

Structural analysis of water-soluble and -insoluble β -glucans of whole-grain oats and barley

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Abstract

Water-soluble and water-insoluble (1 \rightarrow 3),(1 \rightarrow 4)- β -D-glucans were isolated from whole-grain oats and barley and digested with lichenase. The oligosaccharides thus produced were analysed using anion-exchange chromatography with pulse-amperometric detection (HPAEC-PAD). The FT-IR, ^1H NMR and solid-state ^{13}C CP-MAS NMR spectra of the β -glucans were also measured. Analyses of the ratio of oligosaccharides with degrees of polymerisation 3 and 4 (DP3:DP4) showed small structural differences between oats and barley and between the water-soluble and water-insoluble β -glucans. The molar masses analysed using the SEC-HPLC method were 500,000 g/mol for the soluble β -glucans of both oats and barley and <200,000 g/mol for the insoluble β -glucans. No differences were found in the FT-IR and NMR spectra.

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Keywords: β -Glucan; Oats; Barley; Structure

1. Introduction

Mixed-linkage (1 \rightarrow 3),(1 \rightarrow 4)- β -D-glucan, or β -glucan, is the most abundant component of the soluble dietary fibre in both oats and barley. It is a linear and partially water-soluble polysaccharide that consists only of glucose. The positive health effects of oats, lowering of serum cholesterol and attenuation of blood glucose levels, are believed to be caused by β -glucan (Braaten et al., 1994; Cavallero, Empilli, Brighenti, & Stanca, 2002; Johansen, Wood, & Knudsen, 1993; Wood, 1994a,b; Wood, Beer, & Butler, 2000). β -Glucan also causes filtering problems in brewing (Bamforth, 1982; Grimm, Krüger, & Burchard, 1995; MacGregor & Fincher, 1993). Water-soluble β -glucan has been extensively studied for its structure and properties (Böhm & Kulicke, 1999a,b; Forrest & Wainwright, 1977; Izydorczyk, Macri, & MacGregor, 1998a,b; Ren, Ellis, Ross-Murphy, Wang, & Wood, 2003; Wood, Weisz, & Blackwell, 1994).

The composition of water-insoluble dietary fibre has been studied in oats (Claye, Idouraine, & Weber, 1996; Heims & Steinhart, 1991; Manthey, Hareland, & Huseby, 1999), barley (MacGregor & Fincher, 1993; Oscarsson, Andersson, Salomonsson, & Åman, 1996; Vasanthan, Gaosong, Yeung, & Li, 2002) wheat (Gruppen, Hamer, & Voragen, 1992a,b) and rye (Härkönen, Pessa, Suortti, & Poutanen, 1997; Roubroeks, Andersson, & Åman, 2000), but few reports are available on the structure of water-insoluble β -glucan. Izydorczyk et al. (1998b) showed that the alkali-soluble β -glucan of barley has a higher ratio of β -(1 \rightarrow 4): β -(1 \rightarrow 3)-linkages, a higher ratio of cellotriosyl: cellotetraosyl units and larger amounts of contiguous β -(1 \rightarrow 4)-linked segments than water-extractable β -glucan. It is important to know the characteristics that affect the solubility and solution behaviour of β -glucans since these features are involved in health effects and brewing problems.

High-performance anion-exchange chromatography with pulse-amperometric detection (HPAEC-PAD) has been used in analysing the oligosaccharides produced from β -glucans using lichenase digestion. Wood et al. (1994) studied the structural differences between β -glucans of oats,

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barley and rye, while Izydorczyk et al. (1998a,b) examined water-soluble and alkali-soluble barley β -glucans and Roubroeks et al. (2000) studied the structure of rye β -glucan. Gas chromatography (GC) has been used to analyse the monosaccharide content of polysaccharides after hydrolysis with strong acids such as trifluoroacetic acid (TFA) and sulphuric acid (H_2SO_4) (Blakeney, Harris, Henry, & Stone, 1983; Olson, Gray, Chiu, Betschart, & Turnlund, 1988; Pettersen & Schwandt, 1991).

Nuclear magnetic resonance (NMR) spectroscopy has been widely used to study the structure of β -glucan (Cui, Wood, Blackwell, & Nikiforuk, 2000; Dais & Perlin, 1982; Johansson et al., 2000; Westerlund, Andersson, & Åman 1993; Wood et al., 1994). Fourier transform-infrared (FT-IR) spectroscopy has also been used for structural analysis of polysaccharides (Barbosa, Steluti, Dekker, Cardoso, & Corradi da Silva, 2003; Hromádková et al., 2003; Kačuráková, Capek, Sasinková, Wellner, & Ebringerová, 2000) but no reports have been found concerning cereal $(1 \rightarrow 3)$, $(1 \rightarrow 4)$ - β -D- β -glucans.

In our earlier work (Johansson et al., 2000) we studied the structure of soluble β -glucan isolated from oat bran. Recently, we examined the composition of the insoluble fibre fraction of oats and barley using sequential extraction with different alkali solutions and water (Virkki, Johansson, Ylinen, Maunu, & Ekholm, 2004).

The aim of the present study was to analyse the possible structural differences between β -glucans of oats and barley as well as the differences between water-soluble and water-insoluble β -glucans. Both oat and barley β -glucans have been studied extensively, but comparison of results is difficult due to differences in the isolation methods used. Here the extraction procedure was the same for both samples, and therefore any possible differences present would have arisen from the structure rather than from the method.

2. Experimental

2.1. Materials

The materials used were whole-grain oats (Yty) and barley (Saana) obtained from Boreal Plant Breeding Ltd (Jokioinen, Finland). The samples were grown and harvested in 1997. The grains were dehulled manually and then milled (Cyclotec 1093, Tecator AB, Höganäs, Sweden) to a particle size of <0.5 mm.

Termamyl 300 L DX was purchased from Novo Nordisk A/S (Bagsvaerd, Denmark), pancreatin 8 \times USP from Sigma Chemical Co. (St Louis, MO, USA) and lichenase (EC 3.2.1.73) from Megazyme, Wicklow, Ireland. The malto-oligosaccharides were obtained from Sigma. Water was purified with a Milli-Q-Plus system (Millipore Corporation, Bedford, MA, USA). For standard monosaccharides, glucose was obtained from J.T. Baker

(Devender, Holland), arabinose and xylose from Merck (Darmstadt, Germany) and myoinositol from Sigma. The NaOH solution was purchased from Fluka (Buchs, Switzerland). All other chemicals used were the purest obtainable.

2.2. Isolation of β -glucans

The method of Westerlund et al. (1993) with minor changes was used for isolating water-soluble β -glucan from oats (OS) and from barley (BS) (Johansson et al., 2000). The ground grains were defatted, using Soxhlet extraction with hot isopropanol and petroleum ether. The polysaccharides were solubilised in water at 96 °C and starch was hydrolysed using Termamyl. The insoluble fraction was separated using centrifugation. Proteins in the supernatant were degraded using pancreatin. The polysaccharides were precipitated using 60% ethanol at 4 °C. The precipitate was removed using centrifugation and dissolved in water at 70–80 °C. β -Glucan was precipitated using 30% $(\text{NH}_4)_2\text{SO}_4$ and separated using centrifugation. The β -glucan precipitate was dissolved in water at 80 °C in the dialysis tube (CelluSep T1, MW cutoff 3500, Membrane Filtration Products, Inc., San Antonio, Texas, USA) and dialysed against purified water at room temperature for 3×24 h. The resulting β -glucan solution was freeze-dried.

The insoluble fibre fractions were isolated using the method of Asp, Johansson, Hallmer, and Siljeström (1983) and further fractionated, using a modified method of Gruppen et al. (1992a). The arabinoxylans were extracted with saturated $\text{Ba}(\text{OH})_2$ solution (fraction 1). The remaining insoluble material was suspended in Milli-Q water, neutralised with acetic acid and extracted 4 times with water (fraction 2). This fraction contained most of the β -glucan and is referred to as insoluble β -glucan (OIS for oats and BIS for barley). Fractions 3–5 of the Gruppen method were not analysed. The monosaccharide contents of fractions 1 and 2 were analysed using GC.

2.3. General analyses

The flours and the insoluble fibre fractions were characterised for their crude fat, protein and β -glucan contents. Fat was analysed using the AOAC 922.06 method (AOAC, 1995). Protein was analysed using the Kjeldahl method ($N \times 6.25$). The amount of β -glucan was determined using the method of McCleary and Codd (1991) (AOAC 995.16) using an assay kit (Megazyme).

The fractionation method includes several sources of metals and therefore the insoluble fractions were analysed for their Na, K, Mg, Al, Ca, Fe, Cu, Zn and Ba contents and soluble β -glucan also for P with a Perkin Elmer ELAN 6000 inductively coupled plasma-mass spectrometer (ICP/MS) equipped with a Perkin Elmer autosampler AS-91 (Perkin Elmer Ltd., Bucks, England). The dried samples and blanks were wet-digested in 10 ml of conc. HNO_3 with a Tecator Digestion System 41 with an autostep 1012 controller.

Rhodium was used as an internal standard at a 0.01 µg/l concentration. NBS (National Bureau of Standards, Gaithersburg, MD, USA) 1567a wheat flour was used as a reference sample. A TotalQuant analysis was performed which gives semi-quantitative results. The ICP Multi element Standard VI (Merck, Darmstadt, Germany) was used.

The statistical analyses were performed using one-way analysis of variance (ANOVA) at the 95% confidence level.

2.4. Gas chromatography

The monosaccharide contents of the samples were determined using GC (Micromat, HRGC 412 (Orion Analytica, Espoo, Finland) as alditole acetates after hydrolysis with H₂SO₄ at 120 °C (Blakeney et al., 1983; Johansson et al., 2000; Olson et al., 1988). The column was a NB-17 (Nordion, Helsinki, Finland) fused-silica capillary column (25 m × 0.32 mm i.d., film thickness 0.25 µm). The column oven was programmed from 190 °C (4-min hold) to 230 °C (6-min hold) at a rate of 4 °C/min. The monosaccharides were identified according to their retention times and quantitated using an internal standard method involving myoinositol. Free sugar residues were corrected, using the factor 0.9, to anhydrosugars as present in polysaccharides (McCleary & Codd, 1991). All analyses were performed in duplicate.

2.5. Enzymatic degradation

The isolated β-glucans were degraded with lichenase enzyme as previously described (Johansson et al., 2000). The method was modified from the McCleary method (AOAC method 995.16). Samples of isolated β-glucan were dried at 70 °C for 3 h. The samples (60–110 mg) were weighed accurately and pretreated with aqueous ethanol (50%), dissolved in phosphate buffer (4.0 ml, 20 mM, pH 6.5) in a boiling water bath and stirred on a vortex mixer. The samples were then incubated with lichenase at 60 °C for 2 h. The resulting solution was incubated in a boiling water bath for 10 min and then diluted with water. The decomposition products (oligosaccharides) were analysed both with capillary electrophoresis (CE) and HPAEC-PAD.

2.6. CE analyses

The CE analyses were performed with a Hewlett Packard ^{3D} CE system with UV detection at 245 nm (Hewlett-Packard, Waldbronn, Germany). An uncoated fused-silica capillary column was used (total length 60 cm, effective length 51 cm, 50 µm i.d.). The injections were performed hydrodynamically (50 mbar, 2 s). The applied voltage was 21 kV. The running electrolyte was an alkaline borate buffer (420 mM H₃BO₃/220 mM NaOH, pH 9.0). The oligosaccharides were derivatised through reductive amination

using sodium cyanoborohydride and 6-aminoquinoline. All analyses were performed in triplicate.

2.7. HPLC analyses

The oligosaccharides produced using lichenase treatment were also analysed using high performance liquid chromatography (HPLC). The system was equipped with Waters 515 HPLC pumps and Waters Automated Gradient Controller (Milford, MA, USA). The analytical column was a Dionex (Sunnyvale, CA, USA) CarboPac PA1 (4 × 250 mm) and the guard column was a PA1 (3 × 25 mm), maintained at 30 °C. The eluents were A: 150 mM NaOH and B: 500 mM sodium acetate in 150 mM NaOH. The flow rate was 1 ml/min. The gradient was from 90% A–10% B to 100% B in 15 min. A Decade detector with gold electrode was used (Antec Layden, The Netherlands). The pulse potentials and durations were: $E_1 = 0.15$ V, $t_1 = 400$ ms, $E_2 = 0.75$ V, $t_2 = 120$ ms, $E_3 = -0.8$ V, $t_3 = 300$ ms, $t_s = 20$ ms. The samples were filtered (0.2 µm, Acrodisc, Pall Gellman Laboratory, Ann Arbor, MI, USA) before analysis. The injection volume was 20 µl. Quantitation was performed with malto-oligosaccharides with degree of polymerisation (DP) 3–6. All analyses were performed in triplicate.

The molar masses of both soluble and insoluble β-glucans of oats and barley were determined using size-exclusion chromatography (SEC-HPLC) with either calcofluor or light-scattering detection (Suortti, 1993; Wilhelmson et al., 2001). Light-scattering detection was used for OS and BS and calcofluor postcolumn detection was used for OIS and BIS.

2.8. Spectroscopic measurements

The ¹H NMR spectra of BS and BIS were obtained using a Varian ^{UNITY}500 NMR spectrometer (Varian NMR Systems, Palo Alto, CA, USA) operating at 500 MHz for protons. The measurements were performed at 80 °C. The samples were dissolved in D₂O and acetone-d₆ ($\delta_H = 2.225$ ppm) was used as the internal reference. The ¹³C CP-MAS spectra of OS, BS, OIS and BIS were obtained with a Varian ^{UNITY}INOVA 300 NMR spectrometer operating at 75 MHz for carbons. A 5-kHz spinning speed and 7-mm rotor were used. The contact time was 0.5 ms, acquisition time 20 ms and delay between pulses 3 s. The chemical shifts were adjusted using external secondary referencing (hexamethylbenzene, methyl line set to 17.3 ppm). The same spectral window was used during the sample measurements.

The FT-IR spectra were recorded with a Perkin Elmer Spectrum One FT-IR instrument (Perkin Elmer) equipped with a Universal ATR sampling accessory and a MIR TGS detector. A total of 200 scans were run from 4000 to 650 cm⁻¹ at a resolution of 8 cm⁻¹.

Table 1
Chemical composition of the whole-grain flours of oats and barley

Sample	Fat % \pm s.d. ^a	Protein % ^b	Insoluble fibre % \pm s.d. ^c	Total β -glucan % \pm s.d. ^c
Oat flour	8.5 \pm 0.9	13	6.1 \pm 0.8	4.0 \pm 0.1
Barley flour	4.4 \pm 0.9	12	13.7 \pm 0.5	3.7 \pm 0.1

^a $n=9$.

^b $n=2$.

^c $n=4$.

3. Results and discussion

3.1. Characterisation of the flours and insoluble fibre fractions

The whole-grain flours were characterised for their fat, protein, insoluble fibre and β -glucan contents (Table 1). The insoluble fractions were then separated and further characterised for their fat, protein and β -glucan contents (Table 2). Fat caused some difficulty in the isolation of the insoluble fibre but did not disturb the analysis of β -glucans. The amount of insoluble fibre was much smaller in oat flour (6.1%) than in barley flour (13.7%). The total amounts of β -glucan in the flours were 4.0% for oats and 3.7% for barley. The amount of β -glucan in the insoluble fibre fraction of oats was higher than in barley (11.5 and 6.7%, respectively). Thus about 18% of the total β -glucan content was insoluble in oats and 25% in barley. This corresponds well with Miller and Fulcher (1995), who found that 20–25% of oat β -glucan is insoluble in water at 65 °C.

The ICP-MAS analyses were performed to ensure that the dialyses were successful. The results showed that the amounts of Ca and Ba in fraction 2 were 1–2%, while the amounts of the other elements measured were negligible (data not shown).

3.2. Characterisation of β -glucans

Monosaccharide analysis using GC showed that the soluble β -glucans (OS and BS) contained only glucose. The contents of glucose were 99% for oats and 90% for barley. Fraction 2 of the insoluble fibre fraction, which was obtained using water extraction after extraction with Ba(OH)₂, contained glucose, arabinose and xylose.

Table 2
Chemical composition of the insoluble fibre of oats and barley

Sample	Fat % \pm s.d. ^a	Protein % ^b	β -glucan % \pm s.d. ^c
Oat insoluble fibre	9.2 \pm 1.0	17	11.5 \pm 0.1
Barley insoluble fibre	4.2 \pm 0.3	22	6.7 \pm 0.1

^a $n=3$.

^b $n=2$.

^c $n=4$.

Table 3
Molar masses of the soluble and insoluble β -glucans of oats (OS and OIS, respectively) and barley (BS and BIS, respectively)

Sample	$M_w \times 10^5$ g/mol	$M_n \times 10^5$ g/mol	$M_w:M_n$
OS	5.1	3.8	1.3
BS	4.7	3.7	1.3
OIS	<2	n.d.	n.d.
BIS	<2	n.d.	n.d.

n.d. = not determined.

Arabinose and xylose are derived from the arabinoxylan present in the insoluble fibre. The amount of glucose was 36.4% for oats and 29.1% for barley. The sums of arabinose and xylose were 10% for oats and 24% for barley. Arabinoxylan is mainly extracted using Ba(OH)₂ into fraction 1, but part of it remains in the precipitate and is extracted along with β -glucan in fraction 2 (Virkki et al., 2004).

Table 3 shows the molar masses of the samples. There were differences between the soluble (OS and BS) and the insoluble (OIS and BIS) samples but not between oats and barley. The weight average molar masses (M_w) of OS and BS were about 500,000 g/mol for both oats and barley as determined using SEC-HPLC with light-scattering detection. The ratio of weight average and number average molar masses ($M_w:M_n$) was the same (1.3) for oats and barley. The M_w of OIS and BIS were determined using calcofluor detection. They were significantly smaller (<200,000 g/mol) than those for OS and BS and there was no difference between oats and barley. Gruppen et al. (1992a) found a molar mass of 150,000 g/mol for wheat β -glucan extracted from water-insoluble material using the present procedure. They also showed that the Ba²⁺-ions keep the β -glucans insoluble. Roubroeks et al. (2000), in their work on rye β -glucan, suggested that intermolecular associations present in water are avoided in alkali, making β -glucan more soluble. Forrest and Wainwright (1977) showed that β -glucan is not covalently bonded to pentosans in barley cell walls. Woodward, Fincher and Stone (1983) detailed the structure of cell walls, using non-covalent interactions between β -glucan and other components of the cell wall. Miller and Fulcher (1995) suggested that β -glucan is entangled and hydrogen-bonded with other components of the cell wall. Izydorczyk et al. (1998b) also suggested the presence of entanglements between β -glucan and arabinoxylan. In conclusion, β -glucan in the insoluble fibre fraction appears to be non-covalently bound to arabinoxylan and therefore remains insoluble despite its low molar mass. When arabinoxylan is removed using Ba(OH)₂ extraction, β -glucan is released and becomes water-extractable.

3.3. Spectrometric analyses

In our previous work (Johansson et al., 2000) we studied β -glucan from oat bran using liquid-state ¹³C NMR and two-dimensional correlation spectroscopy. These studies

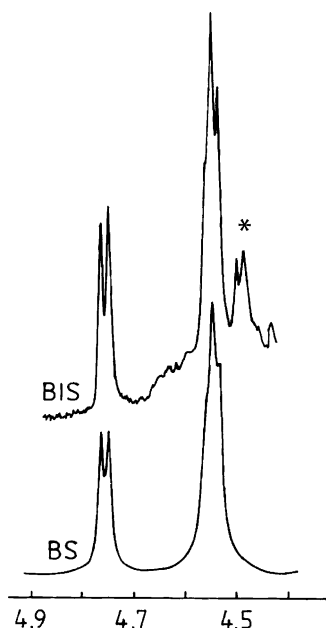


Fig. 1. ^1H NMR spectra of the anomeric regions of soluble (BS) and insoluble (BIS) barley β -glucans (* impurity).

confirmed the structure revealed by Dais and Perlin (1982) and showed no evidence of consecutive (1 \rightarrow 3)-linkages. In the present paper, liquid-state ^1H NMR and solid-state ^{13}C CP-MAS were used to obtain direct information on the materials extracted. Fig. 1 shows the ^1H NMR spectra of BS and BIS with the typical partially overlapping anomeric signals of a β -glucan. The ^1H NMR spectra of OS and OIS were also similar (not shown). Fig. 2 shows the ^{13}C CP-MAS spectra of the β -glucans of oats and barley, the spectra are similar. Broad resonances in the region 50–110 ppm are partially overlapping signals of β -glucan and arabinoxylan carbons. Resonances in the region 10–40 ppm are probably from polyethylene chains originating mainly from fat residues, these signals are only seen

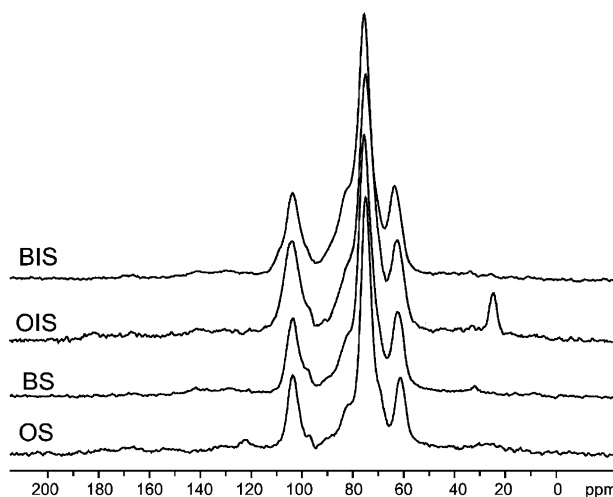


Fig. 2. ^{13}C CPMAS spectra of the soluble and insoluble oat (OS and OIS) and barley (BS and BIS) β -glucans.

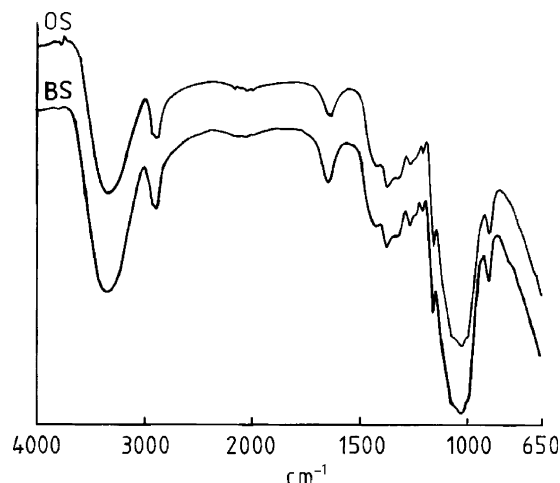


Fig. 3. IR spectra of soluble oat (OS) and barley (BS) β -glucans.

in OIS. Fig. 3 shows the IR spectra of OS and BS. The spectra are similar for oats and barley and show the typical signals of glucose polysaccharides. The spectra of the insoluble β -glucans (not shown) were essentially similar to those of the soluble β -glucans.

3.4. Chromatographic analyses

Table 4 shows the amounts of oligosaccharides with DP 3–6 obtained in enzymatic hydrolyses of the β -glucans of oats and barley analysed using HPAEC-PAD. The same samples were also analysed using CE compared to these methods. The results of the CE analyses were similar to those of HPAEC-PAD. In the present paper, the HPAEC-PAD method showed a higher reproducibility than CE and therefore only the results of HPAEC-PAD are used in the discussion. Oligosaccharides with higher DP were also detected but not identified, due to lack of suitable standards. Roubroeks et al. (2000) in their work on rye β -glucan, reported glucose, cellobiose and laminaribiose as products of lichenase and cellulase hydrolyses. In the present paper, cellobiose and laminaribiose were not found. Statistically significant differences ($P < 0.05$) in the amounts of the oligosaccharides were observed between OS and OIS and between BS and BIS, and also between oats and barley.

The main products of lichenase digestion are oligosaccharides with DP 3 and 4. The ratio of their amounts, DP3:DP4, is a measure of structural differences. Table 4 shows that this ratio is higher for barley than for oats for both soluble (1.6 for BS and 1.4 for OS) and insoluble β -glucans (1.8 for BIS and 1.7 for OIS). The differences are small but statistically significant ($P < 0.05$). In other words, OS and OIS have fewer cellotriose segments than those of BS and BIS. The difference between soluble and insoluble β -glucans is significant for both oats and barley ($P < 0.05$), suggesting that soluble β -glucan has fewer cellotriose units than insoluble β -glucan. The ratios DP3:DP5 and DP3:DP6 were also calculated (Table 4). Although the differences in

Table 4

Relative amounts of oligosaccharides with degrees of polymerisation 3–6 produced using lichenase digestion from soluble and insoluble oat (OS and OIS) and barley (BS and BIS) β -glucans as measured using HPLC-PAD

DP	3 w% \pm s.d	4 w% \pm s.d	5 w% \pm s.d	6 w% \pm s.d	DP3:DP4	DP3:DP5	DP3:DP6
OS	54.2 \pm 1.9	39.8 \pm 1.2	4.7 \pm 0.4	3.5 \pm 0.4	1.4 (1.8) ^a	13.2 (15.2) ^a	18.7 (20.5) ^a
BS	59.2 \pm 4.1	36.0 \pm 2.8	5.4 \pm 0.6	3.4 \pm 0.8	1.6 (2.2) ^a	10.9 (13.5) ^a	17.9 (23.0) ^a
OIS	66.6 \pm 4.9	38.7 \pm 5.7	5.0 \pm 1.4	3.2 \pm 1.4	1.7 (2.3) ^a	13.3 (17.2) ^a	20.2 (27.5) ^a
BIS	61.5 \pm 7.2	33.3 \pm 6.8	5.0 \pm 0.2	2.5 \pm 0.3	1.8 (2.4) ^a	12.1 (16.3) ^a	23.7 (32.5) ^a

^a Values in parenthesis are molar percentages.

these ratios between the samples are all statistically significant, the results do not allow conclusions to be drawn on the solubility or differences between oats and barley.

The molar ratios DP3:DP4 for OS and BS (1.8 and 2.2, respectively) were lower than those reported by Cui et al. (2000) (2.2 and 3.3, respectively) and Wood (1994a,b) (2.1 and 2.8, respectively) but well in accordance with Izydorczyk et al. (1998a,b) who reported values between 1.8 and 2.1 for water-soluble barley β -glucan and 2.1–2.4 for alkali-soluble β -glucans, depending on the conditions of extraction. The results correspond well with those of Colleoni-Sirghie, Fulton and White (2003), who reported a ratio of 1.6 for β -glucan extracted from oat lines, and with Jiang and Vasanathan (2000) who found ratios of 2.0 and 1.8 for barley glucans. Böhm and Kulicke (1999b) reported ratios for oat β -glucan, barley β -glucan and lichenan to be 1.9, 2.5 and 23, respectively. The value for DP3:DP4 varied in these reports but it always seems to be higher for barley than for oats, which is also shown in our work.

It is generally believed that the more β -glucans contain long sequences of (1 \rightarrow 4)-bonds, the higher is their tendency to associate, owing to the rigidity of these polymer segments (Doublier & Wood, 1995; Fincher & Stone, 1986; Izydorczyk et al., 1998a; MacGregor & Fincher, 1993; Woodward et al., 1983). Tvaroska, Ogawa, Deslandes and Marchessault (1983) studied lichenan and barley β -glucan. They showed that a high value for the ratio DP3:DP4 increases the probability that cellotriosyl units would appear regularly, which causes aggregation through formation of helices. This type of aggregation was found in lichenan but not in barley β -glucan. Góméz, Navarro, Garnier, Horta and Carbonell (1997) studied the flow and viscoelasticity of barley β -glucan to elucidate the aggregation of this molecule. They concluded that barley β -glucan forms structured solutions through aggregation involving links between short chain segments. Böhm and Kulicke (1999b), in their work on lichenan and β -glucans of oats and barley, reported an increased tendency to gel formation with increased amounts of consecutive cellotriose units. They concluded that consecutive cellotriose units rather than cellulose like sequences are responsible for the association. Oat β -glucan has the least regular structure and is therefore less able to gelatinise than barley β -glucan and much less so than lichenan.

4. Conclusions

Structural differences between oats and barley β -glucans were found. The soluble and insoluble β -glucans differed from each other for both oats and barley. These differences are detectable in the ratio of oligosaccharides DP3 and DP4 released by hydrolysis with lichenase. The ratio was higher for barley than for oats for both soluble and insoluble β -glucans. A higher ratio of DP3:DP4 means a higher number of cellotriose segments. The molar masses were the same for soluble β -glucans of oats and barley. The molar masses were significantly lower for insoluble β -glucans than for the soluble ones but again the same for both oats and barley. The NMR and IR spectra showed no differences between the samples.

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