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Contents of starch and non-starch polysaccharides in barley varieties of different origin

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Abstract

A large number of barley varieties were extensively analyzed with emphasis on polysaccharides. Interrelationships among the different parameters were studied by using principal component analysis (PCA).

The results showed that barley varieties have a wide diversity in polysaccharide content and composition with the variation mainly due to differences in hull and starch types. However, a relative wide variation was also detected within these groups, which can be exploited further to improve quality in barley. A strong negative correlation between the amount of arabinoxylans (AX) and the degree of branching was found as well as a negative correlation between β-glucan and arabinoxylan. A strong positive correlation was also seen between the β-glucan and the amount of soluble non-starch polysaccharides (NSP), as well as β-glucans and protein contents.

The analyzed hull-less and atypical amylose varieties seem suitable for human consumption where high soluble fibre and nutritive contents are desirable. These varieties contained high contents of β-glucans, soluble NSP, protein, and lower starch content, and could therefore also be suitable for functional food products aimed at health benefits and cancer prevention.

Keywords: Non-starch polysaccharides; Arabinoxylan; β-glucan; Hull-less barley; Waxy and high amylose

1. Introduction

Barley (*Hordeum vulgare*) is an important crop in Scandinavia and other northern parts of the world due to its early maturing ability, making it suitable for areas with a short growing season. On a worldwide basis, only about 5% of the barley production is used for food (FAO, 2001), while most is used in the feed industry. Improving the agronomic performance and, in certain areas, the malting quality have therefore been the main research aims. However, hull-less barley varieties, rich in soluble fibres, have the potential to become more attractive for human consumption.

The dominating fibres components in barley are the β-glucans and the arabinoxylans, located mainly in the cell walls of the endosperm and the aleurone layer. Cereal β-glucans (hereafter simply referred to as β-glucans) are linear homopolysaccharides (of glucose) with approximately 70% (1 → 4)-linkages and 30% (1 → 3)-linkages. On average, two or three (1 → 4)-linked units are separated by a single (1 → 3)-linkage. Nevertheless, longer sequences of homogeneously (1 → 4)-linked monomers do exist (Cui, Wood, Blackwell, & Nikiforuk, 2000; MacGregor & Rattan, 1993). The (1 → 3)-linkages cause irregularities in the structure of the molecule, which influence their properties and make

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the β-glucans partly soluble by preventing close packing of the chains (Jadhav, Lutz, Ghorpade, & Salunkhe, 1998; Jiang & Vasanthan, 2000). β-Glucan content in barley varies with genetic background and environmental conditions (Lehtonen & Aikasalo, 1987a; Oscarsson, Andersson, Aman, Olofsson, & Jonsson, 1998), and among all cereal grains, oat and barley 63, contain the highest levels of β-glucan, with the latter at 2–11% of dry weight (Charalampopoulos, Wang, Pandiella, & Webb, 2002; Jadhav et al., 1998; Lehtonen & Aikasalo, 1987a).

Arabinoxylans are composed of a backbone of (1 → 4)-linked β-D-xylopyranosyl residues. Some of these are substituted at position 2 and/or 3 with α-L-arabinofuranosyl (Dervilly et al., 2002; Han, 2000). Arabinoxylans have been reported to constitute 3–11% of the barley kernel (Han & Schwarz, 1996; Jadhav et al., 1998; Lehtonen & Aikasalo, 1987b).

β-Glucans, as well as arabinoxylans, form viscous solutions in water and can contribute to extraction, filtration, and haze formation problems in the brewing industry (Jadhav et al., 1998; MacGregor & Rattan, 1993). In addition, the high viscosity slows down digestibility in animal intestines, thus reducing the nutritive value of the feed and therefore also feed efficiency. Other problems associated with these polysaccharides are sticky faeces when fed to poultry (Jadhav et al., 1998; MacGregor & Rattan, 1993; Svihus, Selmer-Olsen, & Brathen, 1995). On the other hand, these polysaccharides are important dietary fibres and influence the quality of food. For example, their water-binding capability contributes to making bread juicy and fresh for a longer period (Ulltveit, 2000).

The non-starch polysaccharides, such as arabinoxylans and especially β-glucans, not only influence nutritional value and functional properties of food, but are also beneficial for human health. β-Glucans increase the viscosity in the small intestine, lower blood cholesterol level and, therefore, reduce the risk of heart disease, in addition to being useful for controlling blood glucose level (Andersson, 1994; Mclntosh, Newman, & Newman, 1995; Mclntosh, Whyte, McArthur, & Nestel, 1991; Newman, Klopfenstein, Newman, Guritno, & Hofer, 1992; Newman, Newman, & Graham, 1989; Pick, Hawrysh, Gee, & Toth, 1998; Sundberg, Xue, Newman, & Newman, 1998). A high intake of cereal fibre (or whole grain) also seems to lower the risk of different cancers, coronary heart disease and diabetes (Bingham et al., 2003; Jacobs, Marquart, Slavin, & Kushi, 1998; Liu et al., 2000; Liu et al., 1999; Peters et al., 2003).

Barley has the same (or higher) fibre content as other cereals (Henry, 1987), and the health-promoting effects of these fibres are well documented (Hecker, Meier, Newman, & Newman, 1998; Mclntosh et al., 1991; Newman et al., 1992; Pick et al., 1998) and barley deserves recognition for its nutritive and health potential. Furthermore, barley's wide diversity in β-glucan content makes it possible to select a genotype for specific beneficial uses. However, more studies are necessary to define barley's unused value and make use of it in products/applications not usually associated with barley.

Most studies presented in the literature on the content and variability of barley non-starch polysaccharides have been performed on relatively small sample sets containing 3–10 barley varieties. Furthermore, the relationships of the different types of non-starch polysaccharides in the barley grain are poorly understood. The objective of this work was to study the content and composition of polysaccharides in a wider range of barley samples, and also by using different analytical methods, to achieve more comprehensive information on content and variability of the main non-starch polysaccharide components. Principal component analysis was used to achieve a deeper knowledge of the relationships among the different polysaccharides in the barley grain. These results will be used to select barley varieties for new field-grown experiments in Norway, followed by reanalysis of NSP to study possible stable/unstable varieties with regards to their grain quality.

2. Materials and methods

2.1. Barley samples

Thirty-nine barley varieties of diverse genetic origin and from several barley-growing areas of the northern hemisphere were selected for the study. Most of the varieties were commercial varieties or new breeding lines adapted to Scandinavian climate. To get a sample set of varieties that represented a wider diversity in barley, hull-less varieties, as well as varieties with atypical amylose/amylopectin ratios, were included, mainly from Canada. The varieties were grown in field trials in the areas where they were adapted. Most (24) were grown in Norway in 2001 (Graminor, Hamar), two were grown in Sweden (Svalöf-Weibull, Svalöf), two were grown in Denmark (Sejet, Horsens), and 11 in Canada (University of Saskatchewan, Saskatoon). An overview of the varieties, their characteristics, breeding companies, and location of field trials, is shown in Table 1. All samples were also analysed for kernel weight and inspected for kernel plumpness. A variation in kernel weight from 38.1–55.8 g was obtained, which revealed that all samples had plump kernels with good grain-filling.

2.2. General methods

The whole grains were ground on a Retsch centrifugal mill (Model ZM1; Retsch GmbH, Haan, Germany) with a 0.5-mm sieve. Dry weights were

Table 1
The different barley varieties and their characteristics

Varieties	2-rowed/6-rowed	Hulled/hull-less	Waxy/normal/high amylose	Breeding company, country	Location of field trial
1 Arve	6	H	n	NK, N	Norway
2 Thule	6	H	n	NK, N	Norway
3 Olsok	6	H	n	NK, N	Norway
4 Ven	6	H	n	NK, N	Norway
5 Lavrans	6	H	n	NK, N	Norway
6 Gaute	6	H	n	NK, N	Norway
7 Fager	6	H	n	NK. N	Norway
8 NK96300	6	H	n	NK, N	Norway
9 NK98268	6	H	n	NK, N	Norway
10 NK96737	6	H	n	NK,N	Norway
11 Åker	6	H	n	NK,N	Norway
12 Tyra	2	H	n	NK, N	Norway
13 Kinnan	2	H	n	SW, S	Norway
14 Sunnita	2	H	n	SW, S	Norway
15 Henni	2	H	n	Nordsaat, DK	Norway
16 Saana	2	H	n	Boreal, FIN	Norway
17 Justina	2	H	n	Nordsaat, DK	Norway
18 Iver	2	H	n	NK, N	Norway
19 Bond	2	H	n	Sejet, DK	Norway
20 Annabell	2	H	n	Nordsaat, DK	Norway
21 SWÅ97150	2	H	n	SW, S	Norway
22 Olve	2	H	n	NK, N	Norway
23 PF 14035-54	2	H	n	Paj Bjergfonden, DK	Norway
24 CDC Dolly	2	H	n	CDC, C	Canada
25 CDC Bold	2	H	n	CDC, C	Canada
26 CDC Helgason	2	H	n	CDC, C	Canada
27 Otira	2	H	n	Sejet, DK	Denmark
28 Chamant	2	H	n	Sejet, DK	Denmark
29 NK95003	2	H-L	n	NK, N	Norway
30 CDC Dawn	2	H-L	n	CDC, C	Canada
31 CDC Gainer	2	H-L	n	CDC, C	Canada
32 CDC Freedom	2	H-L	n	CDC, C	Canada
33 CDC McGwire	2	H-L	n	CDC, C	Canada
34 CDC Speedy	2	H-L	n	CDC, C	Canada
35 CDC Candle	2	H-L	w	CDC, C	Canada
36 CDC Alamo	2	H-L	w	CDC, C	Canada
37 SB94897	2	H-L	h	CDC, C	Canada
38 SW 2680	2	H-L	w	SW, S	Sweden
‘39 SW Cindy	2	H	w	SW, S	Sweden

NK, Norsk Kornforedling; N, Norway; SW, Svalöf-Weibull; S, Sweden; CDC, crop development center; C, Canada; DK, Denmark; FIN, Finland.

determined by drying 200 mg of flour at 105 °C for 4 h. Nitrogen was determined by total combustion in a Carlo Erba (NA 1500) at the Department of Biotechnology, Norwegian University of Science and Technology (NTNU), Trondheim, Norway, and the protein content was calculated as $N \times 6.25$. Results are averages of triplicates and are presented on a dry weight basis. Kernel weight was determind by counting a sample of 250–300 kernels using a Numerical Seed Counter, EPL, weighing the samples and calculating kernel weight in mg/per grain.

2.3. Carbohydrate analysis

The mixed linked β-glucan contents of the barley samples were determined using a Megazyme mixed-linkage β-glucan assay kit (Megazyme International Ireland Ltd., Bray Business Park, Bray, Co. Wicklow, Ireland). Total starch and amylose contents were also quantified enzymatically by a total starch assay kit and an amylose/amylopectin assay kit from Megazyme.

Total and insoluble non-starch polysaccharide (T-NSP and I-NSP) contents and their sugar compositions were determined according to the method described by (Englyst, Quigley, Hudson, & Cummings, 1992), by measuring the neutral sugars in acidic hydrolysates by gas chromatography (GC) as alditol acetates. The soluble fraction (S-NSP) was calculated by difference. All of the NSP fractions include cellulose. The amount of arabinoxylans (AX) was estimated by correcting for the presence of arabinogalactans (AG), as described by (Loosveld, Grobet, & Delcour, 1997). Cellulose content was estimated as the difference between glucose and β-glucan.

2.4. Statistical analysis

The relationships between the chemical constituents were studied by a principal component analysis (PCA) using the Unscrambler software package (Version 8.0.5; CAMO A/S, Trondheim, Norway). Analysis of variance and significant differences among means were tested by one-way ANOVA, using Minitab (version 13.3; Minitab Inc., State College, PA, USA). Significant differences were declared at $P < 0.05$. A simple correlation (Pearson correlation) was also computed using Minitab ($P < 0.05$).

3. Results and discussion

3.1. General composition

In this study, different barley varieties (Table 1) were characterized with focus on polysaccharide contents and compositions. Starch was the major constituent, accounting for 51.3–64.2%, followed by non-starch polysaccharides (NSPs), accounting for 22.6–41.1% (Table 2). The NSPs in cereal grains are composed mainly of arabinoxylans (pentosans), β-glucans, and cellulose (Choct, 1997; Henry, 1987). The predominating sugar components analyzed were glucose (11.9–24.3%), xylose (5.3–12.9%) and arabinose (3.7–5.7%), whereas the contents of mannose and galactose were considerably lower (0.7–1.1% and 0.8–1.3%, respectively). Rhamnose and fucose were detected only in trace amounts.

The samples were compared individually and by grouping to investigate possible associations between barley type and the chemical composition of carbohydrates in the grain. Since it is known that many parameters are affected by differences in hull content and starch type, the material was grouped according to hull type, starch type, and also according to 6- or 2-rowed as well as according to growth location of the different samples (Table 3). Differences from the comparisons, between the Norwegian hulled 2-rowed grown in Norway vs. Foreign hulled 2-rowed grown elsewhere, may be due to different properties of the varieties, or to the growth conditions at the different locations. Also, since many of the hull-less varieties had an atypical starch type, the hulled–hull-less comparison was made only among the varieties of normal starch. Furthermore, to investigate the effect of starch type, comparisons were made only within the hull-less varieties.

3.2. Starch and amylose

The lowest content of starch was in a Norwegian hulled 2-rowed variety, Olve (Table 2). Also, the high amylose genotype had a low amount of total starch, as reported earlier (Andersson, Elfverson, Andersson, Regner, & Aman, 1999). The highest concentration of starch was found in Chamant (Table 2), one of the hulled, 2-rowed varieties grown in Denmark. The variation in starch content within the hulled varieties covered the whole variation seen in the total samples (Table 2). As seen in Table 3, no significant differences in starch content were found in the comparisons made within the hulled varieties (6rd-2rd, N2rd-F2rd). For the comparison between hulled and hull-less varieties within the normal starch type, the hull-less samples had significantly higher starch content. The comparison between the atypical and normal starch type was not significant; however, there was a tendency toward a lower starch content for atypical starch types as reported elsewhere (Bhatty & Rossnagel, 1998; Oscarsson, Andersson, Salomonsson, & Aman, 1996; You & Izydorczyk, 2002), with the exception of Olve of normal starch type and the lowest starch content.

This study included four waxy amylose varieties (2.5–8.3% amylose) and one high-amylose (35.5% amylose) sample. The amylose content corresponded well with other typical amylose contents of waxy and high amylose barleys reported elsewhere (Sundberg et al., 1998; Zheng & Bhatty, 1998). However, the amylose content of the variety CDC Alamo was determined to be 2.5% although this variety has been reported as a zero-amylose variety (Li, Vasanthan, Rossnagel, & Hoover, 2001b). Different analytical methods could be the reason for the observed difference.

3.3. Protein

Protein content varied from 8.2% to 18.5% and was in agreement with earlier findings of the protein content in barley ranging from 6% to 20% (Jadhav et al., 1998; Verma, Kasana, Sangwan, & Dhindsa, 1996). The highest amount of protein was found in the high-amylose variety SB 94897. The lowest contents were found in Chamant and Otira, the two varieties from Denmark (Table 2). The Norwegian 6- and 2-rowed varied less in protein content compared to the other foreign samples. Still, a significant difference was seen between the Norwegian hulled 2-rowed and the Norwegian hulled 6-rowed varieties, with the former having the higher amount (Table 3) . The normal hull-less varieties had higher protein contents than the normal hulled varieties, as reported earlier (Andersson et al., 1999; Oscarsson et al., 1996).

3.4. Non-starch polysaccharides

Total NSP content was in the range of 22.6–41.1%. Olve, the variety with the lowest starch content, had the highest amount of T-NSP, while CDC McGwire and CDC Gainer, hull-less varieties, had the lowest T-NSP content (Table 2). The Norwegian 6- and 2-rowed

Table 2
Results of the starch, protein and non-starch polysaccharide analyses of the barley varieties

Varieties	Starch	Amylose	β-Glucan	Protein	T-NSP	I-NSP	S-NSP	T-AX	I-AX	S-AX	A/X (T-AX)	A/X (I-AX)	A/X (S-AX)	T-AG	I-AG	S-AG	Cellulose
1 Arve	57.80	25.30	3.10	10.70	32.80	22.80	9.99	12.90	11.60	1.34	0.37	0.36	0.41	0.98	0.37	0.61	12.13
2 Thule	57.30	24.20	3.46	11.13	38.10	27.21	10.90	15.02	13.43	1.59	0.36	0.34	0.49	1.05	0.42	0.63	14.24
3 Olsok	58.70	24.30	2.64	11.20	29.03	24.10	4.94	12.21	11.90	0.36	0.36	0.35	1.13	0.86	0.39	0.47	10.52
4 Ven	59.10	24.00	3.37	11.50	32.20	22.30	9.91	13.20	11.50	1.67	0.38	0.37	0.43	0.89	0.35	0.54	11.30
5 Lavrans	58.01	25.43	3.79	12.00	33.14	21.80	11.40	12.80	11.01	1.76	0.36	0.37	0.33	0.94	0.36	0.58	12.10
6 Gaute	57.50	24.12	3.26	10.63	36.30	25.54	10.80	14.60	12.90	1.68	0.36	0.37	0.34	1.03	0.42	0.61	13.30
7 Fager	60.44	23.51	3.31	10.44	36.21	25.34	10.90	14.04	12.40	1.64	0.35	0.36	0.28	1.08	0.40	0.68	13.70
8 NK96300	59.63	23.02	3.14	10.30	31.60	22.91	8.64	12.01	11.60	0.42	0.37	0.37	0.30	1.09	0.40	0.68	11.50
9 NK98268	60.70	25.52	3.29	11.61	33.20	21.40	11.80	13.20	10.90	2.32	0.37	0.38	0.34	1.12	0.37	0.76	11.70
10 NK96737	59.20	24.70	3.08	12.30	34.30	22.70	11.60	14.00	11.52	2.46	0.37	0.38	0.36	1.10	0.37	0.73	12.22
11 Åker	56.04	25.72	3.90	10.44	35.02	26.43	8.59	13.70	12.93	0.74	0.39	0.36	1.10	0.92	0.44	0.48	12.90
12 Tyra	59.50	26.00	3.77	12.40	34.12	23.00	11.13	12.80	11.60	1.18	0.38	0.37	0.49	0.98	0.43	0.55	13.20
13 Kinnan	59.14	25.00	3.57	12.00	34.02	22.70	11.34	13.00	11.30	1.71	0.41	0.40	0.42	1.03	0.38	0.65	12.80
14 Sunnita	56.50	24.50	4.06	12.80	37.20	25.30	11.93	13.90	12.84	1.03	0.38	0.37	0.47	1.00	0.40	0.60	14.90
15 Henni	59.90	24.10	3.77	10.72	36.70	25.90	10.80	13.90	12.72	1.14	0.35	0.35	0.32	1.12	0.43	0.69	14.00
16 Saana	59.13	23.00	2.75	12.03	33.30	21.50	11.80	12.90	10.84	2.02	0.39	0.39	0.38	0.94	0.36	0.58	13.20
17 Justina	60.30	24.40	3.15	12.03	33.12	24.70	8.46	12.34	12.20	0.18	0.34	0.34	0.59	1.13	0.42	0.71	12.80
18 Iver	58.40	24.90	3.59	11.92	33.00	21.14	11.90	12.24	10.80	1.44	0.37	0.38	0.31	1.00	0.37	0.63	12.60
19 Bond	59.63	24.72	3.29	11.80	34.13	23.72	10.41	13.10	11.84	1.23	0.36	0.37	0.22	1.13	0.41	0.71	12.63
20 Annabell	59.50	24.72	3.03	11.52	32.80	22.42	10.40	12.31	11.22	1.09	0.38	0.35	0.74	1.00	0.41	0.59	12.74
21 SWÅ97150	56.84	25.22	3.68	11.94	33.34	22.00	11.34	12.60	11.12	1.48	0.36	0.38	0.25	0.91	0.36	0.55	12.80
22 Olve	51.31	24.60	4.59	13.40	41.10	27.32	13.80	15.70	13.70	2.01	0.38	0.36	0.50	1.11	0.45	0.66	15.62
23 PF 14035-54	59.22	24.30	3.53	10.80	33.00	21.50	11.60	12.30	11.00	1.27	0.39	0.39	0.35	1.02	0.33	0.69	12.60
24 CDC Dolly	58.50	26.60	5.03	14.50	36.50	21.02	15.43	12.70	10.70	1.96	0.37	0.37	0.35	0.92	0.31	0.61	14.50
25 CDC Bold	58.33	26.20	2.95	11.40	26.92	18.20	8.77	10.63	9.26	1.38	0.41	0.41	0.41	0.77	0.29	0.48	9.60
26 CDC Helgason	59.50	25.71	3.71	12.32	31.80	19.70	12.11	11.44	9.84	1.60	0.39	0.40	0.37	0.95	0.35	0.60	12.20
27 Otira	60.60	24.70	3.13	8.23	33.04	26.50	6.57	13.00	13.00	0.00	0.38	0.36	–	0.91	0.42	0.49	12.70
28 Chamant	64.20	23.71	2.41	8.42	29.70	20.30	9.42	11.90	10.22	1.65	0.40	0.41	0.33	0.94	0.33	0.60	11.10
29 NK95003	62.43	24.71	3.69	13.21	24.90	16.12	8.77	9.32	8.71	0.62	0.52	0.50	0.91	0.84	0.34	0.51	8.18
30 CDC Dawn	59.64	24.52	3.91	16.93	31.20	12.80	18.44	11.92	6.89	5.03	0.39	0.62	0.17	0.90	0.26	0.65	11.60
31 CDC Gainer	63.30	25.20	3.39	13.93	22.60	11.64	10.96	8.27	6.43	1.84	0.55	0.66	0.27	0.89	0.29	0.59	9.21
32 CDC Freedom	59.70	25.70	4.21	16.10	26.00	11.90	14.10	8.30	6.73	1.57	0.57	0.64	0.33	0.87	0.25	0.62	9.61
33 CDC McGwire	60.20	25.70	4.01	13.40	22.63	12.20	10.50	7.41	4.36	3.05	0.60	0.60	0.59	0.75	0.29	0.45	7.95
34 CDC Speedy	59.80	24.80	3.96	15.50	23.70	11.82	11.90	7.99	6.52	1.47	0.56	0.62	0.32	0.91	0.29	0.63	8.54
35 CDC Candle	58.50	4.87	6.36	15.62	28.13	10.60	17.53	7.37	5.91	1.47	0.59	0.67	0.31	0.82	0.26	0.56	11.12
36 CDC Alamo	53.70	2.45	7.19	18.30	38.70	11.73	26.92	9.77	6.35	3.42	0.60	0.65	0.51	1.08	0.33	0.75	17.10
37 SB94897	53.50	35.54	8.25	18.52	34.70	12.52	22.20	8.85	6.80	2.05	0.59	0.68	0.34	0.89	0.26	0.63	14.00
38 SW 2680	62.30	6.62	4.81	12.62	27.54	11.91	15.63	8.94	6.61	2.33	0.55	0.60	0.42	0.93	0.31	0.62	9.79
39 SW Cindy	55.20	8.26	6.49	11.60	40.74	22.33	18.41	12.50	10.94	1.55	0.37	0.38	0.34	0.97	0.39	0.58	17.70
5%, LSD	3.56	–	0.19	3.06	2.43	2.11	3.39	0.95	1.03	1.35	0.04	0.03	0.78	0.14	0.09	0.16	1.48

Data are averages of triplicates, presented as % of dry weight except for amylose contents, which are % of starch. T, total; I, insoluble; S, soluble; NSP, non-starch polysaccharides; AX, arabinogalactans; AG, arabinogalactans; A/X, degree of branching in arabinoxylans.

Table 3
Results from one-way ANOVA for analysing differences between the different groups

Parameters	Hulled		Normal	Hull-less
	N 2-rd/N 6-rd	N 2-rd/F 2-rd	Hull-less/hulled	Atypical/normal
Starch	–	–	0.032	–
Protein	0.010	–	0.000	–
β-Glucan	–	–	–	0.002
T-NSP	–	–	0.000	0.030
I-NSP	–	–	0.000	–
S-NSP	–	–	–	0.015
T-AX	–	0.043	0.000	–
I-AX	–	–	0.000	–
S-AX	–	–	0.023	–
A/X (T-AX)	–	–	0.000	–
A/X (I-AX)	–	–	0.000	–
A/X (S-AX)	–	–	–	–
T-AG	–	0.005	0.002	–
I-AG	–	0.032	0.000	–
S-AG	–	0.009	–	–
Cellulose	0.036	–	0.000	0.030

Significant differences are shown by the *p*-values. Significant difference determined at 5% level; N 6-rd, Norwegian 6-rowed; N 2-rd, Norwegian 2-rowed; FH 2-rd, Foreign hulled 2-rowed; T, total; I, insoluble; S, Soluble; NSP, non-starch polysaccharides; AX, arabinoxylans; A/X, degree of branching in arabinoxylans; AG, arabinogalactans.

varieties, with a few exceptions, had total NSP contents above 30%. And seen from Table 3, there was no difference in the T-NSP levels between 6- or 2-rowed varieties. The hulled varieties had a significantly higher content of total NSP than did to the hull-less, probably due to the contribution of cellulose and arabinoxylans from the hull in the hulled samples. Furthermore, the atypical starch varieties had a significantly higher amount of T-NSP compared to the normal ones among the hull-less varieties.

Insoluble NSP contents varied from 10.6% to 27.3%, with a Norwegian 2-rowed and a Norwegian 6-rowed variety, Olve, and Thule, respectively, having the highest amounts, while the hull-less, waxy variety, CDC Candle, had the lowest (Table 2). All the Norwegian 6-rowed varieties, as well as the Norwegian 2-rowed, with the exception of the hull-less NK 95003, contained a high amount of insoluble NSP (>20%). The atypical amylose samples and the hull-less contained less than 17%. The hull-less had significantly lower contents of I-NSP than the hulled varieties (Table 3). This might indicate that there was more I-NSP in the hull than in the kernel.

Soluble NSP was in the range of 4.5–26.9% of dry weight, corresponding to 16.4–69.7% of T-NSP. The highest amount of S-NSP was found in the hull-less variety with the lowest amylose content, CDC Alamo. The atypical amylose barley varieties contained the highest amount of S-NSP, while the Norwegian 6- and 2-rowed had the lowest amounts. The samples with the lowest amount of I-NSP, were highest in S-NSP. Furthermore, the hull-less samples had a wide range of S-NSP content, with the atypical in the higher range and the normal in the lower (Table 3). No differences were found between the normal hulled and normal hull-less varieties in S-NSP. Furthermore, the atypical hull-less genotypes contained more soluble than insoluble NSP, contrary to the hulled and normal varieties.

3.5. β-Glucan

A range of 2.4–8.3% was observed in total β-glucan content. The high-amylose sample contained the highest amount of β-glucan, while the lowest content was found in Chamant (Table 2). With two exceptions (Olve and Sunnita), all Norwegian samples were found to contain less than 4% β-glucans, while the atypical amylose genotypes had a β-glucan content above 6%, with the exception of SW 2680. The hull-less atypical amylose varieties had a significantly higher concentration of β-glucan than the normal amylose ones, as reported elsewhere (Andersson et al., 1999; Baidoo & Liu, 1998; Izydorczyk, Storsley, Labossiere, MacGregor, & Rossnagel, 2000). The difference in β-glucan content between the hulled and hull-less varieties of normal starch type was not significant; however, there was a tendency towards a lower β-glucan content in the hulled samples. The main S-NSP component was β-glucan, which was also indicated by a strong correlation between β-glucan and soluble NSP ($r = 0.88$).

3.6. Arabinoxylans

Faurot et al. (1995) stated that 30% of the pentosans in wheat were soluble and this fraction was constituted mainly of arabinoxylans and a smaller amount of arabinogalactans. Since arabinogalactans are also found in barley (Cyran, Izydorczyk, & MacGregor, 2002), the arabinose residue measured would therefore originate from both arabinoxylans and arabinogalactans. The amount of arabinoxylan was calculated by correcting for the presence of arabinogalactans, as described by (Loosveld et al., 1997), and not as the sum of arabinose and xylose residues. However, since this correction is based on wheat, the correction factor used could be slightly different for barley.

The reported total content of arabinoxylans in barley, 3–11% (Han & Schwarz, 1996; Jadhav et al., 1998; Lehtonen & Aikasalo, 1987b), is somewhat lower than in our study, where the amounts were found to be 7.4–15.7%. The variety with the highest amount of T-NSP (Olve) also had the highest amount of total arabinoxylans (T-AX). The lowest amount was found among the hull-less varieties (Table 2). Both 6-rowed and the Norwegian 2-rowed contained more than 12% T-AX, with one exception in each group. The foreign hulled samples had less then 13%. The hulled varieties contained a significantly higher amount of T-AX than did the hull-less samples (Table 3), which was in agreement of earlier reports (Andersson et al., 1999). This can be explained by the presence of the arabinoxylans in the hull, and show that the amount of hull influences the T-AX level. There was also a significantly higher level of T-AX in the Norwegian hulled 2-rowed compared to the Foreign hulled 2-rowed varieties. Since these were varieties with the same characteristics, but grown in different places, it indicated that growing conditions may also influence the level of T-AX.

Also, the amount of insoluble arabinoxylans (I-AX) varied much between the different varieties, with a range of 4.4–13.7% (Table 2). Olve had the highest amount, while CDC McGwire had the lowest. Both the Norwegian 6- and 2-rowed varieties contained high amounts, and showed a small variation in I-AX content. The hull-less had generally little (<7%) I-AX, which was significantly less than the hulled samples (Table 3).

Two varieties, Justina and Otira, contained no or little soluble arabinoxylans (S-AX), while a hull-less sample contained the most (5.0%) (Table 2). The hull-less genotypes also had a wider variation in the content of S-AX. 0–42.2% were soluble (of the total arabinoxylans) with the hull-less varieties having a significantly higher content of soluble arabinoxylans than the hulled samples (Table 3). Overall, there were more insoluble arabinoxylans than soluble arabinoxylans, as reported for oats (Frolich & Nyman, 1988; Pettersson, Graham, & Aman, 1987; Westerlund, Andersson, & Aman, 1993).

3.7. Degree of branching in arabinoxylans

The degree of branching in the arabinoxylans (A/X) was generally the same for both the total and insoluble fraction (Table 2). Hull-less, waxy, and high-amylose varieties had the highest degree of substitution in these fractions. Hulled and hull-less varieties were significantly different giving a higher substitution with less hull (Table 3). In the soluble arabinoxylans, the substitution pattern was different from those in the total and insoluble arabinoxylans. Generally the A/X ratio was higher, except for the hull-less genotypes (not NK 95003), which had a lower degree of branching than did their total and insoluble fractions. Two of the Norwegian 6-rowed (Olsok and Åker) had the highest A/X ratio in the S-AX fraction.

3.8. Arabinogalactan

The calculated amount of total arabinogalactans (T-AG) varied from 0.8% to 1.1% (Table 2). The content of arabinogalactans was significantly higher in the hulled varieties than in the hull-less samples in both total and insoluble AG (Table 3). The amount of arabinogalactan also seemed to be influenced by growing conditions since the Norwegian, hulled 2-rowed varieties contained significantly more arabinogalactan than did the Foreign hulled 2-rowed samples. In all samples, there were more soluble than insoluble arabinogalactans.

3.9. Cellulose

Cellulose content varied from 8.0% to 17.7% with the highest amounts of cellulose in the waxy, hulled SW Cindy, the waxy, hull-less CDC Alamo, the high amylose variety SB 94897, as well as in the Norwegian hulled variety Olve. The lowest amount was found in CDC McGwire (Table 2). These results were rather unexpected since both CDC Alamo and SB 94897 were hull-less. A significant difference was seen between the Norwegian hulled 2-rowed and the Norwegian hulled 6-rowed varieties with the former group having a higher amount of cellulose (Table 3). Also, as expected, the hull-less varieties had a significantly lower content of cellulose than did the hulled among the normal starch types. Within the hull-less group, the atypical varieties had a higher amount of cellulose. This could imply that starch type somehow influences the cellulose content. The calculated content of cellulose might be slightly too high since glucomannans and pure $(1 \rightarrow 3)$-β-glucans have been reported as minor components in the cereal grains (Jadhav et al., 1998) and could contribute to the amount of glucose. However, this contribution was not considered to be significant.

3.10. Principal component analysis

The PCA plots in Fig. 1 are combined score and loading plots (biplots), including both the varieties (Table 1) and the analyzed parameters (Table 2). It provides an overview of interrelationships between the analyzed chemical components, but also helps to detect and interpret sample patterns. It is possible to see similarities or

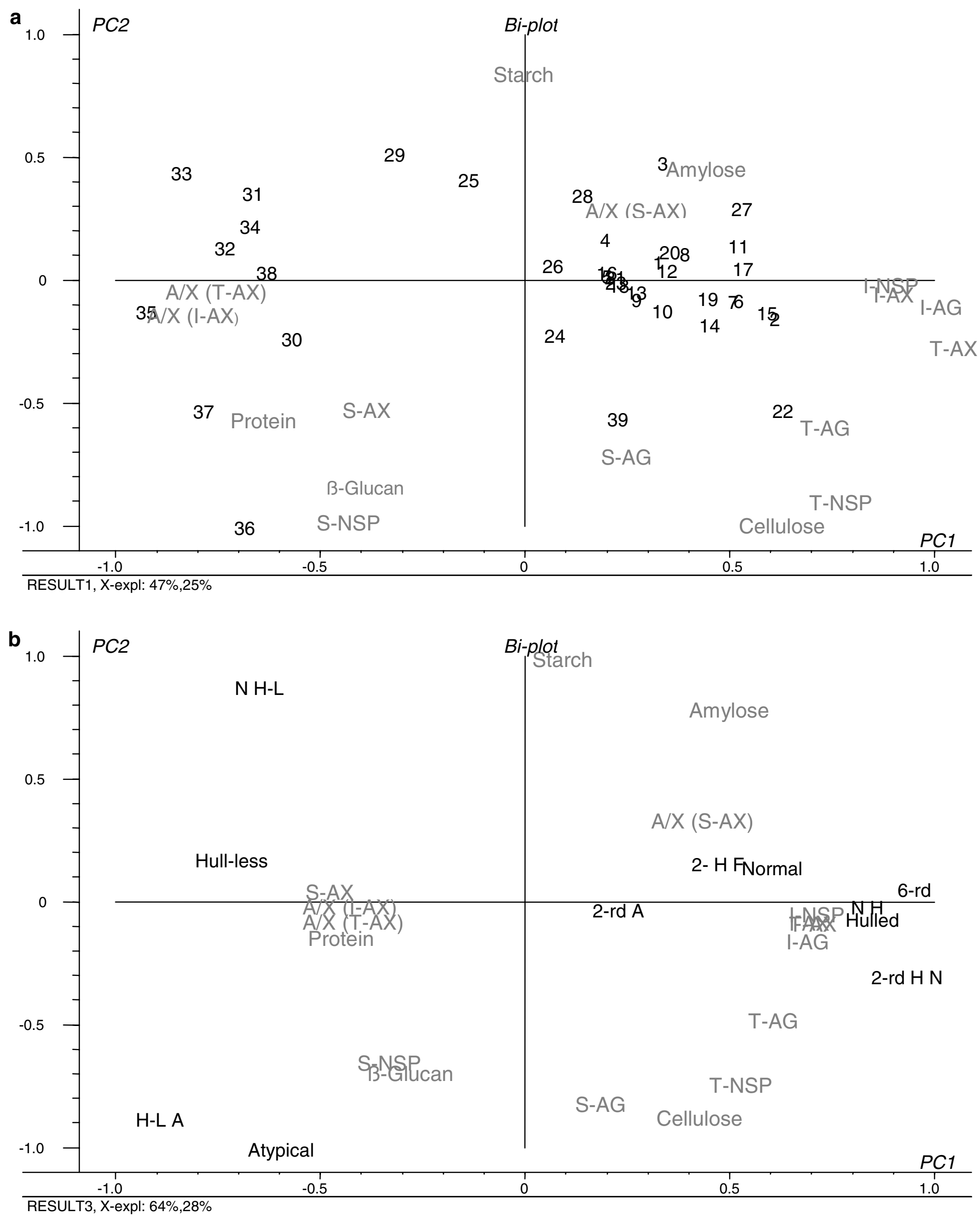

Fig. 1. PCA biplots over (a) the barley varieties (numbers) and (b) the groups and the parameters analyzed. The cluster under sample 4 in (a) includes samples 5, 16, 18, 21 and 23, while the cluster in (b) next to the hulled are I-NSP, T-AX og I-AX.

differences and then make a classification of the varieties into groups. If varieties are located close to each other, they have similarities in the analyzed parameters and thus similarities in their composition. Fig. 1(a) shows that the hull-less varieties (nos. 29–38) are clustered and isolated to the far left of the plot, while the hulled (nos. 1–28, 39) are generally to the right. The normal varieties were located in the upper left quadrant and to the right in the biplot, depending on their hull type. As mentioned, the hull-less varieties are located to the left of the plot with the normal starch types clustered in the upper quadrant (with the exeption of CDC Dawn), while the atypical (nos. 35–38, 39) are scattered in the lower left quadrant. Some varieties appear to differ from this pattern. SW Cindy (no. 39) differs from the other atypical varieties, most likely because it is hulled, while the others are hull-less. Number 29, NK 95003, is located far to the right compared to the other hull-less varieties. Even if this variety is reported to be hull-less, our sample of this variety was not totally hull-less, which can explain its position in the plot. CDC Bold (no. 25) is also an outsider compare to the hulled samples. This variety has low contents of T-NSP, T-AX, I-AX and cellulose, and is therefore more similar to the hull-less samples. Also, the Norwegian variety Olve (no. 22) is atypical among the hulled samples due to its low starch content and high amounts of T-NSP, I-NSP, T-AX, I-AX and cellulose. The high-amylose variety (no. 37) does not differ from other atypical starch varieties in the biplot, but is located close to the protein and β-glucan contents, as this variety had the highest protein and β-glucan contents, and a lower amount of starch.

Seen from both Fig. 1(a) and (b), the characteristic of hull and hull-less is explained by PC1, as found by (Andersson et al., 1999), while the type of starch is explained by both PC1 and PC2.

The PCA plots also give information about the inter-correlations between the analyzed chemical parameters. The chemical components lying close to each other will be positively related, and the components, located in opposite directions along one of the PC axes, will be negatively related. As seen from Fig. 1(a), and the simple correlation study (not shown), the content of β-glucan was significantly positively correlated with all the parameters in its quadrant, with a strong correlation to S-NSP and protein. β-Glucan content was significantly and negatively related to starch, cellulose and amylose contents as well, as the parameters in the cluster far to the right on the PC1 axis. In contrast to our findings, Bhatty (1999) found that β-glucans were positively correlated with total NSP content in barley, as Asp, Mattsson, and Onning (1992) had shown in oats. Furthermore, our results were not in agreement with those of Li, Vasanthan, Rossnagel, and Hoover (2001a), who reported no correlation between β-glucan content and amylose content.

All the parameters in the quadrant down to the right were also significantly correlated. Insoluble NSP was strongly correlated with the amount of total and insoluble arabinoxylans. This could indicate that the insoluble NSP fraction and the insoluble arabinoxylans had similar variation and distribution in their contents.

Interestingly, the amounts of total and insoluble arabinoxylans (T-AX, I-AX) were strongly negatively correlated with their substitution patterns (A/X). This means that, the higher content of arabinoxylans (AX), the less was the branching. Also, since there was a significantly negative relationship between the amount of AX and β-glucan content, the varieties with more β-glucans had less arabinoxylans.

Total starch content and total cellulose content were significantly negatively correlated. Starch was also negatively correlated with total NSP and β-glucan contents as reported by Newman and Newman (1991). A weak, but significantly negative correlation between protein content and starch was observed, as reported by Li et al. (2001a).

As seen from the principal component analysis (PCA) plot (Fig. 1(b)), the hull-less and atypical amylose varieties had high contents of β-glucans, protein, soluble NSP, and relativly high amounts of soluble arabinoxylans. The hull-less varieties had relatively high degrees of branching in the total and insoluble arabinoxylans, and a lower content of I-NSP as well as lower A/X ratio in S-AX.

Hulled and normal amylose samples had a lower amounts of β-glucans, protein, soluble NSP, and a low degree of substitution in the T-AX and I-AX. In contrast, the contents of insoluble NSP and total and insoluble arabinoxylans were high. A higher amount of arabinogalactans was also seen in all fractions (T-AG, I-AG, S-AG) compared to the hull-less and the atypical varieties.

The Norwegian 6- and 2-rowed genotypes contained little β-glucans, protein, S-NSP, or S-AX. Also, the A/X ratio was generally low in all fractions, with some exceptions in the soluble part. However, the amounts of total NSP and total and insoluble arabinoxylans and arabinogalactans were high.

The results from the present study show that barley varieties have a wide diversity in polysaccharide content and composition, and that these variations are mainly associated with differences in hull and starch types. A relatively wide variation was also detected within these groups, which can be exploited further to improve quality in barley for different applications in many areas, such as in health and nutrition, food and feed, as well as the brewing industry. The analyzed hull-less and atypical amylose varieties seem suitable for human consumption where high soluble fibre and nutritive contents are desirable. These varieties had high contents of β-glucans, S-NSP (S-AX), protein and lower starch content, and could therefore also be suitable for functional food products aimed at health benefits and cancer prevention.

For the feed and the brewing industries, which prefer a low content of β-glucans, the Norwegian 6- and 2-rowed varieties would, in addition to hulled and normal samples, be appropriate. These samples also contained high amounts of total and insoluble NSP and had high contents of total arabinoxylan, which may contribute to problems similar to those of β-glucans.

Stable quality characteristics and chemical compositions are claimed from the industry. Since the variation in chemical composition are large, depending on both varietal differences and environmental factors, further investigations are needed to identify varieties with a desirable and stable grain quality for industrial and other purposes.

4. Conclusion

Starch was the major constituent of barley, accounting for 51–64%, followed by total non-starch polysaccharides (23–41%). The content of total arabinoxylans in this material was higher (7–16%) than reported in earlier findings. Due to the absence of husk, the hull-less barley varieties were lower in non-starch polysaccharide content, but higher in protein and β-glucans than the hulled samples. The waxy and high-amylose varieties were high in protein, β-glucans, and soluble fibre. Generally, the normal hulled varieties contained a high amount of total NSP and had more insoluble than soluble NSP. On the other hand, atypical hull-less and atypical amylose genotypes had more soluble than insoluble NSP.

By PCA and the large number of analysis of the different barley varieties, an opportunity to study the correlation between the different chemical components and to classify the different barley samples into groups of different chemical grain quality was possible. This provides a helpful tool for choosing varieties suitable for different applications. A negative correlation between β-glucan and arabinoxylan content was found as well as a strong negative correlation between the amount of AX and the degree of branching. A strong positive correlation was also seen between the β-glucan and protein contents, as well as β-glucans and the amount of soluble NSP.

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