

Content and Molecular-Weight Distribution of Dietary Fiber Components in Whole-Grain Rye Flour and Bread

ROGER ANDERSSON,* GUNNEL FRANSSON, MARKUS TIETJEN, AND PER ÅMAN

Department of Food Science, Swedish University of Agricultural Sciences (SLU),
Post Office Box 7051, SE-750 07 Uppsala, Sweden

Content of dietary fiber and dietary fiber components in whole-grain rye ($n = 18$) were analyzed. The average total content, when fructan was included, was for dietary fiber 19.9% (range of 18.7–22.2%) and for extractable dietary fiber 7.4% (range of 6.9–7.9%). Arabinoxylan was the main dietary fiber component, with an average total content of 8.6%, followed by fructan (4.1%). During baking of whole-grain rye bread, only small changes in total content of arabinoxylan, arabinogalactan, and β -glucan occurred, while the content of resistant starch increased and the content of fructan decreased in a baking-method-dependent manner. The molecular-weight distribution of extractable arabinoxylan in the flour was analyzed with a new method and ranged from 4×10^4 to 9×10^6 g/mol, with a weight average molecular weight of about 2×10^6 g/mol. During crisp bread making, only a limited degradation of arabinoxylan molecular weight was detected, while a notable degradation was observed in sour-dough bread. The molecular weight of extractable β -glucan in the whole-grain rye flour ranged from 10^4 to 5×10^6 g/mol, with a weight average molecular weight of 0.97×10^6 g/mol. During bread making, the molecular weight of the β -glucan was substantially degraded.

KEYWORDS: Rye kernels; rye bread; dietary fiber; arabinoxylan; β -glucan; molecular weight

INTRODUCTION

Rye is a traditional cereal, highly used in whole-grain foods in northern and eastern Europe. It is considered a healthy ingredient and adds variety to the bread market. Rye containing whole-grain foods are rich in dietary fiber, including arabinoxylan, fructan, and mixed-linkage (1 \rightarrow 3, 1 \rightarrow 4)- β -D-glucan (in the following referred to as β -glucan), as well as in a whole range of bioactive components, such as cinnamic acids, alkylresorcinols, lignans, sterols, vitamins, and minerals, in the so-called dietary fiber complex (1–5). Traditional methods for the analysis of total dietary fiber does not include fructan and oligosaccharides in the raffinose series. There is an increasing interest for separate analyses of these components to include them into the dietary fiber value, which can be of great importance for rye products that may be rich in fructan.

Whole grain is reported to have several positive effects on human health, including protection against the development of overweight, heart disease, and type 2 diabetes, as well as certain cancers (6). It has been shown that certain partly soluble dietary fiber, such as β -glucan and arabinoxylan, have serum cholesterol-lowering properties, and cholesterol is an independent risk factor for the development of cardiovascular diseases (7, 8). This effect

can, at least partly, be related to viscosity of soluble dietary fiber in the gut, which is dependent upon content, structure, and molecular-weight distribution of the soluble dietary fiber components. We have recently studied the effect of baking on molecular-weight distribution of β -glucan in yeast-leavened bread (9–11). From these studies, it is evident that β -glucan can be highly degraded during the mixing and fermentation step of the bread-making process. It has also been suggested that this degradation may be one of the reasons why oat-bran-based yeast-fermented bread seems to have lost at least some of its cholesterol-lowering properties (12).

Dietary fiber in whole-grain rye has been studied extensively with traditional methods, excluding fructan, and total content varies between 150 and 210 g kg⁻¹, with significant effects of both genotype and environment (2, 13–15). Total content of arabinoxylan is reported to vary between 8.0 and 12.1%; water-extractable arabinoxylan is reported to vary between 2.6 and 4.1%; β -glucan is reported to vary between 1.3 and 2.2%; and fructan is reported to vary between 4.5 and 6.4% (2). The yield of extractable arabinoxylan has been shown to be reduced during bread making, possibly because of oxidative or other types of cross-linking, making part of the polymers insoluble, and the molecular-weight distribution of the extractable arabinoxylan was found to be changed: in dough, the high-molecular-mass fraction increased, while in bread, it was the medium-molecular-mass fraction that increased (16).

* To whom correspondence should be addressed: Department of Food Science, Swedish University of Agricultural Science (SLU), P.O. Box 7051, SE-750 07 Uppsala, Sweden. Telephone: +46(0)-18-671000. Fax: +46(0)-18-672995. E-mail: roger.andersson@lmv.slu.se.

Table 1. Content and Extractability (within Parenthesis) of Dietary Fiber Polysaccharide Residues, Klason Lignin, and Fructan in Whole-Grain Rye (% of Dry Samples)^a

sample	arabinose	xylose	mannose	galactose	glucose	uronic acids	Klason lignin ^b	fructan ^c	TDF
Amilo	2.8 (34)	4.7 (31)	0.6 (38)	0.3 (31)	5.1 (9)	0.2 (29)	0.9	4.0	18.7 (39)
SW 99507	3.0 (27)	5.2 (25)	0.7 (31)	0.4 (24)	4.4 (11)	0.3 (28)	1.2	3.9	18.9 (36)
SW 99176	3.1 (29)	5.4 (26)	0.6 (29)	0.3 (27)	4.1 (11)	0.3 (28)	1.3	3.9	19.1 (37)
Esprit	3.2 (27)	5.3 (25)	0.7 (32)	0.4 (22)	3.9 (10)	0.2 (29)	1.1	4.2	19.1 (38)
Rorik	3.2 (30)	5.4 (28)	0.6 (31)	0.5 (25)	4.1 (11)	0.2 (27)	1.0	4.4	19.3 (40)
SW 001212	3.1 (29)	5.4 (27)	0.6 (29)	0.4 (23)	4.2 (12)	0.2 (28)	1.0	4.3	19.3 (39)
SWHY 000810	3.0 (28)	5.1 (26)	0.7 (27)	0.4 (19)	4.1 (10)	0.3 (27)	1.2	4.6	19.4 (39)
Picasso	3.4 (28)	5.5 (28)	0.7 (36)	0.5 (20)	4.6 (12)	0.2 (33)	0.9	3.7	19.4 (37)
Kubik	3.3 (28)	5.7 (26)	0.6 (30)	0.4 (28)	4.1 (11)	0.2 (32)	1.0	4.3	19.7 (38)
SW 001216	3.2 (29)	5.6 (27)	0.6 (28)	0.4 (25)	4.2 (11)	0.2 (29)	1.1	4.4	19.8 (39)
Hagrid	3.4 (30)	5.7 (28)	0.6 (33)	0.4 (20)	4.1 (12)	0.2 (29)	1.2	4.3	19.9 (39)
Gandalf	3.2 (31)	5.6 (29)	0.7 (28)	0.4 (24)	4.1 (11)	0.3 (26)	1.2	4.5	20.0 (40)
Kaskelott	3.5 (29)	6.0 (27)	0.6 (26)	0.4 (22)	4.3 (10)	0.3 (25)	1.0	4.3	20.3 (38)
LI 20025	3.6 (26)	6.0 (28)	0.6 (22)	0.5 (27)	4.9 (15)	0.2 (30)	1.1	3.6	20.4 (36)
LI 20035	3.9 (24)	6.2 (26)	0.7 (22)	0.5 (23)	4.8 (7)	0.2 (30)	1.0	3.6	20.8 (33)
LI 20001	3.7 (29)	5.9 (29)	0.7 (33)	0.5 (23)	4.6 (10)	0.3 (29)	1.2	4.2	20.9 (37)
LI 20002	3.6 (28)	6.0 (28)	0.7 (28)	0.5 (23)	4.6 (11)	0.2 (31)	1.3	4.2	21.1 (37)
LI 20019	3.9 (25)	6.4 (28)	0.7 (23)	0.5 (20)	5.0 (8)	0.3 (28)	1.4	4.0	22.2 (34)
average	3.3 (28)	5.6 (27)	0.6 (29)	0.4 (24)	4.4 (11)	0.2 (29)	1.1	4.1	19.9 (37)
CV	9.0	7.4	7.0	14.3	8.1	8.3	13.2	7.4	4.6

^a Fructan is included in the total dietary fiber (TDF) value, and results are given as an average of at least duplicate analyses. Deviations between duplicates were below 5% of the average for components with levels above 2%. ^b Klason lignin is completely unextractable by definition. ^c Fructan is completely extractable.

In this paper, we have studied the content of total and extractable dietary fiber components in rye and investigated how the bread-making process will affect the content of these components, as well as the molecular-weight distribution of extractable arabinoxylan and β -glucan.

MATERIALS AND METHODS

Rye Kernel Samples. Samples of rye kernels were obtained from Svalöf Weibull AB (Svalöv, Sweden). From the 2002 harvest, 18 samples (see **Table 1**) were collected from an experimental field near Landskrona. Two cultivars (Esprit and Kaskelott) were grown during 2002 at three different locations (Bjertorp, Kölbäck, and Landskrona). During 2003, four cultivars (Amilo, Esprit, and Kaskelott) were grown at four different locations in Sweden (also Haga).

Rye Breads. Rye of the cultivar Kaskelott (harvested in 2003) was obtained from Svalöv Weibull AB. The kernels were milled at Lilla Harrie Valskvarn AB (Kävlinge, Sweden) into whole-grain flour. This flour was used to bake a typical yeast-fermented sour-dough bread by Lantmännen AB (Järna, Sweden) and typical yeast-fermented and nonfermented air-leavened rye crisp breads by Wasabröd AB (Filipstad, Sweden). Five different commercial whole-grain rye breads were obtained from local stores. These breads include a yeast-fermented rye crisp bread baked with whole-grain and sifted rye flour (A), a yeast-fermented rye crisp bread baked with whole-grain rye flour (B), a thin crisp bread baked with whole-grain rye flour (C), a sour-dough soft bread baked with sour dough of rye, whole-grain rye flour, and whole rye kernels (D), and a yeast-fermented soft bread baked with whole-grain rye flour, wheat flour, and whole-grain wheat flour (E). A yeast-fermented soft bread baked with sifted wheat and rye flours was also included (F).

Chemical Analysis. Before analysis, grain, crisp bread, and freeze-dried soft bread samples were ground in a cyclone sample mill (Retsch, Haan, Germany) to pass a 0.5 mm screen. All analyses were carried out in at least duplicate, and results are reported on a dry matter basis, determined by drying samples for 16 h at 105 °C.

Contents of extractable, unextractable, and total dietary fiber components (not including fructan) were determined by the Uppsala method (17) as modified by Andersson et al. (18) for separate analysis of extractable and unextractable components. In this method, non-resistant starch is removed by α -amylase and amyloglucosidase, and remaining polysaccharides are precipitated by 80% ethanol. Polysaccharides are hydrolyzed by acid and quantified as alditolacetates by gas chromatography. In the whole-grain flour, arabinoxylan was calculated as the sum of arabinose and xylose residues, not taking into account the fact that some of the arabinose residues are present in

arabinogalactan. For the samples in the baking experiments, arabinoxylan and arabinogalactan were computed from the xylose, galactose, and arabinose values, assuming an arabinose/galactose ratio of 0.69 in the extractable arabinogalactan (19). Total β -glucan content was analyzed with the AOAC method 32-23 using the Megazyme kit K-BGLU (Megazyme, Bray, Ireland). Fructo-oligosaccharides and fructan (in the following referred to as fructan) were also analyzed with a Megazyme kit K-FRUC with an established enzymatic method, including treatment with α -galactosidase to avoid interference of raffinose series oligosaccharides (20).

Analysis of Molecular Weight. Calcofluor average molecular weight (M_w) and molecular-weight distribution of extractable β -glucan were determined according to Rimsten et al. (21), except for the Calcofluor concentration, which was changed to 0.0025%. β -Glucan in the milled samples was extracted in hot water and simultaneously starch-digested with α -amylase. β -Glucan in extracts was fractionated by high-performance size-exclusion chromatography and detected with Calcofluor. This detection method is selective for β -glucan but will exclude molecules with molecular weights below 10^4 . Molecular weights are therefore given as Calcofluor molecular weight, which is the same as weight molecular weight for samples that only contain high-molecular-weight β -glucan (above 10^4).

Molecular-weight distribution of extractable arabinoxylan was determined by size-exclusion chromatography and light scattering. Endogenous enzymes were inactivated by incubating 1 g of milled sample in 5 mL of 50% aqueous ethanol for 15 min in a boiling waterbath. After cooling to room temperature, another 5 mL of 50% ethanol was added and the sample was centrifuged for 10 min at 1000g. The supernatant was discarded, and the pellet was washed with 10 mL of 50% ethanol, followed by centrifugation and decantation. The pellet was suspended in 20 mL of sodium acetate buffer (0.1 M, pH 5.0), and 50 μ L of thermostable α -amylase (3000 units/mL, Megazyme, Bray, Ireland) was added. The sample was mixed and incubated for 90 min in a boiling waterbath with occasional mixing. After cooling to room temperature, 1 mL of amyloglucosidase (140 units/mL, Megazyme, Bray, Ireland) was added and the sample was incubated at 60 °C overnight. The sample was cooled and centrifuged for 15 min at 1500g. An aliquot of 15 mL of supernatant, 450 μ L of 0.5 M sodium phosphate, 1 mg of pancreatin (P1750, Sigma, St Louis, MO), and 100 μ L of lichenase (1000 units/mL, Megazyme, Bray, Ireland) was mixed and incubated for 2 h at 40 °C under occasional stirring. The samples were thereafter placed on magnetic stirring; 135 mL of 99% ethanol was added; and the sample was kept on ice for 2 h. The precipitate was collected by centrifugation (5 min, 1000g) and dissolved in 2 mL of 0.1 M sodium nitrate by heating in a boiling water bath for 10 min. The sample was centrifuged for 10 min at 18000g and filtered through a 0.45

μm filter, and 75 μL was injected to a high-performance size-exclusion (HPSEC) system with three serially connected columns (OHPak SB-806 M HQ, OHPak SB-804 HQ, and OHPak SB-803 HQ, Shodex, Showa Denko KK, Miniato, Japan) kept at 35 °C. The eluent was 0.1 M NaNO_3 , containing 0.02% NaN_3 at 0.5 mL/min. Detectors were refractive index (RI) and multiple-angle laser light scattering (MALLS; Dawn DSP equipped with a He-Ne laser at 632.8 nm, Wyatt Technology Corp., Santa Barbara, CA). Data for molecular-weight determinations were analyzed using ASTRA software (version 4.70.07, Wyatt Technology Corp., Santa Barbara, CA) based on a dn/dc of 0.147. The angular fit was based on the Debye procedure. Molecular-weight distributions were obtained following a first-order polynomial curve fitting of $\log M$ versus the elution volume. Results are given as the average of five analyses.

RESULTS AND DISCUSSION

Dietary Fiber Components in Rye Grain. To look for variation in the content of dietary fiber components, rye grain from different cultivars and breeding lines ($n = 18$) were harvested from one experimental field in southern Sweden during 2002. The samples were analyzed for their content of extractable and unextractable dietary fiber constituents with the Uppsala method, which does not include any fructan molecules (Table 1). The content of arabinoxylan was calculated as the sum of arabinose and xylose residues, not taking into account the part of the arabinose residues originating from arabinogalactan (22). Arabinoxylan was the dominating dietary fiber component in the rye samples, with an average content of 8.9% (range of 7.5–10.3%). The average ratio of arabinose to xylose residues was 0.59%, and the average arabinoxylan solubility was 27% (range of 25–31%). This means that the average content of extractable arabinoxylan in the samples was 2.4% (range of 2.1–2.7%). The samples also contained glucose residues (average of 4.4%), originating mainly from cellulose and β -glucan, Klason lignin (average of 1.1%), mannose residues (average of 0.6%), galactose residues (average of 0.4%), and uronic acid residues (average of 0.2%). Average dietary fiber content as analyzed with the Uppsala method was 15.8% (range of 14.7–17.2%), and the average dietary fiber solubility was 21%, with only a small variation (19–22%). The contents of dietary fiber and dietary fiber components in these Swedish samples are similar to what previously has been reported (13, 15).

Fructan, which is highly soluble in aqueous solutions, was analyzed in the samples with a separate method, and the average content was 4.1% (range of 3.6–4.6%) (Table 1). In Sweden and certain other countries, fructan content can be added to the dietary fiber value, resulting in an average total dietary fiber content of 19.9% (range of 18.7–22.2%), with an average extractability of 37% (range of 33–40%).

The content of dietary fiber components was also analyzed with the Uppsala method in grains from two cultivars (Esprit and Kasklott) harvested at two different sites in Sweden during 2002 and from three different cultivars (Esprit, Amilo, and Kasklott) harvested at four different sites in Sweden during 2003. The total content of dietary fiber and total and soluble arabinoxylan contents in these samples (individual results not shown) were generally also highest in Kasklott, with values ranging from 15.1–16.4% for dietary fiber (not including fructan), 8.6–9.7% for total arabinoxylan, and 2.1–2.6% for soluble arabinoxylan. A batch of Kasklott was therefore selected for further studies.

Dietary Fiber Components in Rye Bread. Yeast-leavened crisp bread, air-leavened crisp bread, and yeast-leavened sour-dough bread were baked with the selected batch of Kasklott whole-grain rye flour. The flour contained 3.3% extractable and 13.0% unextractable dietary fiber, giving a total of 16.3% dietary fiber

Table 2. Content of Main Extractable and Unextractable Dietary Fiber Polysaccharides of Whole-Grain Rye Flour (Kasklott) and Breads Made from This Flour (Average of at Least Duplicate Analysis^a)

	arabinoxylan ^{b,c}	arabinogalactan ^b	β -glucan ^d	cellulose and resistant starch ^e	fructan	TDF ^f
Rye Flour						
extractable	2.4 (0.58)	0.2			5.0	8.3
unextractable	6.6 (0.52)					13.0
total	9.0 (0.53)	0.2	1.5	2.7	5.0	20.6
Sour-Dough Rye Bread						
extractable	2.8 (0.53)	0.2			1.9	5.8
unextractable	5.9 (0.49)					12.9
total	8.7 (0.51)	0.2	1.4	3.5	1.9	18.1
Yeast-Leavened Rye Crisp Bread						
extractable	2.8 (0.55)	0.2			3.4	7.2
unextractable	5.7 (0.52)					11.5
total	8.5 (0.53)	0.2	1.4	2.6	3.4	18.1
Air-Leavened Rye Crisp Bread						
extractable	2.6 (0.53)	0.2			4.7	8.5
unextractable	5.7 (0.49)					11.5
total	8.3 (0.50)	0.2	1.5	2.6	4.7	19.2

^a Deviations between replicates were below 5% of the average for components with levels above 1%. ^b Computed from xylose, galactose, and arabinose values, assuming an arabinose/galactose ratio of 0.69 in extractable arabinogalactan. ^c Arabinose/xylose ratio within parenthesis. ^d Total content analyzed separately; mostly unextractable in rye. ^e Dietary fiber total glucose value minus the β -glucan value; mainly unextractable. ^f Also including mannose and uronic acid residues and Klason lignin.

when analyzed with the Uppsala method. The main dietary fiber constituent was arabinoxylan (9.0%), of which 26.6% was extractable (Table 2). It also contained 2.7% cellulose and enzyme-resistant starch, 1.5% β -glucan, 1.1% Klason lignin, and 0.9% arabinogalactan. The fructan content of the flour was 5.0%; the total dietary fiber content was 21.3%; and the extractable dietary fiber content was 8.3% when fructan was included. The three whole-grain breads contained 3.8–3.9% extractable dietary fiber and 11.5–12.9% unextractable dietary fiber when analyzed with the Uppsala method. Arabinoxylan content (8.3–8.7%) was somewhat lower than in the flour, probably because of a dilution effect because some salt and yeast was added to the dough and a small degradation of arabinoxylan during the bread making to low-molecular-weight fragments not included in the analysis. The arabinose/xylose ratio was lower in both the extractable and unextractable fractions of arabinoxylan compared to those in the flour. Very similar contents of extractable and unextractable arabinogalactan and total β -glucan were found in the breads compared to the flour. Air-leavened nonfermented crisp bread contained a similar amount of fructan as the flour. The yeast-fermented and especially the sour-dough bread (1.9%) had lower contents of fructan, showing that fructan can be degraded during the bread-making process and, thus, when included, resulting in lower contents of total and extractable dietary fiber in the bread. Previous studies have shown that a significant degradation of fructan can occur during bread making (23), and this will lower the dietary fiber content in the breads compared to that in the raw materials, as well as lower the content of prebiotic carbohydrates (24). The content of cellulose and resistant starch was higher in the sour-dough bread compared to the rye flour and the crisp breads. This can be explained by a formation of resistant starch in the crumb during bread making (25).

Molecular Weight of Extractable Arabinoxylan and β -Glucan. Molecular-weight distribution of extractable arabinoxylan in Kasklott whole-grain rye flour and different types of bread made from this flour was determined with a newly developed method. Endogenous enzymes in the samples were completely inactivated by treatment in aqueous ethanol; arabinoxylan was extracted with sodium acetate; and starch, β -glucan,

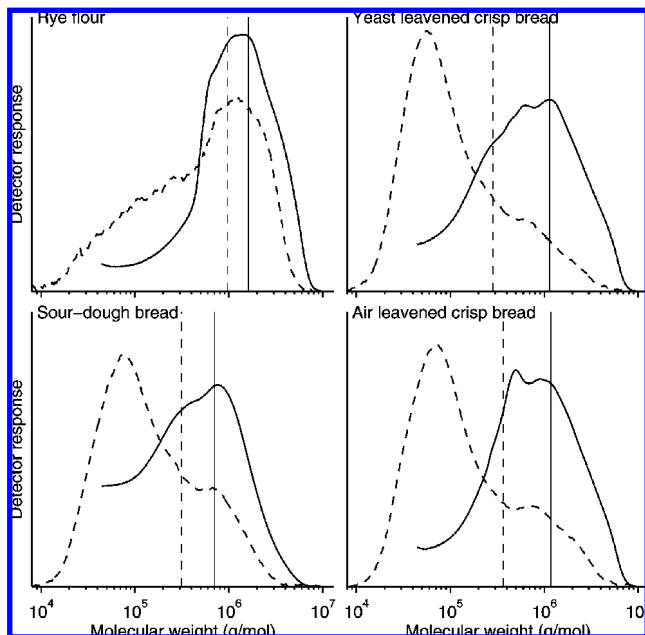


Figure 1. Molecular-weight distributions of extractable β -glucan (---) and arabinoxylan (—) in whole-grain rye flour and bread. Vertical lines denote weight average molecular weight, and their coefficients of variation between replicates were below 10%.

fructan, and protein were removed from the extracts by enzymatic treatments and ethanol precipitation. The highly purified extracts of arabinoxylan were analyzed by HPSEC–MALLS–RI. Molecular weights smaller than 4×10^4 g/mol cannot be detected with high precision by this technique and were therefore excluded from the results. This means that arabinogalactan peptides, which have a molecular weight of around 3×10^4 g/mol (22), are at least mostly excluded from these molecular-weight determinations. The arabinoxylan molecular-weight distribution in the flour ranged from 4×10^4 to about 9×10^6 g/mol with a polymodal distribution and a weight average molecular weight of about 2×10^6 g/mol (Figure 1). Extractable arabinoxylan in the two crisp breads had similar molecular-weight ranges but somewhat lower weight average molecular weights (about 1×10^6 g/mol). Extractable arabinoxylan in the sour-dough bread had, however, a narrower molecular range (from 4×10^4 to about 7×10^6 g/mol) and a lower weight average molecular weight (about 7×10^5 g/mol). These results show that bread making reduces the proportion of high-molecular-weight extractable arabinoxylan and increases the proportion of more low-molecular-weight arabinoxylan and that these changes depend upon the baking process used. Five commercial whole-grain breads and bread made with mainly sifted wheat and rye flours were also studied to compare the Kaskelott whole-grain breads with breads on the commercial market (Figure 2). Extractable arabinoxylan from all six breads showed a similar multimodal arabinoxylan molecular-weight distribution, but the weight average molecular weights were somewhat lower and varied from 6×10^5 to 9×10^5 g/mol. It is interesting to note that also in this case the sour-dough bread (D) had the lowest arabinoxylan average molecular weight and that the soft bread baked with sifted wheat and rye flours (F) had a somewhat higher average molecular weight than this commercial sour-dough bread. Because there was no significant differences in arabinoxylan extractability between these breads, this difference is probably not due to cross-linking but different activities of endogenous arabinoxylan-degrading enzymes.

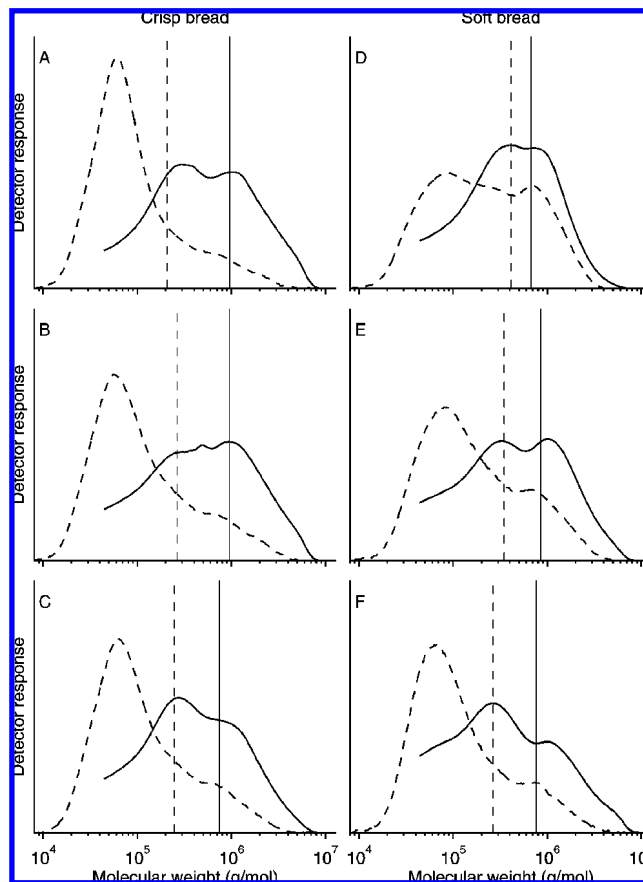


Figure 2. Molecular-weight distributions of extractable β -glucan (---) and arabinoxylan (—) in selected commercial rye products. Crisp (A–C) and soft (D–F) breads are described in detail in the Materials and Methods. Vertical lines denote weight average molecular weight, and their coefficients of variation between replicates were below 10%.

Molecular weight of analyzed extractable β -glucan in Kaskelott whole-grain rye flour ranged from 10^4 to 5×10^6 g/mol with essentially a bimodal distribution (Figure 1). The Calcofluor weight average molecular weight was 0.97×10^6 g/mol, which is similar to the average molecular weights previously reported for whole-grain wheat and rye but much lower than for oats (about 2.2×10^6 g/mol) and barley (1.6×10^6 g/mol) (11, 21). In the three whole-grain rye breads baked, similar molecular-weight ranges as in the flour were found. The distributions were essentially bimodal, but in these cases, the low-molecular-weight fraction was dominating. The proportion of the high-molecular-weight fraction diminished in the order sour-dough bread, air-leavened crisp bread, and yeast-fermented crisp bread. The Calcofluor weight average molecular weights of β -glucan in the three breads were 31×10^4 , 37×10^4 , and 29×10^4 g/mol, respectively. The molecular-weight distribution of extractable β -glucan was also determined in the five commercial whole-grain breads (A–E) and in one bread made with mainly sifted wheat and rye flours (F). Also in this case, the extracted β -glucan had a wide range of β -glucan molecular weights with an essentially bimodal distribution. The whole grain soft breads (D and E) had the highest proportion of high-molecular-weight β -glucan and the highest Calcofluor weight average molecular weights, 41×10^4 and 35×10^4 g/mol, respectively. The three crisp breads and the bread with mainly sifted flour had a lower proportion of the high-molecular-weight β -glucan and also the lowest Calcofluor weight average molecular weights, 21 – 26×10^4 g/mol. These results for extractable β -glucan molecular weights are in agreement with a

previous study, which has shown that the molecular weight decreased during yeast fermentation of rye crisp bread but was almost unchanged during oven baking (11). In that study, the molecular-weight decrease was smallest when the dough was made with flour with a high falling number (i.e., lowest enzyme activity), indicating that the endogenous β -glucan-degrading enzymes in the flour mixture were responsible for the decrease. The reduced molecular weight of the extractable β -glucan in the breads may be of nutritional importance because it is well-known that the concentration, conformation, and molecular weight of polymers are related to viscosity and that gut viscosity is related to many nutritional effects, including both glucose regulation and cholesterol-lowering properties.

CONCLUSIONS

Swedish rye contained 15–18% dietary fiber and 3.6–4.6% fructan. If fructan is included in the total dietary fiber value, it will be raised to 18.7–22.2%, an increase by an average of 26%. Extractable dietary fiber will increase by 124%. Of the rye cultivars studied, Kaskelott was generally found to have the highest content of total and extractable dietary fiber and arabinoxylan and was therefore used to produce sour-dough bread and yeast and air-leavened crisp breads. The breads contained 2.6–2.8% extractable arabinoxylan, 1.4–1.5% β -glucan, and 1.9–4.7% fructan. Sour-dough and yeast fermentation resulted in a significant degradation of the rye fructan. Extractable arabinoxylan in all breads had a wide molecular-weight distribution and, when compared to the flour, relatively well-retained average molecular weights. On the other hand, the β -glucan was highly degraded during the bread-making processes. The baking-method-dependent change in content and molecular weight of extractable dietary fibers may be of significant importance for the nutritional and technological properties of the rye dietary fiber.

ACKNOWLEDGMENT

The authors acknowledge Elisabeth Gunnarsson for providing the rye samples.

LITERATURE CITED

- Åman, P. The dietary fibre complex in whole grain cereals. In *Whole Grain and Human Health*; Liukkonen, K., Kuokka, A., Poutanen, K., Eds; VTT Symposium 213; Technical Research Centre of Finland: Espoo, Finland, 2001; pp 20–22.
- Hansen, H. B.; Rasmussen, C. V.; Bach Knudsen, K. E.; Hansen, Å. Effects of genotype and harvest year on content and composition of dietary fibre in rye (*Secale cereale* L.) grain. *J. Sci. Food Agric.* **2003**, *83*, 76–85.
- Liukkonen, K. H.; Katina, K.; Wilhelmsson, A.; Myllymaki, O.; Lamoi, A. M.; Kariluoto, A. S.; Piironen, V.; Heinonen, S. M.; Nurmi, T.; Adlercreutz, H.; Peltoketo, A.; Pihlavan, J. M.; Hietaniemi, V.; Poutanen, K. Process-induced changes on bioactive compounds in whole grain rye. *Proc. Nutr. Soc.* **2003**, *62*, 117–122.
- Mattila, P.; Pihlavan, J.-M.; Hellström, J. Content of phenolic acids, alkyl- and alkenylresorcinols, and avenanthramides in commercial grain products. *J. Agric. Food Chem.* **2005**, *53*, 8298–8295.
- Kamal-Eldin, A.; Åman, P.; Zhang, J.-X.; Bach Knudsen, K.-E.; Poutanen, K. Rye bread and other rye products. In *Technology of Functional Cereal Products*; Hamaker, B. R., Ed.; CRC Press: Boca Raton, FL, 2008; pp 233–260.
- Richardson, D. P. Whole grain health claims in Europe. *Proc. Nutr. Soc.* **2003**, *62*, 161–169.
- Brown, L.; Rosner, B.; Willett, W. W.; Snacks, F. M. Cholesterol-lowering effects of dietary fiber: A meta-analysis. *Am. J. Clin. Nutr.* **1999**, *69*, 30–42.
- Leinonen, K. S.; Poutanen, K. S.; Mykkänen, H. M. Rye bread decreases serum total and LDL cholesterol. *J. Nutr.* **2000**, *130*, 164–170.
- Åman, P.; Rimsten, L.; Andersson, R. Molecular weight of β -glucan in oat-based foods. *Cereal Chem.* **2004**, *81*, 356–360.
- Andersson, A. A. M.; Armö, E.; Grangeon, E.; Fredriksson, H.; Andersson, R.; Åman, P. Molecular weight and structure units of (1 \rightarrow 3, 1 \rightarrow 4)- β -glucans in dough and bread made from hull-less barley milling fractions. *J. Cereal Sci.* **2004**, *40*, 195–204.
- Andersson, A. A. M.; Rüeegg, N.; Åman, P. Molecular weight distribution and content of water-extractable β -glucan in rye crisp bread. *J. Cereal Sci.* **2008**, *47*, 399–406.
- Frank, J.; Sundberg, B.; Kamal-Eldin, A.; Vessby, B.; Åman, P. Yeast-leavened oat breads with high or low molecular weight β -glucan do not differ in their effects on blood concentrations of lipids, insulin, or glucose in humans. *J. Nutr.* **2004**, *134*, 1384–1388.
- Pettersson, D.; Åman, P. The variation in chemical composition of triticales grown in Sweden. *Acta Agric. Scand.* **1987**, *37*, 20–26.
- Plaami, S.; Saastamoinen, M.; Kumpulainen, J. Effects of variety and environment on dietary fibre content of winter rye in Finland. *J. Cereal Sci.* **1989**, *10*, 209–215.
- Nilsson, M.; Andersson, R.; Andersson, R. E.; Autio, K.; Åman, P. Heterogeneity in a water-extractable rye arabinoxylan with a low degree of disubstitution. *Carbohydr. Polym.* **2000**, *41*, 397–405.
- Hartmann, G.; Piber, M.; Koehler, P. Isolation and chemical characterisation of water-extractable arabinoxylans from wheat and rye during breadmaking. *Eur. Food Res. Technol.* **2005**, *221*, 487–492.
- Theander, O.; Åman, P.; Westerlund, E.; Andersson, R.; Pettersson, D. Total dietary fiber determined as neutral sugar residues, uronic acid residues and Klason lignin (the Uppsala method): Collaborative study. *J. AOAC Int.* **1995**, *10*, 149–156.
- Andersson, A. A. M.; Merker, A.; Nilsson, P.; Sorensen, H.; Åman, P. Chemical composition of the potential new oilseed crops *Barabrea vulgaris*, *Barbarea verna* and *Lepidium campeatre*. *J. Sci. Food Agric.* **1999**, *79*, 179–186.
- Loosveld, A.-M.; Grobet, A.; Delcour, J. A. Content and structural features of water-extractable arabinogalactan in wheat flour fractions. *J. Agric. Food Chem.* **1997**, *45*, 1998–2002.
- McCleary, B. V.; Murphy, A.; Mugford, D. C. Determination of oligofructans and fructan polysaccharides in foodstuffs by an enzymatic/spectrophotometric method: Collaborative study. *J. AOAC Int.* **1997**, *83*, 356–364.
- Rimsten, L.; Stenberg, T.; Andersson, R.; Andersson, A.; Åman, P. Determination of β -glucan molecular weight using SEC with Calcofluor detection in cereal extracts. *Cereal Chem.* **2003**, *80*, 485–490.
- Van den Bulck, K.; Swennen, K.; Loosveld, A.-M.; Courtin, C. M.; Brijs, K.; Proost, P.; Van Damme, J.; Van Campenhout, S.; Mort, A.; Delcourt, J. A. Isolation of cereal arabinogalactan-peptides and structural comparison of their carbohydrate and peptide moieties. *J. Cereal Sci.* **2005**, *41*, 59–67.
- Fretzdorff, B.; Welge, N. Abbau von getreideeigenen Fructanen während der Herstellung von Roggen. Villkornbrot. *Getreide Mehl Brot* **2003**, *57*, 147–151.
- Nilsson, U.; Nyman, M. Short-chain fatty acid formation in the hindgut of rats fed oligosaccharides varying in monomeric composition, degree of polymerisation and solubility. *Br. J. Nutr.* **2005**, *94*, 705–713.
- Westerlund, E.; Theander, O.; Andersson, R.; Åman, P. Effects of baking on polysaccharides in white bread. *J. Cereal Sci.* **1989**, *10*, 149–156.

Received for review August 20, 2008. Revised manuscript received December 28, 2008. Accepted January 9, 2009. The authors acknowledge the Swedish cereal and baking industry for technical and financial support.