2011).

2.4. Isolation of hemicelluloses A and B

The hemicellulose A (Hemi. A) and hemicellulose B (Hemi. B) were extracted from the plant material according to the procedure of Yadav, Cooke, Johnston, & Hicks, 2010 with some modification. In brief, the ground plant material was boiled at 85 °C with efficient mechanical stirring in the presence of heat stable Termamyl α-amylase at pH 6.8 for 1 h to hydrolyze starch. Then the pH of this suspension was raised to 11.5 by adding 50% NaOH and the boiling and stirring were continued for additional 30 min. During the reaction, pH was maintained at 11.5 by adding 50% NaOH and the reaction volume was maintained by adding water as needed to compensate water loss due to evaporation. The hot slurry of the deconstructed material was immediately sheared using a high speed Polytron (PT 10/35 GT) equipped with 12 mm probe (Kinematica Inc., Bohemia, NY) at 10,000 rpm for 30 min and cooled to room temperature. The solid residue was separated from the reaction mixture by centrifugation at 14,000 × g for 10 min and discarded. The supernatant was collected in a beaker and its pH was adjusted to 4.0–4.5 by adding concentrated HCl to precipitate acid insoluble Hemi. A, which was collected by centrifugation at 10,000 g for 30 min. Two volumes of ethanol were gradually added to the supernatant with stirring to precipitate the acid soluble

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