Food Research International 65 (2014) 423–436

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Extraction and modification technology of arabinoxylans from cereal by-products: A critical review

Zhengxiao Zhang, Christopher Smith, Weili Li *

Department of Food and Tourism Management, Manchester Metropolitan University, Manchester M15 6BG, UK

ARTICLE INFO

Article history:
Received 14 March 2014
Received in revised form 24 May 2014
Accepted 30 May 2014
Available online 9 June 2014

Chemical compounds studied in this article:
Beta-D-xylopyranose (PubChem CID 125409)
Arabinose (PubChem CID 5460291)
Endo-1,4-beta-xylanase (PubChem CID 16132247)
Sodium hydroxide (PubChem CID 14798)
Barium hydroxide (PubChem CID 28387)
Hydrogen peroxide (PubChem CID 784)
Hydrochloric acid (PubChem CID 313)
Ethanol (PubChem CID 702)
Ammonium sulphate (PubChem CID 6097028)
Water (PubChem CID 962)

Keywords:
Arabinoxylans
Extraction
Yields
Modification
Molecular weight
Ara/Xly

ABSTRACT

Arabinoxylans (AXs) are one of the most important groups of hemicelluloses in the endosperm and outer layers of cereal grains. However, the macromolecular characteristics of extracted AXs and the extraction yields achieved exhibit huge differences. These differences are apparently dependent on the different extraction and modification methods used. This paper aims to review the extraction and modification methods used in the separation of AXs from cereal by-products as reported in previous studies. The effects of different extraction and modification methods on AX extraction yields, molecular characteristics and properties were evaluated. The influence of various extraction methods including chemical solvent extraction, enzymatic extraction and modification, and mechanically-assisted extraction on molecular structure (the ratio of arabinose to xylose and molecular weight distribution) of AXs are compared and discussed in this paper.

1. Introduction

Arabinoxylans (AXs) are an important group of hemicelluloses found in the out-layer and endosperm cell walls of cereals (Izydorczyk & Biliaderis, 1995; Saeed, Pasha, Anjum, & Sultan, 2011; Vries, Prosky, Li, & Cho, 1999). Hemicelluloses are branched polymers formed by combinations of various monosaccharides and cellulose with a linear backbone composed of glucose subunits linked by β-(1,4)-glucosyl (Xu et al., 2006). In the 1920s, a polysaccharide, named 'Pentosan', with high viscosity, which was found to be composed mainly of xylose and arabinose, was extracted from wheat flour (Freeman & Gortner, 1932; Hoffmann & Gortner, 1927). Subsequently, polysaccharides with a high AX content were found in the outer-layers of cereal grains such as wheat, corn, rice, barley, oat, rye, and sorghum, and have been studied extensively over the last few decades (Fincher & Stone, 1986; Saeed et al., 2011; Vinkx & Delcour, 1996). Since the 1980s, AXs are of interest to cereal chemists, as they have been found to have a significant influence on the quality of bread dough and bread (Courtin & Delcour, 1998; Li, Hu, Wang, & Brennan, 2013). Furthermore, as a result of their high viscosity and excellent water-holding properties, AXs have been used as food thickening agents and stabilising agents (Carvajal-Millan, Guilbert, Doublier, & Micard, 2006; Lapierre, Pollet, Ralet, & Saulnier, 2001; Yadav, Parris, Johnston, & Hicks, 2008). More recently, AXs have been reported to possess various biological activities, such as lowering serum cholesterol, blood sugar level modification, antioxidant activity and post-prandial glycaemic response reduction and immunity enhancement as well as an ability to reduce the risk of coronary heart

Abbreviations: AXs, arabinoxylans; A/X, the ratios of arabinose to xylose; WEAXs, water-extractable AXs; WUAXs, water un-extractable AXs; AS-AXs, alkali-solubilised AXs; ES-AXs, enzyme-solubilised AXs; MW, molecular weight; AXOS, arabinoxylo-oligosaccharides; GAX, glucuronoarabinoxylans; GH, glycoside hydrolase; DMSO, dimethylsulfoxide.

* Corresponding author at: Righton Building, Cavendish Street, Department of Food and Tourism Management, Manchester Metropolitan University, Manchester M15 6BG, UK. Tel.: +44 1612472698.
E-mail address: w.li@mmu.ac.uk (W. Li).

http://dx.doi.org/10.1016/j.foodres.2014.05.068
0963-9969/

disease and applications in weight management systems (Benko et al., 2007; Lu, Walker, Muir, Mascara, & O'Dea, 2000; Lu, Walker, Muir, & O'Dea, 2004; Swennen, Courtin, & Delcour, 2006).

As summarised in Table 1, cereal bran contains relatively high AXs in various fractions. So, cereal bran is a cost effective source of AXs, which is a by-product of cereal processing. As a result of their high Mw and high ferulic acid content AXs readily form covalent/non-covalent linkages between AX chains and with other components of the cell wall such as proteins, β-glucans, lignin and cellulose, hence a high proportion of AXs cannot be extracted by water (Beaugrand, Cronier, Thiebeau, et al., 2004; Saulnier, Sado, Branlard, Charmet, & Guillon, 2007). Therefore, various methods have been developed for the extraction and purification of AXs from cereal by-products, including alkaline and acid extraction (Höije, Gröndahl, Tommeraas, & Gatenholm, 2005; Hollmann & Lindhauer, 2005; Zhou et al., 2010), enzyme hydrolysis (Beaugrand, Chambat, et al., 2004; Li et al., 2013; Maes, Vangeneugden, & Delcour, 2004), microwave-assisted extraction (Rose & Inglett, 2010), ultrasound-assisted extraction (Ebringerova, Hromadkova, Alfoldi, & Ibalova, 1998; Hromadkova, Kovacikova, & Ebringerova, 1999), steam explosion extraction (Allen et al., 2001), hot compressed water extraction (Dien et al., 2006), twin-screw excursion extraction (Marechal, Jorda, Pontalier, & Rigal, 2004; Zeitoun, Pontalier, Marechal, & Rigal, 2010), ethanol purification and ammonium sulphate precipitation (Izydorczyk & Biliaderis, 2007). It has been found that the extraction yields and macromolecular characteristics of AXs vary depending upon the extraction and modification methods used. Previous studies have demonstrated that the bioactivities of AXs may be associated with their specific molecular characteristics by modification. Modified wheat bran AXs with low Mw (6.6×10^4 Da) have potential prebiotic properties *in vitro* (Hughes et al., 2007) and the modified rice bran with Mw (30–50 kDa) has immune-modulating activities *in vitro* and *in vivo* studies (Ghoneum, 1998; Ghoneum & Brown, 1999; Ghoneum & Matsuura, 2004). In contrast, higher molecular weight AXs have demonstrated an ability to lower the post-prandial glycaemic response *in vivo* (Lu, Walker, Muir, Mascara et al., 2000; Lu, Walker, Muir and O'Dea, 2004). It would seem that the macromolecular characteristics; variations in the degree of branching, molecular weight and spatial arrangement of AXs recovered by different methods influence their functionality (Saulnier et al., 2007). This review focuses on methods for the extraction and modification of AXs from cereal by-products, and also investigates and compares the effects of these methods on the yields and chemical properties of AXs.

2. Arabinoxylans of cereals

2.1. Structure

AXs are composed of a backbone of β-1,4 linked D-xylopyranosyl residues. Monomeric α-L-arabinofuranoside can be present at the C (O)-3 and/or the C (O)-2 positions of the xylose moieties (Izydorczyk & Biliaderis, 2007). Comparison of molecular structures of AXs from whole cereal grains and cereal by-products, (Izydorczyk & Biliaderis, 2007) indicated that the AXs from cereal brans from rice, sorghum, finger millet, and maize have more complex side chains (including xylopyranose, galactopyranose, and α-D-glucuronic acid or 4-O-methyl-α-D-glucuronic residues) than those from cereals such as wheat, rye, and barley. The general structure of AXs from cereal bran is shown in Fig. 1. The AXs can be cross-linked to ferulic acid at the C (O)-5 positions *via* an ester linkage (Izydorczyk & Biliaderis, 1995, 2007; Saeed et al., 2011). Ferulic acid side chains can also form linkages with β-glucan/cellulose/glucose/protein (Andersson & Aman, 2000; Dervilly, Rimsten, Saulnier, Andersson, & Aman, 2001; Izydorczyk & MacGregor, 2000).

The main differences between the various cereal brans are the manner of arabinose residue substitution in the xylan backbone, in the relative proportions and sequence of the various linkages between these two sugars (xylose and arabinose), and in the presence of other substituents (Izydorczyk & Biliaderis, 1995). A/X of AXs from wheat

Table 1
AX contents of various cereals and cereal by-products (dry basis) (adapted from Izydorczyk & Biliaderis, 2007).

Raw materials	Tissues	Total AXs (%)	WEAXs (%)	References
Wheat	Whole grain	5.77	0.59	Hashimoto, Shogren, & Pomeranz (1987a)
	Bran	21.4	/	Courtin & Delcour (2001)
	Bran	25	1	Hollmann & Lindhauer (2005)
	Bran	19	/	Bataillon et al. (1998)
	Bran	19.38	0.88	Hashimoto et al. (1987a)
	Flour	/	0.43	Ganguli & Turner (2008)
	Flour	1.37–2.06	0.54–0.68	Izydorczyk et al. (1991)
	Durum wheat	4.07–6.02	0.37–0.56	Lempereur, Rouau, & Abecassis (1997)
Barley	Whole grain	6.11	0.35	Hashimoto, Shogren, & Pomeranz (1987b)
	Whole grain	3.4–4.1	/	Izydorczyk & MacGregor (2000)
	Whole grain	/	0.40–0.88	Oscarsson, Andersson, Salomonsson, & Åman (1996)
	Whole grain	6.36–8.58	0.379–0.808	Fleury et al. (1997)
	Pearled grain	4.45	0.27	Hashimoto et al. (1987b)
	Pearling	14.14	0.54	Hashimoto et al. (1987b)
	Pearled flour	/	0.3–1.08	Dervilly, Rimsten, Saulnier, Andersson, & Aman (2001)
Corn	Bran	27.2	/	Yadav et al. (2007)
	Bran	29.86	0.28	Hashimoto et al. (1987b)
Rye	Whole grain	7.6	/	Bengtsson & Aman (1990)
	Whole grain	8–12.1	2.6–4.1	Hansen, Rasmussen, Knudsen, & Hansen (2003)
	Bran	/	1.7	Figueroa-Espinoza, Poulsen, Borch Soe, Zargahi, & Rouau (2004)
	Flour	3.2–3.64	2.2–2.65	Cyran et al. (2003)
Oats		2.73	0.17	Hashimoto et al. (1987b)
	Whole grain	8.79	0.1	Hashimoto et al., 1987b
	Hulls	3.5	0.33	Beaugrand, Crônier, Debeire, & Chabbert (2004)
	Bran	3	0.15	Hashimoto et al. (1987b)
	Pearled grain			Hashimoto et al. (1987b)
Rice	Whole grain	2.64	0.06	Hashimoto et al. (1987b)
	Hulls	8.36–9.24	0.11–0.11	Hashimoto et al. (1987b)
	Bran	4.84–5.11	0.35–0.77	Hashimoto et al. (1987b)
Sorghum	Whole grain	1.8	0.08	Hashimoto et al. (1987b)
	Pearling	5.4	0.35	Hashimoto et al. (1987b)
Soybean	Hulls	13.1	1.33	Hashimoto et al. (1987b)