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Polysaccharides from *Sesamum indicum* meal: Isolation and structural features

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Abstract

Defatted *Sesamum indicum* seed cake was extracted, following two separate sequences, and the effects of extraction medium on yield and composition of the extracts were compared. Polysaccharides extracted sequentially with dilute acid and alkali represented 250 mg/g of defatted meal. The isolated polymers contained arabinan, rhamnogalacturonan I (RG I) and arabinogalactan proteins. Polysaccharides extracted during chlorite treatment and with dilute alkali had a higher proportion of rhamnose, suggesting a more branched variety of polymer. Three extracts, which were further characterized by size exclusion chromatography, gave two overlapping peaks. Structural characterisation of hemicellulosic polysaccharides, isolated with KOH, using specific enzyme hydrolysis, ion exchange chromatography (HPAEC) and matrix assisted laser desorption ionisation-time-of-flight (MALDI-TOF) mass spectroscopy, showed that sesame meal xyloglucan (XG) contained XXXG, XXFG and XXLG, and XLLG (named according to Fry et al., 1993) as the major building sub-units in the ratio of 1:0.9:0.3. Hydrolysis with endo-β-(1 → 4)-D-xylanase and analysis of the xylan derived oligosaccharides showed the presence of monomeric xylose (40%), xylobiose (46%) and acidic xylan oligosaccharides containing 4-*O*-methyl-D-glucuronic acid residues (14%).

Keywords: *Sesamum indicum*; Seed cake; Arabinan; RGI; Arabinogalactan protein; Xyloglucan; Xylan

1. Introduction

Sesamum indicum L. syn *S. orientale* L. is an erect, branched or unbranched annual and one of the most ancient of cultivated crops in India. The average yield of mustard seed is about 157 kg/ha (Wealth of India, 1972). The agronomic value of the plant lies in the seed. Most of the sesame seed produced in India is utilised for production of oil, with seed cake as by-product. Sesame meal is the residue obtained from seed after extraction of oil. However, due to the limited degradation of these plant cell wall polysaccharides in the digestive tract of monogastric animals, sesame meal is poorly utilised in animal feed. This is likely caused by the complex structure of the walls, which makes them not easily accessible to enzymic degradation. One interesting feature of sesame meal is its richness in polysaccharides and protein, which can be used for its functional/or biological properties in the making of suitable functionalised derivatives (Zaghloul & Prakash, 2002), for the preparation of modified protein (Bandyopadhyay & Ghosh, 2002) or hypoglycaemic activity (Takeuchi, Mooi, Inagaki, & He, 2001). Understanding the composition, structure and location of cell wall polysaccharides is therefore, essential for the development of a better use of this agricultural by-product.

To date, most studies on *Sesamum* have concerned glycosides (Suzuki, Miyase, & Ueno, 1993), quinones

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(Hasan, Furumoto, Begum, & Fukui, 2001), flavonoids (Anila & Vijayalakshmi, 2000), sugars (Wealth of India, 1972) and proteins (Tzen, Cao, Laurent, Ratnayake, & Huang, 1993). Less attention has been paid, however, to the structural features of polysaccharides present in sesame cultivated in India. To the best of our knowledge, only one study dealing only with the sugar composition (Wankhede & Tharanathan, 1976) has been reported, and detailed structural information is missing. Unfortunately, partial structural characterization is not sufficient for interpretation in terms of functional properties and behaviour, and further knowledge is required. This report is part of a larger study aimed at characterizing different polysaccharide families of sesame meal. The structural analysis was carried out using enzymatic degradation of the hemicellulosic fractions with specific enzymes and analysis of the resulting fragments by combination of GC, GC–MS, HPAE–PAD chromatography and MALDI-TOF mass spectrometry. In addition, as sesame meal is an important source of water soluble polysaccharides, we have used mild acidic treatment, a process used for the industrial extraction of pectin from apple pomace and citrus peels (Aravantinos-Zafiris & Oreopoulou, 1992) for the extraction of polysaccharides. The yields and compositions of the dilute alkali- and water-extracted polysaccharides are also presented and discussed.

2. Materials and methods

2.1. General analyses

The analyses were made at least in duplicate and the results presented are their mean values. All evaporations were carried out under reduced pressure temperature below $\leqslant 50$ °C. Klason lignin was determined as previously described (Adams, 1965).

2.2. Material and preliminary treatments

The seed cake was obtained from the local market and was treated sequentially with hexane (48 h) and acetone (24 h) in a Soxhlet apparatus to remove lipids. The defatted sesame meal (DM) was then air dried and ground.

2.3. Isolation of polysaccharides

2.3.1. Extraction with water

The defatted seed meal (DM, 5 g) was extracted sequentially with: (i) water (300 ml, pH 5.5) for 16 h at 4 °C and then for 4 h at 35 °C (CWE, 360 mg), followed by (ii) hot water (300 ml, pH 5.5) at 80 °C for 30 min (HWE, 480 mg).

2.3.2. Dilute HCl extraction

In a separate experiment DM (4 g) was thrice extracted with 0.05 M HCl (200 ml, pH 1.8) solution at 80 °C for 30 min (designated as 'A', yield 520 mg).

2.3.3. Delignification

Lignins were removed from the acid-extracted residue using sodium chlorite in acidic solutions (pH 4.7) at 80 °C for 15 min (twice) and the material recovered was dialyzed and referred to as sodium chlorite soluble material (SC, yield 400 mg).

2.3.4. Alkali extraction

Polymers were extracted from the delignified material using the following extraction conditions (Fig. 1): (i) 0.05 M KOH + 0.4% $NaBH_4$ for 16 h at 4–6 °C, followed by 4 h at 30–35 °C, (OH, 480 mg), (ii) 1 M KOH + 0.4% $NaBH_4$ for 4 h at 30–35 °C, followed by 16 h at 4–6 °C (1OH, 160 mg) and (iii) 4 M KOH + 0.4% $NaBH_4$ for 4 h at 30–35 °C followed by 16 h at 4–6 °C (4OH, 150 mg).

All alkaline extracts were acidified to pH 5 over an ice-bath, dialyzed exhaustively and finally lyophilized. The resulting 4 M KOH-insoluble residue was washed thoroughly with water containing acetic acid, and then with deionized water, and finally dried by solvent exchange to yield the INS residue (1200 mg).

2.3.5. Isolation of arabinogalactan proteins with β-glucosyl Yariv reagent

AGPs were isolated according to Schultz, Johnson, Currie, and Bacic (2000). Briefly, to a solution of A in 1% NaCl (w/w) an equal volume of Yariv reagent, also in 1% NaCl was added. The mixture was kept at 4–6 °C for 16 h and then centrifuged. The pellet was washed with 1% NaCl, followed by pure methanol (3 times each). The pellet was then dried and treated with sodium metabisulphite (10%). The resulting solution was then dialyzed and freeze dried to yield the sesame arabinogalactan proteins (AGPs).

2.4. Preparation of xyloglucan oligosaccharides

The two hemicellulosic fractions 1OH or 4OH (15 mg) were separately dissolved in 6 ml of 50 mM NaOAc (pH 5.0) and the mixtures incubated with 30 units of endoglucanase (Megazyme International, Ireland) for 24 h at 37 °C with constant shaking. The enzyme resistant polymers were then precipitated in 80% ethanol (v/v) and removed by centrifugation. The soluble fractions containing the xyloglucan oligosaccharides (1XGose and 4XGose) were concentrated under reduced pressure and finally lyophilised.