Nuclear Magnetic Resonance and Methylation Analysis-Derived Structural Features of Water-Extractable Arabinoxylans from Barley (*Hordeum vulgare* L.) Malts

Winok Debyser,*,† Margot E. F. Schooneveld-Bergmans,‡ Guy Derdelinckx,§ Piet J. Grobet,|| and Jan A. Delcour†

Laboratory of Food Chemistry, Center for Malting and Brewing Science, and Center for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, B-3001 Heverlee, Belgium, and Department of Food Science, Wageningen Agricultural University, P.O. Box 6700 EV, Wageningen, The Netherlands

Water-extractable arabinoxylans (WEAX) were precipitated with ethanol (65%, v/v) in water extracts of six barley malts. The precipitates consisted of 82−89% arabinoxylan (carbohydrate basis) with arabinose to xylose ratios from 0.60 to 0.76. The WEAX recovered represented up to 50% of all WEAX present in barley malt (43−49.5%). Methylation analysis of these WEAX showed a low proportion of *O*-3 monosubstituted xylose residues (5.1−7.1%), a high proportion of disubstituted xylose residues (24.8−28.0%), and the presence of *O*-2-monosubstituted xylose residues (5.1−6.8%). Relative proportions of unsubstituted, monosubstituted, and disubstituted xylose resulting from the methylation analysis were confirmed by ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectral data. Calculations from ^{1}H-NMR spectral data appear to overestimate the level of *O*-2-monosubstituted xylose residues. Size exclusion chromatography could not reveal significant differences in WEAX molecular weight profiles between the six malts. The molecular weight profiles showed a peak at about 38 kDa.

Keywords: *Arabinoxylan; barley malt; structure; nonstarch polysaccharides*

INTRODUCTION

Arabinoxylans constitute 4−10% of the barley grain (Henry, 1986; Lehtonen and Aikasalo, 1987). They comprise respectively 20−25% (Fincher, 1975; Ballance and manners, 1978) and 85% (McNeil et al., 1975) of the cell wall polysaccharides of endosperm and aleurone layers. The detailed study of barley arabinoxylans is recent, and contradictory results concerning the importance in the brewing process (Cach and Annemuller, 1995; Schwarz and Han, 1995), more particullary with regard to wort viscosity and/or filtration (Ducroo and Frelon, 1989; Viëtor et al., 1993) and beer haze formation (Coote and Kirsop, 1976), necessitate further work in this area. For barley, structural features of both water- and alkali-extractable arabinoxylans have been reported in the past (Viëtor et al., 1992, 1994; Oscarsson et al., 1996). Viëtor et al. (1992, 1994) studied structural features of alkali-extractable arabinoxylans of barley malt, but structural data of water-extractable arabinoxylans (WEAX) from barley malt are, to the best of our knowledge, not available.

Arabinoxylans consist of a backbone of β-(1→4)-D-xylopyranosyl residues (Xyl), substituted mainly with α-L-arabinofuranosyl residues at *O*-2 (2-Xyl), *O*-3 (3-Xyl), or both *O*-2 and *O*-3 (2,3-Xyl) (Figure 1). Viëtor et al. (1992, 1994) elucidated the structure of water-insoluble cell wall (WIS) material extracted with barium hydroxide solutions from dehusked barley and malt.

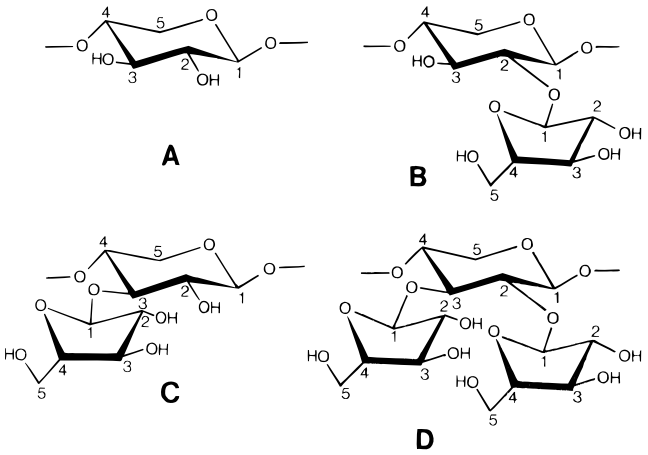

Figure 1. Structural elements of arabinoxylans from barley: (A) unsubstituted xylose residue, (B) xylose residue substituted at *O*-2 with arabinose, (C) xylose residue substituted at *O*-3 with arabinose, and (D) xylose residue substituted at *O*-2 and *O*-3 with arabinose.

Graded ethanol precipitation of WIS resulted in fractions in which the arabinose to xylose (Ara/Xyl) ratio increased with ascending ethanol concentration. Cleemput et al. (1995) found similar properties for wheat WEAX. In line with findings for rye (Vinkx, 1995), Viëtor et al. (1992) found a strong correlation between the Ara/Xyl ratio of malt WIS fractions and the relative levels of 2-Xyl and 2,3-Xyl. Arabinoxylans were partly degraded during malting. Malt WIS tended to precipitate at somewhat lower ethanol concentrations than barley WIS, but there was no significant difference in molecular weight distribution between barley and malt WIS. Recently, Oscarsson et al. (1996) studied the WEAX isolated from 16 covered or naked barleys.

* Author to whom correspondence should be addressed [tel, (+32) 16 32 15 82; fax, (+32) 16 32 19 97; e-mail, jan.delcour@agr.kuleuven.ac.be].
† Laboratory of Food Chemistry.
‡ Department of Food Science.
§ Center for Malting and Brewing Science.
|| Center for Surface Chemistry and Catalysis.

S0021-8561(97)00001-0 CCC: $14.00

About 44% of the Xyl residues were substituted, of which a considerable part only at *O*-2.

In this study we isolated WEAX from barley malts. The arabinoxylans were characterized to investigate potential differences between malts from different varieties and to investigate whether structural features of WEAX from barley malt can be related to structural data concerning the water- and alkali-extractable arabinoxylans from barley and the alkali-extractable arabinoxylans from barley malt.

EXPERIMENTAL PROCEDURES

Chemicals. All chemicals were of analytical or best available grade. β-D-Allose and α-amylase solution (type XII-A, from *Bacillus licheniformis*, A3403) were from Sigma, St. Louis, MO. Standard pullulans (P-82) were delivered by Showa Denko K.K., Tokyo, Japan.

Barley Malt. Six commercial barley malts, i.e., three two-rowed spring barley varieties (Alexis, Caruso, and Prisma), one two-rowed winter barley variety (Clarine), and two malts from a six-rowed winter barley variety (Plaisant malt samples 1 and 2), were kindly supplied by Cargill Malt Division, Herent (Belgium). For the isolation of WEAX, malts were ground to pass a 1.0 mm sieve using a Cyclotec sample mill from Tecator, Höganäs, Sweden.

Isolation of WEAX. Arabinoxylans were isolated from barley malt according to the procedure of Cleemput et al. (1993) with preheating (5 h at 130 °C) of samples of ground barley malt (150 g) prior to extraction with water (5/1, v/w; 15 min, 30 °C). Arabinoxylans were precipitated in the water extracts at 65% ethanol (v/v). The precipitates were dissolved in water and reprecipitated at a final ethanol concentration of 65%. The precipitates were washed with aliquots of ethanol (95%) and acetone and dried for 24 h at 45 °C.

Determination of Neutral Sugar Composition. The neutral sugars of the WEAX were estimated by gas chromatography (GC). Samples were hydrolyzed in 2.0 M trifluoroacetic acid for 60 min (110 °C). The sugars were reduced and acetylated (Englyst and Cummings, 1984). Alditol acetates were analyzed by GC as described by Cleemput et al. (1993). WEAX contents of barley were determined as described by Cleemput et al. (1993) and calculated as [(Ara + Xyl) − 0.67Gal] to correct for the presence of arabinogalactan (Fincher and Stone, 1974) in the water extracts. All analyses were carried out at least in duplicate.

Protein Determination. Protein contents were determined by the method of Lowry et al. (1951) with bovine serum albumin as standard.

Methylation Analysis. The method of Hakamori (1964), modified by Sandford and Conrad (1966), was used for methylation analysis. After methylation, samples were hydrolyzed (2.0 M trifluoroacetic acid, 1 h, 121 °C) and converted to alditol acetates (Gruppen et al., 1992). The samples were analyzed with GC and gas chromatography−mass spectrometry (GC−MS) as described by Gruppen et al. (1992). Relative proportions of the methylated alditol acetates could be calculated with the GC results. Due to the coelution of 2-*O*-methylxylitol and 3-*O*-methylxylitol acetates with GC, their relative amounts were calculated from the relative abundance of the peaks at the ratio molecular mass to charge 117 and 129 specific for respectively 2-*O*-methylxylitol and 3-*O*-methyl xylitol.

^{1}H-NMR Spectroscopy. ^{1}H-NMR spectra were recorded with a Bruker AM 300 spectrometer (Karlsruhe, Germany) at 85 °C. Samples were deuterium exchanged by dissolving (two times) in D_2O and lyophilization (two times). Acetone was used as internal standard (δ 2.2). Pulse repetition time was 2 s. The number of scans was typically 7000. Signals were assigned based on previous literature spectral data (Viëtor et al., 1992; Vinkx et al., 1993; Hoffman et al., 1992b). As done previously by Oscarsson et al. (1996), the difference in integral of the two peaks corresponding to the anomeric region of Ara residues doubly bound to Xyl (δ 5.29 and 5.22) was taken as a measure for the relative amount of 2-Xyl. This assumption, the ^{1}H-NMR spectral data, and the Ara/Xyl ratios allowed calculation of the proportions of unsubstituted Xyl (u-Xyl), 2-Xyl, 3-Xyl, and 2,3-Xyl.

Table 1. Water-Extractable Arabinoxylan Contents (% of dry malt) of Six Barley Malts and Their Arabinose to Xylose Ratios[a]

barley malt	total WEAX		WEAX preparations						
	%	Ara/Xyl	Ara	Xyl	Man	Gal	Glu	Ara/Xyl	protein
Alexis	0.68	0.62	33	56	3	4	5	0.60	19.5
Caruso	0.66	0.65	35	53	3	4	5	0.66	23.1
Clarine	0.49	0.67	37	48	4	3	8	0.76	18.1
Plaisant 1	0.69	0.69	34	48	1	3	14	0.72	18.4
Plaisant 2	0.67	0.67	33	49	2	2	13	0.68	18.3
Prisma	0.69	0.65	36	51	1	5	7	0.70	24.4

[a] Neutral sugar composition (% of total sugar content), arabinose to xylose ratio, and protein content (%) of water-extractable arabinoxylan preparations from six barley malts. Abbreviations: WEAX, water-extractable arabinoxylan; Ara/Xyl, arabinose to xylose ratio; Ara, arabinose; Xyl, xylose; Man, mannose; Gal, galactose; Glu, glucose.

Size Exclusion Chromatography. Samples (2.0 mg) of the dissolved isolated arabinoxylans were dissolved in 1.0 mL of 0.3% NaCl and separated on a Jordi aqueous GPC (Alltech, Bellingham, MA) glucose-bound column (100 nm, 250 × 10 mm) by elution with 0.3% NaCl (1.5 mL/h at room temperature). Sugars were measured using a R-400 refractive index detector (Waters Associates, Milford, MA). Molecular weight markers were Shodex standard P-82 pullulan (Showa Denko K.K., Tokyo, Japan), 1.0 mg/mL, with molecular weights of 78.8×10^4, 40.4×10^4, 21.2×10^4, 11.2×10^4, 3.74×10^4, 2.28×10^4, 1.18×10^4, and 0.59×10^4 Da.

RESULTS AND DISCUSSION

Isolation of Water-Extractable Malt Arabinoxylans. Precipitation with 65% ethanol yielded up to 50% of the total WEAX present in barley malt (Table 1). Higher ethanol concentrations yielded too high arabinogalactan and glucan contaminations (data not shown).

Neutral Sugar Analysis. The neutral sugar composition of the isolated WEAX is given in Table 1. The arabinoxylan content (carbohydrate basis) varied from 82% to 89%. The Ara/Xyl ratios varied from 0.60 to 0.76. The protein content of the WEAX preparations varied from 18.1% to 23.4%, indicating that malt contains a fraction of protein or enzymatically hydrolyzed protein that is extractable with water and coprecipitates with ethanol upon raising the ethanol concentration.

Methylation Analysis. The relative proportions of u-Xyl, 2-Xyl, 3-Xyl, and 2,3-Xyl are given in Table 2.

Variation in Levels of u-Xyl. The lowest variation was found in the percentage for u-Xyl (58.2−61.5%). A greater variation in the percentage for u-Xyl (47−62%) was mentioned for WEAX from 16 unmalted barleys (Oscarsson et al., 1996). Viëtor et al. (1992) found comparable results for alkali-extractable barley and malt (cv. Triumph) arabinoxylans, respectively, 57% and 59% u-Xyl. The barley aleurone cell wall arabinoxylans have a higher level of u-Xyl (67−68%) (McNeil et al., 1975; Bacic and Stone, 1981). A lower proportion of u-Xyl was found (59%) (Bacic and Stone, 1981) for the water-extractable fraction of these aleurone cell wall arabinoxylans.

Variation in Levels of 2-Xyl. The levels of 2-*O*-monosubstituted Xyl varied from 5.1% to 6.8%, rather low levels in comparison with levels in WEAX from barley (6−15%) (Oscarsson et al., 1996) and from barley and malt WIS (respectively 10% and 11%) (Viëtor et al., 1992).

Table 2. Proportions (%) of Un-, Mono-, and Disubstituted Xylose in Water-Extractable Arabinoxylan from Barley Malts, Calculated from Methylation Analysis Data and ^{1}H-NMR Spectral Data[a]

barley malt	u-Xyl	2-Xyl	3-Xyl	2,3-Xyl	t-Xyl
		Methylation Analysis			
Alexis	61.5	5.2	6.9	24.8	1.52
Caruso	60.9	6.6	6.1	24.8	1.60
Clarine	58.2	6.8	5.1	28.0	1.55
Plaisant 1	58.4	6.7	5.5	27.4	2.03
Plaisant 2	59.6	5.1	7.1	26.7	1.47
Prisma	58.9	13.3[b]		26.0	1.88
		^{1}H-NMR Analysis			
Alexis	59.7	10.1	10.4	19.7	
Caruso	59.0	9.6	6.3	25.0	
Clarine	54.4	9.3	5.9	30.4	
Plaisant 1	57.0	9.8	3.6	29.0	
Plaisant 2	57.8	10.2	6.2	25.8	
Prisma	55.4	12.4	6.8	25.4	

[a] Abbreviations: u-Xyl, β-(1→4)-linked D-xylopyranosyl residue unsubstituted; 2-Xyl, β-(1→4)-linked D-xylopyranosyl residue substituted with α-L-arabinofuranosyl residue at *O*-2; 3-Xyl, β-(1→4)-linked D-xylopyranosyl residue substituted with α-L-arabinofuranosyl residue at *O*-3; 2,3-Xyl, β-(1→4)-linked D-xylopyranosyl residue substituted with α-L-arabinofuranosyl residues at *O*-2 and *O*-3; t-Xyl, terminal D-xylopyranosyl residue. [b] Sum of 2-Xyl and 3-Xyl.

Variation in Levels of 3-Xyl. The amounts of 3-Xyl varied from 5.1% to 7.1% (Table 2). WEAX from barley contain relatively more 3-Xyl (11−20%) (Oscarsson et al., 1996). The levels of 3-Xyl from barley and malt WIS are also higher (14%) (Viëtor et al., 1992). Comparison with other literature data is difficult as several authors did not separately mention the levels of 3-Xyl and 2-Xyl. For barley aleurone cell wall arabinoxylans 23−24% of the Xyl residues were 2-Xyl or 3-Xyl (McNeil et al., 1975; Bacic and Stone, 1981). For the water-extractable fraction of barley aleurone cell walls, the proportion of 2-Xyl and 3-Xyl was 29% (Bacic and Stone, 1981).

Variation in Levels of 2,3-Xyl. About 24 to 28% of the Xyl residues were disubstituted (Table 2). This is more than was found in WEAX from barley (18−24%) (Oscarsson et al., 1996). Alkali-extractable arabinoxylans from barley and malt have 19% and 16% 2,3-Xyl, respectively (Viëtor et al., 1992). The proportion of 2,3-Xyl was 8−10% for arabinoxylans from barley aleurone cell walls (McNeil et al., 1975; Bacic and Stone, 1981) and 12% for the water-soluble fraction of these arabinoxylans (Bacic and Stone, 1981).

^{1}H-NMR Analysis. Details of the ^{1}H-NMR spectra of WEAX are shown in Figure 2. There were only low levels of 3-Xyl (δ 5.39) and high levels of 2,3-Xyl (δ 5.29 and 5.22) present. The unresolved signals downfield from the peaks at δ 5.29 and 5.22 are the result of two neighboring 2,3-Xyl residues (Hoffman et al., 1992a; Vinkx et al., 1993; Cleemput et al., 1993). The unresolved signal downfield of the peak at δ 5.29 could also be assigned to 2-Xyl (Vietor, 1992; Vinkx, 1995). Table 2 lists the proportion of un-, mono-, and disubstituted Xyl residues in WEAX of the different malts.

The highest discrepancy between ^{1}H-NMR and methylation data was found for the 2-*O*-monosubstituted Xyl residues. Apparently, with the ^{1}H-NMR spectral data, an overestimation of the levels of 2-Xyl is made. Methylation analysis data showed smaller differences in WEAX fine structure between malts than the ^{1}H-NMR calculations, especially in the levels of 3-Xyl. However, the reliability of integrating 3-Xyl ^{1}H-NMR signals can be questioned as the peak is broad and of low relative intensity (Figure 2).

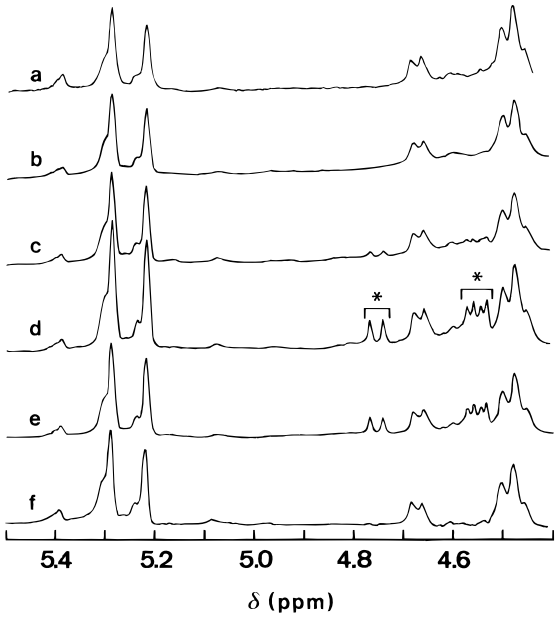

Figure 2. Details of ^{1}H-NMR spectra of water-extractable arabinoxylan isolated from six barley malts (D_2O, 85 °C, 300 MHz). δ 5.2−5.4: region of signals from arabinofuranosyl residues. δ 4.4−4.7: signals from xylopyranosyl residues (Vietor, 1994). Signals from β-glucan are indicated with an asterisk (Vinkx, 1995); a, Alexis; b, Caruso; c, Clarine; d, Plaisant 1; e, Plaisant 2; f, Prisma.

The WEAX preparations of Plaisant 1 and 2 and, to a lesser extent, for Clarine contained some β-glucan (Vinkx, 1995) as indicated in Figure 2.

Gel Permeation Analysis. Gel permeation profiles of the WEAX are shown in Figure 3. The profiles are very similar, and the average molecular weight was about 38 kDa. However, small amounts of high molecular weight compounds are present. The molecular weight estimations for water-soluble arabinoxylans from barley are as high as 10^6 Da (Forrest and Wainwright, 1979; Voragen et al., 1987). This confirms the degradation of water-soluble arabinoxylans during malting (Vietor et al., 1992). According to Henry (1988), the total pentosan content during malting changes relatively little, when compared to that of β-glucan. Thus, the degradation of arabinoxylans during malting apparently does not result in a great loss of pentosan from the grain, in contrast with observations for β-glucan (Bamforth, 1982; Henry, 1988). Both barley and barley malt contain comparable levels of WEAX arabinoxylans (Oscarsson, 1996; Debyser et al., 1997). As a result, we can conclude that malting does not lead to great increases in arabinoxylan solubility.

CONCLUSIONS

Arabinoxylan preparations precipitated from water extracts at 65% contained up to 89% arabinoxylan (on carbohydrate basis). Methylation and ^{1}H-NMR analysis revealed some differences in substitution patterns for WEAX of malts of different barley varieties. The isolated WEAX had a relative high proportion of 2,3-Xyl and a low proportion of 3-Xyl. Compared with other barley and barley malt arabinoxylan literature data, the level of u-Xyl seems to be less variable. ^{1}H-NMR seems to overestimate the levels of 2-Xyl. Gel permeation profiles of the WEAX showed an average molecular weight of 38 kDa, illustrating the degradation of WEAX during malting.

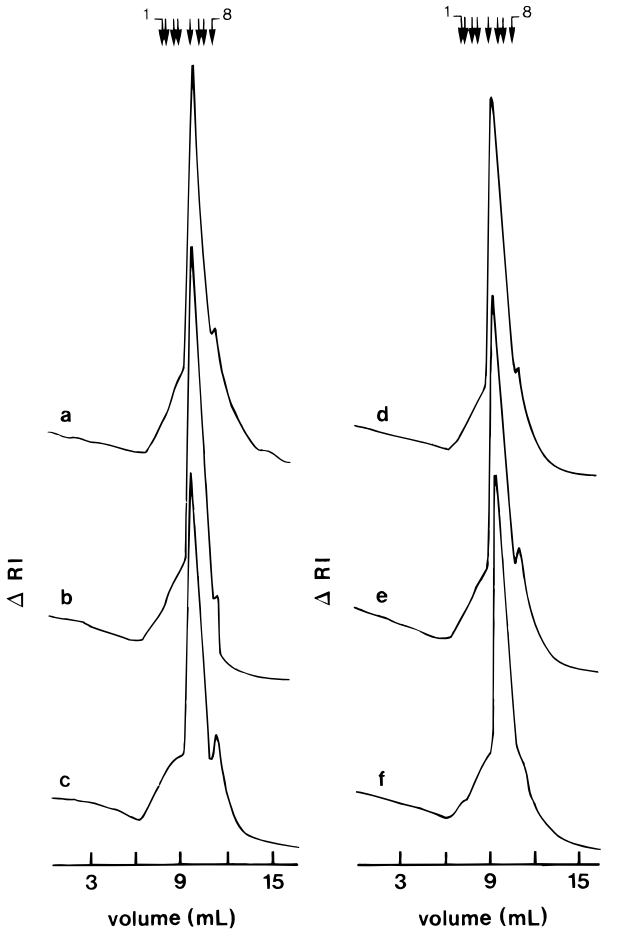

Figure 3. Gel permeation profiles from water-extractable arabinoxylans isolated from six barley malts. Retention times of pullulan standards with molecular weight 78.8×10^4, 40.4×10^4, 21.2×10^4, 11.2×10^4, 3.74×10^4, 2.28×10^4, 1.18×10^4, and 0.59×10^4 are indicated as 1−8, respectively; a, Alexis; b, Caruso; c, Clarine; d, Plaisant 1; e, Plaisant 2; f, Prisma.

ABBREVIATIONS USED

Ara, arabinose; Ara/Xyl, ratio of arabinose to xylose; Gal, galactose; GC, gas chromatography; GC-MS, gas chromatography−mass spectrometry; Glu, glucose; Man, mannose; NMR, nuclear magnetic resonance; Xyl, xylose; WEAX, water-extractable arabinoxylans; WIS, water-insoluble cell wall material.

ACKNOWLEDGMENT

We thank L. Van Den Ende for technical assistance.

LITERATURE CITED

Bacic, A.; Stone, B. A. Chemistry and organization of aleurone cell wall components from wheat and barley. *Aust. J. Plant Physiol.* **1981**, *8*, 475−495.

Ballance, G. M.; Manners, D. J. Structural analysis and enzymic solubilisation of barley endosperm cell walls. *Carbohydr. Res.* **1978**, *61*, 107−118.

Bamforth, C. W.; Martin, H. L. β-Glucan and β-glucan solubilase in malting and mashing. *J. Inst. Brew.* **1981**, *87*, 365−371.

Cach, N. C.; Annemuller, G. Ein Beitrag über die Pentosane im Prozeβ der Bierherstellung - sind sie wichtig oder technologisch unbedeuted (Contribution on the pentoses in the beer process−are they important or insignificant technologically?). *Monatssch. Brauwiss.* **1995**, *48*, 232−241.

Cleemput, G.; Roels, S. P.; van Oort, M.; Grobet, P. J.; Delcour, J. A. Heterogeneity in the structure of water-soluble arabinoxylans in European wheat flours of variable bread-making quality. *Cereal Chem.* **1993**, *70*, 324−329.

Cleemput, G.; van Oort, M.; Hessing, M.; Bergmans, M. E. F.; Gruppen, H.; Grobet, P. J.; Delcour, J. A. Variation in the degree of D-xylose substitution in arabinoxylans extracted from an European wheat flour. *J. Cereal Sci.* **1995**, *22*, 73−84.

Coote, N.; Kirsop, B. H. A haze consisting largely of pentosan. *J. Inst. Brew.* **1976**, *82*, 34.

Debyser, W.; Derdelinckx, G.; Delcour, J. A. Arabinoxylans and arabinoxylan hydrolysing activities in barley malts and the worts derived from them. *J. Cereal Sci.* **1997**, *26*, 67−74.

Ducroo, P.; Frelon, P. G. Improvement of beer production by the use of β-glucanase-pentosanase from *Disporotrichum dimorphosporum*. *European Brewery Convention. Proceedings of the 22nd Congress*; Oxford University Press Inc.: New York, 1989; pp 445−452.

Englyst, H. N.; Cummings, J. H. Simplified method for the measurement of total non-starch polysaccharides by gas - liquid chromatography of constituent sugars as alditol acetates. *Analyst* **1984**, *109*, 937−942.

Fincher, G. B. Morphology and chemical composition of barley endosperm cell walls. *J. Inst. Brew.* **1975**, *81*, 116−122.

Fincher, G. B.; Stone, B. A. A water-soluble arabinogalactan-peptide from wheat endosperm. *Aust. J. Biol. Sci.* **1974**, *27*, 117−132.

Fincher, G. B.; Stone, B. A. Cell walls and their components in cereal grain technology. In *Advances in Cereal Sciences and Technology Vol. VIII*; Pomeranz, Y., Ed.; American Association of Cereal Chemists: St. Paul, MN, 1986; pp 207−295.

Forrest, I. S.; Wainwright, T. The mode of action of β-glucans and pentosans in barley endosperm cell walls. *J. Inst. Brew.* **1977**, *83*, 279−286.

Gruppen, H.; Hamer, R. J.; Voragen, A. G. J. Water-unextractable cell wall material from wheat flour. I. Extraction of polymers with alkali. *J. Cereal Sci.* **1992**, *16*, 41−51.

Hakomori, S. A. A rapid permethylation of glycolipid, and polysaccharide catalysed by methylsulfinyl carbanion in dimethyl sulfoxide. *J. Biochem.* **1964**, *55*, 205−208.

Henry, R. J. Genetic and environmental variation in the pentosan and β-glucan contents of barley, and their relation to malting quality. *J. Cereal Sci.* **1986**, *4*, 269−277.

Henry, R. J. Changes in β-glucan and other carbohydrate components of barley during malting. *J. Sci. Food Agric.* **1988**, *42*, 333−341.

Hoffmann, R. A.; Geijtenbeek, T.; Kamerling, J. P.; Vliegenthart, J. F. G. ^{1}H-n.m.r. study of enzymically generated wheat-endosperm arabinoxylan oligosaccharides: structures of hepta- to tetradecasaccharides containing two or three branched xylose residues. *Carbohydr. Res.* **1992a**, *223*, 19−44.

Hoffmann, R. A.; Kamerling, J. P.; Vliegenthart, J. F. G. Structural features of a water-soluble arabinoxylan from the endosperm of wheat. *Carbohydr. Res.* **1992b**, *226*, 303−311.

Lehtonen, M.; Aikasalo, R. Pentosans in barley varieties. *Cereal Chem.* **1987**, *64*, 133−134.

Lowry, O. H.; Rosebrough, N. J.; Farr, A. L.; Randall, R. Y. Protein measurement with the folin phenol reagent. *J. Biol. Chem.* **1951**, *193*, 265−275.

McNeil, M.; Albersheim, P.; Taiz, L.; Jones, R. L. The structure of plant cell walls. *Plant Physiol.* **1975**, *55*, 64−68.

Oscarsson, R.; Andersson, R.; Salomonsson, A.-C.; Åman, P. Chemical composition of barley samples focussing on dietary fibre components. *J. Cereal Sci.* **1996**, *24*, 161−170.

Sanford, P. A.; Conrad, H. E. The structure of the Aerobacter aerogenes A3(S1) polysaccharide. I. A reexamination using improved procedures for methylation analysis. *Biochemistry* **1996**, *5*, 1508−1517.

Schwarz, P. B.; Han, J.-Y. Arabinoxylan content of commercial beers. *J. Am. Soc. Brew. Chem.* **1995**, *53*, 157−159.

Viëtor, R. J.; Voragen, A. G. J. Composition of non-starch polysaccharides in wort and spent grain from brewing trials with malt from a good malting quality barley and a feed barley. *J. Inst. Brew.* **1993**, *99*, 243−248.

Viëtor, R. J.; Angelino, S. A. G. F.; Voragen, A. G. J. Structural features of arabinoxylans from barley and malt cell wall material. *J. Cereal Sci.* **1992**, *15*, 213−218.

Viëtor, R. J.; Hoffmann, R. A.; Angelino, S. A. G. F.; Voragen, A. G. J.; Kamerling, J. P.; Vliegenthart, J. F. G. Structures of small oligomers liberated from barley arabinoxylans by endoxylanase from Aspergillus awamori. *Carbohydr. Res.* **1994**, *254*, 245−255.

Vinkx, C. J. A. Structure and properties of arabinoxylans from rye. Ph.D. Dissertation, Katholieke Universiteit Leuven, Belgium, 1995.

Vinkx, C. J. A.; Reynaert, H. R.; Grobet, P. J.; Delcour, J. A. Physicochemical and functional properties of rye nonstarch polysaccharides. V. Variability in the structure of water-soluble arabinoxylans. *Cereal Chem.* **1993**, *70*, 311−324.

Voragen, A. G. J.; Schols, H. A.; Marius, J.; Rombouts, F. M.; Angelino, S. A. G. F. Non-starch polysaccharides form barley: structural features and breakdown during malting. *J. Inst. Brew.* **1987**, *93*, 202−208.

Received for review December 31, 1996. Revised manuscript received May 20, 1997. Accepted May 28, 1997.[⊗] The receipt of a scholarship from the Vlaams Instituut voor de Bevordering van het Wetenschappelijk-Technologisch Onderzoek in de Industrie (Brussels) is gratefully acknowledged.

JF970001J

[⊗] Abstract published in *Advance ACS Abstracts,* July, 15, 1997.