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Rapid Communication

Characterisation of dietary fibre components in rye products

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ABSTRACT

In this study, dietary fibre (DF) was characterised in rye products from a local supermarket. Soft breads generally had lower DF contents (8–18%) than had crisp breads (13–20%) due to high inclusion of wheat flour. For some products, the labelled DF values contained fructan, but others did not. However, for most products, the DF values analysed exceeded those declared. Arabinoxylan (AX) and fructan were generally the main DF components in the products, followed by cellulose and resistant starch, β-glucan, Klason lignin and arabinogalactan. In the soft breads, cellulose and resistant starch concentrations were relatively high, due to significant formation of resistant starch. During bread manufacturing, the molecular weight of β-glucan was highly degraded, while that of AX was more resistant. Extruded products had the highest β-glucan extractability and the extracted β-glucan retained its molecular weight most, which may be of nutritional significance. In rye milling fractions, about 50% of the fructan content analysed had a degree of polymerisation below 10, i.e. it comprised oligosaccharides. The crisp breads produced without yeast had the highest DF and fructan contents and the highest proportion of low-molecular weight fructan. These results indicate that, during bread-making, the low-molecular weight fraction of fructan was most available for degradation by yeast or by endogenous enzymes present in the ingredients.

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1. Introduction

Rye (*Secale cereale* L.) is a widely grown cereal in northern, central and eastern Europe. Its main use is in bread and other products aimed for human consumption or animal feed (Kamal-Eldin, Åman, Zhang, Bach Knudsen, & Poutanen, 2008). Among commonly grown cereals, whole grain rye has the highest dietary fibre (DF) content, ranging from 13% to 17% (Bengtsson & Åman, 1990; Nilsson, Saulnier, Andersson, & Åman, 1996) or 18% to 22% when fructan (including fructo-oligosaccharides) is included in the analysis (Andersson, Fransson, Tietjen, & Åman, 2009). The new definition of DF in the EU includes fructan and fructo-oligosaccharides and discussions are underway in the Codex Alimentarius Commission (CAC) about their universal inclusion (Lunn & Buttriss, 2007). Many consumers obtain a significant part of their DF intake from rye in the form of different types of soft and crisp breads. The typical Western diet contains less than 20 g DF day^{-1}, which is lower than the recommended daily intake value of 25–35 g (Drehner, 1987). The major components of rye DF are arabinoxylan, fructan and β-glucan, with contents ranging from 8.0% to 12.1%, 4.5% to 6.4% and 1.3% to 2.2%, respectively, in rye grain (Hansen, Rasmussen, Bach Knudsen, & Hansen, 2003). Rye is considered to be a healthy cereal with its high content of DF and associated components (Kamal-Eldin et al., 2009). The physiological effects of rye DF are at least partly related to properties such as solubility, content and molecular weight of the fibre components, which are influenced by processing (Lunn & Buttriss, 2007; Thebaudin, Lefebvre, Harrington, & Bourgeois, 1997).

Arabinoxylan is a major component of cereal cell walls, especially rye. The water-extractable AX exerts a positive influence on the baking quality of rye flour, while the non-extractable part can have negative effects. Therefore both the amount and extractability of AX are important in determining its role in bread making (Vinkx & Delcour, 1996). Because of its high water-holding capacity, rye AX plays an important role in starch retrogradation and bread staling (Izydorczyk & Biliaderis, 1995). β-Glucan is present in lower amounts in rye than in oats and barley. In human studies, it has been reported to have both cholesterol-lowering and glucose-attenuating effects, depending upon the dose, viscosity and molecular weight (Wood, 2007).

Fructans are polydisperse molecules with a degree of polymerisation (DP) normally ranging from 2 to 60. Naturally occurring fructans are non-reducing carbohydrates with a sucrose residue at the reducing end and, based on the linkages between fructosyl-fructose units, they are classified into different groups. In cereals, levan with β-(2 → 6) fructosyl-fructose linkages predominates, while the most widely studied fructan is inulin with β-(2 → 1) fructosyl-fructose linkages (Izydorczyk, Cui, & Wang, 2005; Roberfroid, 2005). Inulin extracted from chicory root or Jerusalem artichoke is today a commercially important food ingredient. Studies have shown that fructan content and molecular weight

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distribution may be affected during food processing (Hansen et al., 2002; Praznik, Cieślik, & Filipiak-Florkiewicz, 2002). Fructan is resistant to endogenous enzymes in the upper gastrointestinal tract, but research has shown that the microorganisms in this part of the tract are few and thus may have a limited capacity to degrade highly available fibre components, such as fructan (Bach Knudsen & Hessov, 1995). In the large intestine, fructan is highly fermented by the colonic microflora. The bifidogenic nature of inulin is well-documented and studies are now focusing on its potential immune-stimulating and anticancer effects (Taper & Roberfroid, 2002; Watzl, Girrbach, & Roller, 2005).

As discussed above, the content and properties of DF are considered important factors for the healthiness of whole grain rye foods. The aim of this study was to investigate the DF content in different commercial breads with whole grain rye as one of the main ingredients, and to compare the content analysed with the content reported on the product labels. The main dietary fibre components in the foods (arabinoxylan, β-glucan and fructan) and the molecular weight distribution of their extractable parts were also investigated.

2. Materials and methods

2.1. Materials

Twelve crisp breads, eight soft breads and two extruded products, declared to contain rye as one of their main ingredients, and varying in ingredient composition and processing method used for their preparation, were obtained from a local supermarket (Table 1). Three rye flour streams (inner endosperm, outer endosperm and milled rye bran) were obtained from Lantmännen AB, Stockholm, Sweden.

2.2. Methods

2.2.1. Sample preparation

Prior to analysis, crisp breads and extruded products were finely ground in a cyclone sample mill (Retsch, Hann, Germany) to pass a 0.5 mm screen. The soft bread samples were freeze-dried before grinding. All milled samples were stored in plastic containers at room temperature until analysis.

2.2.2. Analytical methods

All the samples were analysed at least in duplicate. Dry matter was determined by drying the samples at 105 °C for 16 h according to AACC method 44-15A (2000). Total dietary fibre and its constituents were quantified according to the Uppsala method (Theander, Åman, Westerlund, Andersson, & Pettersson, 1995). Weight-average molecular weight (M_w) and number-average molecular weight (M_n) of arabinoxylan were determined by high performance size-exclusion chromatography, coupled with multiple angle laser light scattering and refractive index detectors (Andersson et al., 2009). Arabinoxylan, with retention time of 30–44 min, was included in the results. The β-glucan content was analysed enzymatically according to McCleary and Codd (1991) and Calcofluor average molecular weight (M_{cf}) of β-glucan was determined using size-exclusion chromatography with Calcofluor detection, according to the method described by Rimsten, Stenberg, Andersson, Andersson, and Åman (2003) with a Calcofluor concentration of 0.0025%. With this detection technique, molecules smaller than 10^4 are excluded from the analysis. Most of the samples were extracted for 1.5 h, except those containing oats, which were extracted for 6 h in boiling water in the presence of thermostable α-amylase (Ajithkumar, Andersson, & Åman, 2005). Fructan quantification was performed according to McCleary, Murphy, and Mugford (2000) using a spectrophotometric method with the enzymatic assay kit K-FRUC (Megazyme, Bray, Ireland). The samples were treated with α-galactosidase from *Aspergillus niger* E-AGLAN (Megazyme, Bray, Ireland) before degradation of starch, maltosaccharides and sucrose, as described in the kit.

2.2.3. Fructan molecular weight distributions

About 200 mg of sample was weighed into a glass tube, together with 200 μl of lactose solution (2 mg lactose ml^{-1} water, Sigma, Steinheim, Germany) as internal standard and 4 ml of 80% ethanol. The sample was capped and extracted in a boiling water bath for

Table 1
Ingredients according to label in crisp breads, soft breads and extruded products.

Sample	Main ingredients
Crisp breads	
A	Whole grain rye flour, yeast, sourdough
B	Whole grain rye flour
C	Whole grain rye flour, yeast
D	Whole grain rye flour, buck wheat, linseed, kibbled soya, sesame seeds, kibbled rye
E	Whole grain rye flour
F	Whole grain rye flour, oat flakes, yeast
G	Whole grain rye flour, yeast
H	Whole grain rye flour, yeast (thin crisp bread)
I	Whole grain rye flour, yeast
J	Whole grain rye flour, yeast
K	Whole grain rye flour, corn flour, yeast
L	Whole grain rye flour, wheat flour, whole grain oat flour, barley flour, millet, poppy seeds, yeast (thin crisp bread)
Soft breads	
M	Whole grain rye flour, sourdough, whole grain wheat flour, rye bran, yeast
N	Rye grains, sourdough, sieved rye flour, malt, wheat fibre, yeast
O	Whole grain rye flour, sourdough, whole grain wheat flour, wheat flour, yeast, rye bran
P	Wheat flour, whole grain rye flour, whole grain wheat flour, yeast, oat fibre
Q	Whole grain wheat flour, whole grain rye flour, wheat flour, whole grain oat flour, linseed, yeast, malt, sugar beet fibre, sourdough
R	Wheat flour, rye fibre, sourdough, whole grain rye flour, yeast
S	Wheat flour, whole grain rye flour, sieved rye flour, rye flakes, sourdough, yeast, wheat germ
T	Wheat flour, rye flour, yeast, rye fibre, rye flakes
Extruded products	
U	Whole grain rye flour, whole grain oat flour, malt (breakfast cereal)
V	Whole grain wheat flour, white wheat flour, whole grain rye flour, corn flour, whole grain barley flour, spelt wheat flour, amaranth flour, quinoa flour (crisp bread)

1 h with occasional mixing, ensuring that no ethanol evaporated during the extraction. The tube was cooled and centrifuged at 1500*g* for 15 min. Supernatant (0.5 ml) was transferred to a separate test tube and the solvent removed by drying with nitrogen. Then 2.5 ml of 0.1 M sodium acetate buffer pH 5.0 were added and the sample incubated for 4 h at 60 °C in the presence of 50 μl of amyloglucosidase (soluble starch 326 U ml^{-1}, E-AMGDF, Megazyme, Bray, Ireland) with frequent stirring, using a vortex mixer. One millilitre of amyloglucosidase-treated solution was transferred to another glass tube and treated with 25 μl of fructanase mixture, E-FRMXLQ (exo-inulinase 2000 U ml^{-1} and endo-inulinase 200 U ml^{-1}, Megazyme, Bray, Ireland) for 1 h at 40 °C. Both fructanase-treated and non-treated samples were filtered through Titan2® HPLC syringe filters (17 mm, 0.45 μm) obtained from Sun Sri, Wilmington (NC), USA.

Both samples were analysed in a Dionex DX 500 Chromatography System (Sunnyvale, CA, USA) equipped with GP 40 gradient pump. The eluent was 150 mM NaOH (A) at 1.0 ml min^{-1} with a gradient of 150 mM NaOH containing 500 mM $NaCH_3COO$ (B); 0–10 min linear gradient 0–20% eluent B; 10–30 min linear gradient 20–100% eluent B; 30–40 min isocratic at 100% B. The system was run with 100% A for 5 min between runs. Chromatography was carried out with a CarboPac™ PA-1 (4 × 250 mm, P/N 35391) anion-exchange column pre-fitted with a CarboPac™ PA-1 Guard Column (P/N 43096). Detection was carried out by an ED40 pulsed amperometric detector. The relative percentage distributions of different DP ranges were calculated, based on the area under the peaks. The area under each peak was calculated by subtracting the area of chromatogram without fructan from that with fructan present.

3. Results and discussion

3.1. General

Crisp breads, soft breads, extruded products and milling fractions were analysed for total DF, arabinoxylan, β-glucan and fructan. The results are reported on a dry weight basis and are the mean of at least two replicates. The deviation between replicates was generally below 5%.

3.2. Total dietary fibre and its components

The bran had the highest total DF content (37.7%, as analysed by the Uppsala method with added fructan), followed by the outer endosperm (21.8%, Table 2). In a previous study (Kamal-Eldin et al., 2009), the DF content in six different rye brans from Sweden, Finland and Denmark were found to range from 41.1% to 47.5%, which is higher than in the present study. Nilsson et al. (1996) reported 38.4% DF in rye bran and 8.4% in rye flour without including fructan, which is more similar to our result. The average DF content

Table 2
Dietary fibre content and composition of crisp breads, soft breads, extruded products and milling fractions (% of dry matter).

Samples	Dietary fibre		Dietary fibre components					
	Total DF[a]	Labelled DF[b]	Arabinoxylan[c]	Arabinogalactan[c]	β-Glucan[d]	Cellulose and resistant starch[e]	Fructan	Klason lignin
Crisp breads								
A	18.7	17.1[f]	8.8 (0.52)	0.7	1.9	2.6	2.2	1.4
B	19.8	18.8	8.3 (0.52)	0.6	1.9	3.0	3.7	1.5
C	18.8	15.9[f]	8.6 (0.54)	0.6	1.9	2.5	2.7	1.5
D	19.0	17.6	7.4 (0.52)	0.8	1.6	3.0	3.4	1.5
E	19.5	16.9[f]	8.0 (0.53)	0.6	2.1	2.6	4.0	1.4
F	17.4	14.9[f]	7.9 (0.54)	0.5	2.2	2.3	2.1	1.5
G	17.9	16.8[f]	8.2 (0.53)	0.6	1.8	2.5	2.8	1.1
H	17.7	19.8	8.1 (0.50)	0.6	2.0	2.3	2.6	1.2
I	17.7	15.9[f]	8.2 (0.53)	0.6	1.9	2.3	2.7	1.1
J	17.5	16.9[f]	8.0 (0.53)	0.6	1.9	2.1	2.9	1.1
K	17.2	15.7[f]	7.4 (0.54)	0.5	1.9	2.0	3.3	1.2
L	13.0	14.7	5.2 (0.55)	0.4	1.8	1.7	1.9	1.2
Average	17.8	16.7	7.8 (0.53)	0.6	1.9	2.4	2.8	1.3
Soft breads								
M	17.5	18.3	8.5 (0.48)	0.6	1.7	2.8	2.0	1.1
N	16.8	14.5[f]	6.9 (0.51)	0.5	1.4	4.1	2.3	0.7
O	15.8	15.5	7.5 (0.51)	0.6	1.5	2.6	1.8	0.9
P	12.1	13.6[f]	5.0 (0.42)	0.4	0.9	3.5	1.1	0.3
Q	11.6	11.8[f]	4.6 (0.55)	0.5	1.1	2.6	1.3	0.5
R	10.5	14.4	4.2 (0.31)	1.1	0.9	1.9	0.8	0.5
S	8.80	9.6[f]	3.5 (0.56)	0.4	0.9	1.8	1.5	0.2
T	7.90	9.1	3.1 (0.56)	0.3	1.0	0.7	1.8	0.2
Average	12.6	13.3	5.4 (0.49)	0.5	1.2	2.5	1.6	0.6
Extruded products								
U	14.3	14.3	5.3 (0.53)	0.4	2.3	1.5	2.8	0.8
V	9.40	11.5[f]	4.1 (0.58)	0.5	0.9	1.1	1.4	0.7
Milling fractions								
Inner endosperm	11.8	NA[g]	4.4 (0.66)	0.3	1.5	1.2	3.4	0.2
Outer endosperm	21.8	NA	9.3 (0.65)	0.5	3.4	2.1	4.6	0.5
Milled rye bran	37.7	NA	18.2 (0.50)	1.3	4.4	4.3	5.0	3.0

[a] Total DF calculated as the sum of fructan and DF analysed by the Uppsala method.
[b] Labelled DF content recalculated on dry matter basis.
[c] Calculated from arabinose, xylose and galactose residue values assuming that the arabinose to xylose ratio was 0.69 in arabinogalactan. Arabinose to xylose ratio of arabinoxylan in brackets.
[d] Total β-glucan determined enzymatically.
[e] Cellulose and resistant starch calculated as the difference between total β-glucan and the glucose residues analysed by the Uppsala method.
[f] The samples did not have fructan included in their labelled DF value.
[g] Not applicable.

in the crisp breads (17.8%) was higher than that in the soft breads (12.6%). The key reason for lower DF content in soft breads is a dilution effect due to high inclusion of wheat flour for gluten development in most breads. Plaami and Kumpulainen (1993) reported similar contents for total DF in three rye breakfast cereal products produced in Finland. The DF content decreases during dough mixing and fermentation (Hansen et al., 2002; Lambo, Öste, & Nyman, 2005). For example, the total DF content has been reported to decrease by 11–28% as a result of added enzymes during production of wheat breads, with or without supplemented rye bran (Laurikainen, Härkönen, Autio, & Poutanen, 1998).

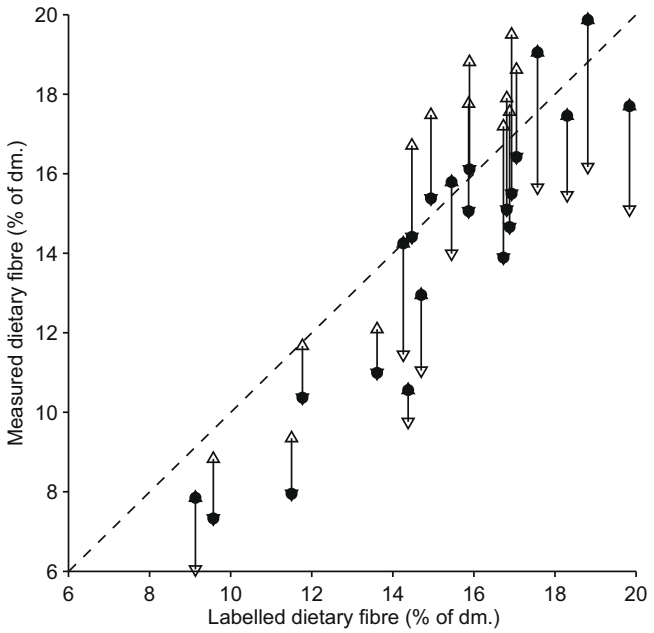

Fig. 1. Comparison of measured and labelled dietary fibre values. The labelled values were recalculated on a dry weight basis. The arrows facing downward represent the samples that included fructan in their labelled DF values, while the vertical distance between two points represents the fructan content in that sample.

The DF contents stated on labels for the breads and extruded products were compared with the measured values (Fig. 1). Labelled values were recalculated on a dry weight basis and comparison was based on whether the manufacturer included fructan in total DF or not, in order to get an unbiased comparison. The labelled and measured values were evenly distributed across the unity line and only a few samples reported a too high DF content. It is interesting to note that some companies include fructan in total DF value while others do not.

Arabinoxylan was the major component contributing to the DF value in all samples analysed (Table 2). Arabinoxylan was calculated as the sum of arabinose and xylose residues, excluding arabinose residues originating from arabinogalactan (Andersson et al., 2009). Kamal-Eldin et al. (2009) reported 23.1% average AX content in rye bran, which is higher than our value of 18.2%. Because of the presence of wheat flour along with rye flour, the average AX content in soft breads (5.4%) was lower than in crisp breads (7.8%) but a little higher than in extruded products. Arabinose/xylose ratio (A/X) showed a more branched structure in inner endosperm (A/X = 0.66) and outer endosperm (A/X = 0.65) AX than in bran (A/X = 0.50, Table 2), which is in agreement with previous studies (Kamal-Eldin et al., 2009). Enzymatic degradation of AX is controlled, not only by arabinose distribution across the xylan back-

Table 3
Weight (M_w) and number (M_n) average molecular weight and polydispersity index (M_w/M_n) of extractable arabinoxylan, as well as extractability and Calcofluor average molecular weight (M_{cf}) of extractable β-glucan.

Sample	Arabinoxylan			β-Glucan	
	M_w (10^5 g mol^{-1})	M_n (10^5 g mol^{-1})	M_w/M_n	Extractability (%)	M_{cf} (10^5 g mol^{-1})
Crisp breads					
A	11.0	3.42	3.2	32	2.02
B	9.70	4.71	2.1	23	4.21
C	9.89	2.96	3.3	28	2.39
D	10.6	4.39	2.4	28	5.97
E	10.7	4.27	2.5	23	7.66
F	9.60	2.90	3.3	37	5.43
G	9.63	2.84	3.4	27	2.87
H	9.73	2.81	3.5	34	2.59
I	8.50	2.33	3.6	25	2.19
J	10.5	3.11	3.4	28	2.89
K	9.48	3.02	3.1	23	3.22
L	9.53	2.88	3.3	40	2.70
Average	9.91	3.30	3.1	29	3.68
Soft breads					
M	20.3	6.61	3.1	29	2.41
N	11.9	4.91	2.4	31	4.38
O	14.2	3.31	4.3	31	2.53
P	22.2	3.48	6.4	37	2.11
Q	13.4	5.35	2.5	44	5.39
R	7.97	2.91	2.7	29	1.86
S	7.98	3.31	2.4	34	2.78
T	8.65	3.00	2.9	44	2.82
Average	13.3	4.11	3.3	35	3.03
Extruded products					
U	9.47	7.00	1.4	54	15.0
V	6.94	2.55	2.7	47	10.6
Milling fractions					
Inner endosperm	10.7	3.71	2.9	26	13.3
Outer endosperm	11.0	5.51	2.0	17	13.1
Milled rye bran	13.8	7.18	1.9	16	8.57

bone, but also by cell wall ultrastructure. Highly branched AX molecules are less prone to AX-hydrolysing enzymes (Vinkx & Delcour, 1996). The heterogeneity of AX molecules affects the intrinsic viscosity and hydrodynamic volume of the AX (Izydorczyk & Biliaderis, 1995). Average A/X value in crisp breads (0.53) was higher than that in soft breads (0.49), indicating less branching in soft breads. Arabinogalactan is a minor component in rye and the average content for crisp breads was similar to that for soft breads and extruded products.

The total content of β-glucan in milling fractions ranged from 1.5% (inner endosperm) to 4.4% (bran) (Table 2). Nilsson et al. (1996) reported 3.4% β-glucan content in rye bran and 1.3% in sieved rye flour. On average, the soft breads (1.2%) were lower in total content of β-glucan than were the crisp breads (1.9%). The extruded breakfast cereal had a higher β-glucan content (2.3%) than had the other food products. The presence of 30% whole grain oat flour in this breakfast cereal explains the high β-glucan content, as oats contain more β-glucan than did rye (Genç, Özdemir, & Demirbaş, 2001).

Cellulose is a component present in all plant cell walls and resistant starch (RS) is formed during hydrothermal treatment of starch-containing food raw materials. Since no specific methods have been used for these components, and both are built up of glucose residues, they are reported together in this study. Differences in cellulose content are mainly due to variations in ingredients, while RS content is dependent on variations in ingredients and in processing (Westerlund, Theander, Andersson, & Åman, 1989). Resistant starch and cellulose content ranged from 1.7% to 3.0% in crisp breads (average 2.4%) and from 0.7% to 4.1% in soft breads (average 2.5%), which was higher than in the inner (1.2%) and outer endosperm (2.1%) fractions (Table 2). Although crisp breads and soft breads had similar average values for RS and cellulose, the wider variation in soft breads indicates a diversity of processing and raw materials. The extruded products were relatively low in RS and cellulose contents, indicating less RS formation due to lower water activity during processing. With recognition of its prebiotic properties, resistant starch in food products has gained increasing interest during recent years.

Fructan content in milling fractions ranged from 3.4% in inner endosperm to 5.0% in bran (Table 2). The fructan content varied from 1.9% to 4.0%, with an average of 2.8% in crisp breads, with sample E being the highest in fructan content as it contained only

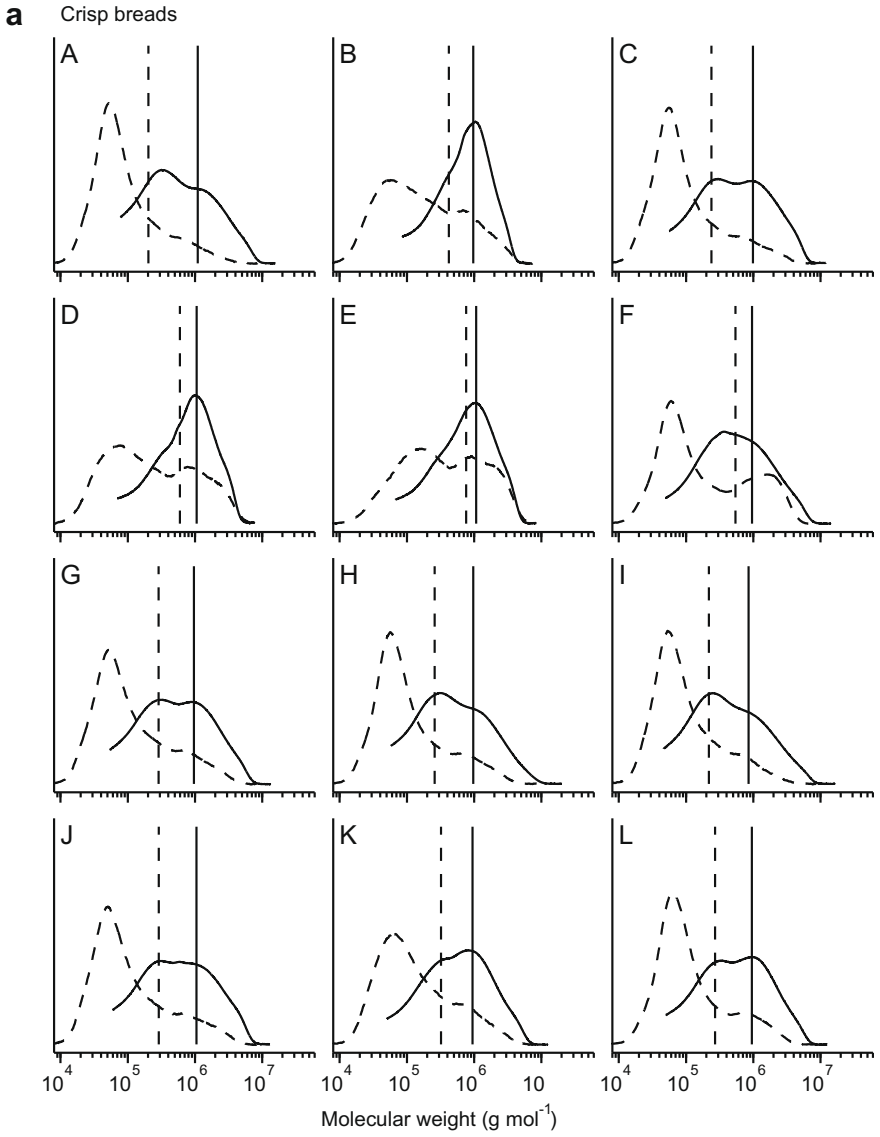

Fig. 2. Molecular weight distributions of extractable β-glucan (. . .) and arabinoxylan (—) in (a) crisp breads (A–L), (b) soft breads (M–T) and extruded products (U and V), and (c) milling fractions. Vertical lines denote the weight-average molecular weights and Calcofluor average molecular weights, respectively.

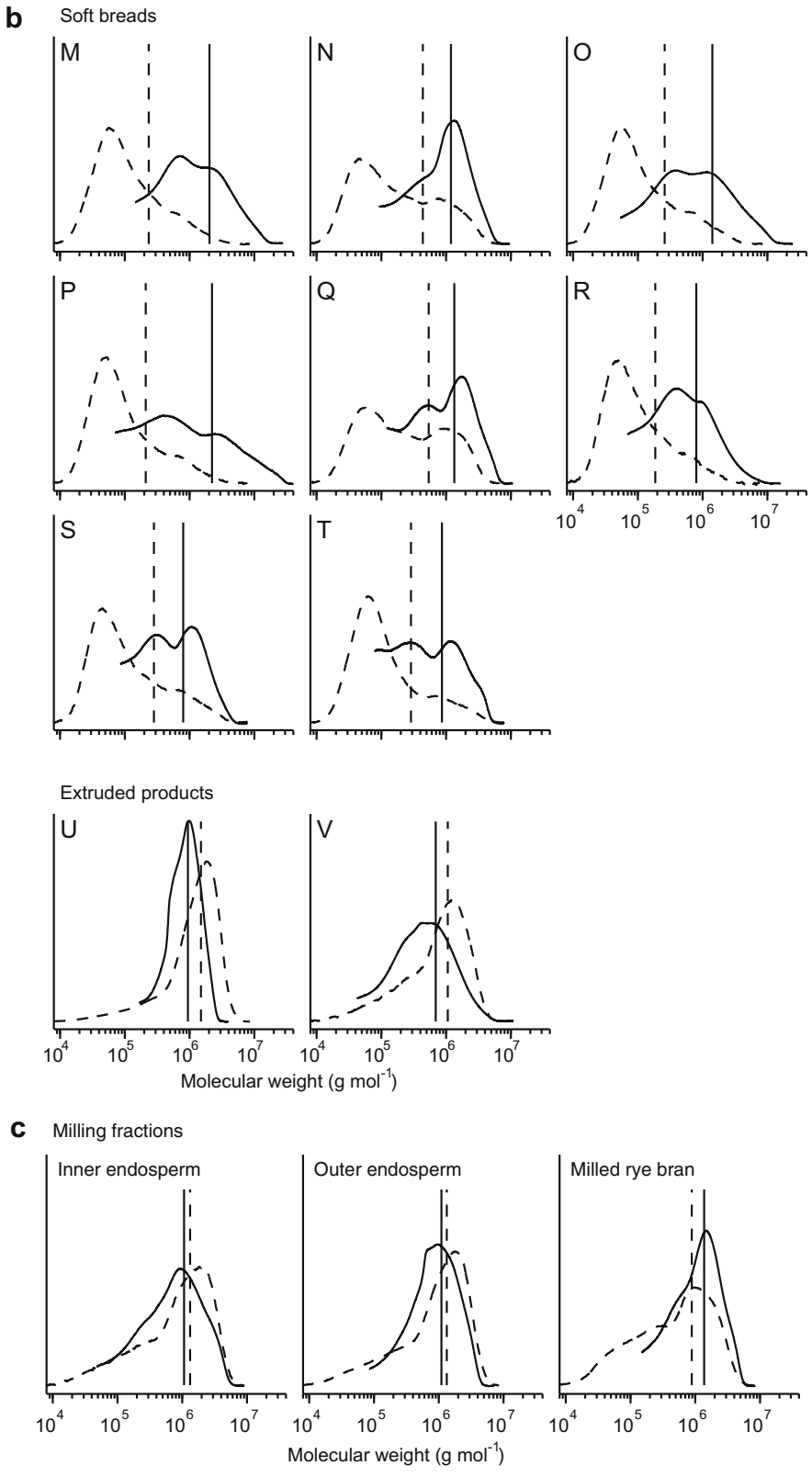

Fig. 2 (*continued*)

whole grain rye flour. In soft breads, fructan content ranged from 0.8% to 2.3%, with an average content of 1.6%. The addition of whole kernels of rye that are less affected by yeast or enzymes, can explain the high fructan content in sample N. The low fructan content in soft breads is most likely due to the presence of sourdough and yeast in most of the breads, since Andersson et al. (2009) recently showed that these ingredients can result in significant degradation of rye fructan. Similar results for fructan content have been reported by Karppinen, Myllymäki, Forssell, and Poutanen (2003) for Finnish rye crisp breads and soft breads. They attrib-

uted the differences in fructan content in different breads to the function of fermentation, the amount of flour used in the baking and the flour itself. Several previous findings also support the decrease in fructan content during various steps in the bread-making process. For example, Hansen et al. (2002) reported a 45% decrease in fructan content during imitated sourdough mixing, proofing and baking. Klason lignin is one of the main components of bran and, in this study, 8.0% of the DF value was constituted of Klason lignin. Average Klason lignin content in crisp breads (1.3%) was considerably higher than that in soft breads (0.6%).

3.3. Molecular weight distributions of arabinoxylan, β-glucan and fructan

The bran AX was higher in both M_w and M_n than was the endosperm AX (Table 3). The average AX M_w of crisp breads, 9.91×10^5 g mol^{-1} (range 8.50×10^5 to 11.0×10^5) was lower than that for soft breads, 13.3×10^5 g mol^{-1} (range 7.97×10^5 to 22.2×10^5). The variation in M_w was wider in soft breads than in crisp breads or milling fractions. A bimodal pattern of M_w was observed in crisp breads, where it was possible to group the distributions into two categories based on the presence or absence (B, D and E; Table 1) of yeast in the recipe (Fig. 2a). In contrast to crisp breads, the soft breads exhibited a multimodal distribution pattern (Fig. 2b). The molecular weight distribution of extruded products (U, V) was similar to that of the milling fractions and showed only minor degradation compared with the other products (Fig. 2b and c). Andersson et al. (2009) reported M_w of 10.0×10^5 g mol^{-1} in two rye crisp breads and 7.0×10^5 g mol^{-1} in sourdough bread with a narrow molecular weight distribution range and concluded that the bread-making process reduced the proportion of high molecular weight arabinoxylan. In the same study, commercial breads showed a polymodal distribution of M_w, which was in agreement with our commercial bread samples. Girhammar and

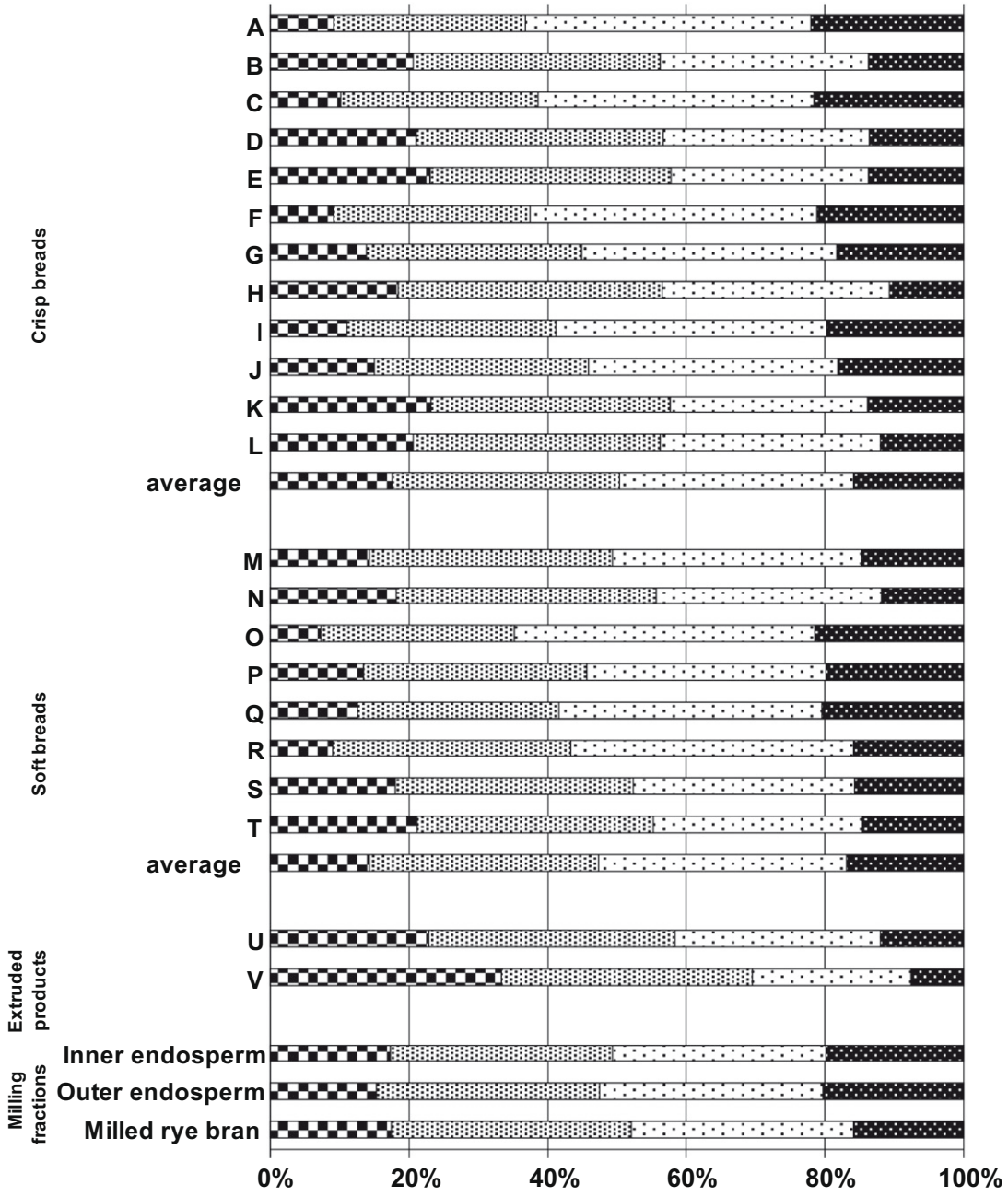

Fig. 3. Relative distributions of degree of polymerisation in crisp breads, soft breads, extruded products and milling fractions (▩ DP 3–4 ▩ DP 5–9 ▩ DP 10–15 ▩ DP > 15).

Nair (1992) reported a molecular weight range for rye arabinoxylan of 2.75×10^5 to 7.70×10^5 g mol^{-1}, using high performance gel permeation chromatography, while, according to Vinkx and Delcour (1996), the M_w of rye bran is 11.7×10^5 g mol^{-1}. Endogenous xylanases in the flour can act on insoluble AX to result in an increase in average molecular mass fractions during proofing and mixing (Hartmann, Piber, & Koehler, 2005).

The M_n of AX was highest in bran (7.18×10^5 g mol^{-1}) compared with all other products, followed by the extruded breakfast cereal (7.00×10^5 g mol^{-1}; Table 3). The M_n of AX ranged from 2.33×10^5 to 4.71×10^5 g mol^{-1} in crisp breads and from 2.91×10^5 to 6.61×10^5 g mol^{-1} in soft breads. The polydispersity value of inner (2.9) and outer endosperm (2.0) was lower than the average value for crisp breads (3.1) and soft breads (3.3; Table 3). The high polydispersity index in soft breads indicates more AX degradation than in the other products. Polydispersities of the extruded breakfast cereal (1.4) and extruded crisp bread (2.7) were also low compared with most of the bread samples. This might be an indication that extrusion does not have a large effect on the AX molecules.

The average β-glucan extractability in soft breads was 35%, which was higher than that for crisp breads (29%) (Table 3). The β-glucan was least extractable in the milling fractions, while about half the amount present was extractable in the extruded products. It is notable that extrusion appears not to degrade the β-glucan, although it renders it more extractable. The high extractability of β-glucan in extruded crisp bread (47%) can explain the higher average molecular weight, as the method calculates the molecular weight of the extractable β-glucan only. Extruded breakfast cereal had the highest extractability (54%), although it contained a significant amount of oats. The results regarding the extractability of the β-glucan during baking are in agreement with Andersson, Rüegg, and Åman (2008), who showed that the content of water-extractable β-glucan increases during bread making but decreases with prolonged fermentation before heat treatment due to the action of endogenous enzymes present in the flour.

Average M_{cf} of β-glucan in crisp breads (3.68×10^5 g mol^{-1}) was higher than that in soft breads (3.03×10^5 g mol^{-1}; Table 3). The low average M_{cf} in soft breads might be due to the presence of sourdough and yeast as ingredients in most of the soft breads or the action of enzymes in the flour before heating in the oven (Andersson et al., 2004). The M_{cf} values of extruded breakfast cereal (15.0×10^5 g mol^{-1}) and extruded crisp bread (10.6×10^5 g mol^{-1}) were far higher than those in crisp breads and soft breads, as discussed above. The presence of oats in breakfast cereal and barley flour in crisp bread, along with short treatment time and low water activity, can explain the high values in the extruded products. It is well established that both oats and barley have higher molecular weights than rye (Ajithkumar et al., 2005; Andersson, Lampi, et al., 2008; Cyran, Courtin, & Delcour, 2003).

The molecular weight distributions of fructan in the milling fractions did not differ much (Fig. 3). Almost 50% of the molecules had DP > 9. As is apparent from Fig. 3, in both crisp and soft breads the majority of the molecules had DP in the range 5–15. Extruded breakfast cereal and extruded crisp bread showed different behaviours and contained 23% and 33% of fructan molecules with DP 3–4, with only 12% and 8%, respectively, of the molecules having DP > 15, due to variations in ingredients and processing. Compared with extruded products, the breads had a smaller proportion of short DP. Most of the crisp breads with yeast were lower in DP 3–9 and higher in DP 10–15 or DP > 15. It can be inferred from this that the yeast uses the lower DP fructan preferentially. A similar overall picture emerged in the results for soft breads, where the samples with sourdough and yeast were lower in shorter DP. Although it is difficult to precisely determine the reason and define a pattern, as the exact processing methods and composition of the raw materials are not known, there is some previous supporting evidence of the preference of yeast invertase for DP 3 and 4 (Escrivá & Martínez-Anaya, 2000). Different processing parameters, such as dough preparation, fermentation and baking, have been found to influence the fructan levels in bread (Böhm, Kaiser, Trebstein, & Henle, 2005). The long-chain molecules are more stable during the baking process, where low pH and high temperature result in significant degradation of fructo-oligosaccharides (Praznik et al., 2002).

4. Conclusions

This study found that various rye-containing foods from a local supermarket had a high content of DF (8–20%) and that AX and fructan were the main DF components in these products. It is notable that some of the DF values declared on the labelling included fructan, while others did not but, for most of the foods analysed, DF values exceeded the declared values. During bread manufacturing, the molecular weight of β-glucan was highly degraded while that of AX was more resistant. The high average M_w and low average M_{cf} in soft breads compared with crisp breads were an indication that AX and β-glucan do not follow the same pattern of degradation during processing. Interestingly, from a nutritional point of view the extruded products had the highest β-glucan extractability and the extracted β-glucan had the most retained molecular weight. Crisp breads produced without yeast fermentation had the highest content of DF and fructan and the highest proportion of low-molecular weight fructan. These results indicate that the low-molecular weight fraction of fructan is that most available for degradation by yeast or endogenous enzymes during bread making. There is a need for further studies to examine the effects of different processing parameters on DF components, particularly fructan and arabinoxylan.

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