Quality Assurance and Safety of Crops & Foods ISSN 1757-8361

ORIGINAL ARTICLE

Arabinoxylan and fructan in the malting and brewing process

M. Krahl, S. Müller, M. Zarnkow, W. Back & T. Becker

Technische Universität München, Lehrstuhl für Brau- und Getränketechnologie, Freising-Weihenstephan, Germany

Keywords
arabinoxylan; β-glucan; brewing; dietary fibre; fructan; malting.

Correspondence
M. Krahl, Technische Universität München, Lehrstuhl für Brau- und Getränketechnologie, Weihenstephaner Steig 20, 85354 Freising-Weihenstephan, Germany.
Email: moritz.krahl@wzw.tum.de

Received 10 June 2009; revised 17 August 2009; accepted 4 September 2009

doi:10.1111/j.1757-837X.2009.00035.x

Abstract

Introduction Soluble dietary fibre is of interest in the malting and brewing process for at least two reasons. In the past, brewers feared them because of possible lautering and filtration problems, and thus a prolonged production time of wort and beer. On the other hand, they have beneficial attributes for colonic and consumer's overall health and are a fermentable part of dietary fibre in the human diet. As diseases caused by poor diet or malnutrition are becoming a severe problem in Western countries, interest in health-beneficial compounds like dietary fibre are of growing interest in the diet. *Objectives* In this work, the influence of the malting and brewing process on the content of soluble dietary fibre in malt, wort and beer derived from it was investigated. *Methods* Arabinoxylan was measured by HPAEC/PAD after acidic hydrolisis. Fructan was determined subsequent to enzymatic digestion β-glucan was analysed using calcoflour. Malt and beer analysis were carried out following the methods outlined in MEBAK and EBC. The amount of water-extractable arabinoxylan (WEAX) rapidly increased during malting whereas the brewing and fermentation process showed no influence on the WEAX content in the finished beer. The amount of fructan in most of the investigated cereals was not affected by malting and wort production but decreased to $< 10\%$ of the initial amount during fermentation. An analysis of 40 German wheat beer samples from different breweries showed arabinoxylan contents ranging from 0.87 up to 2.88 $g\,l^{-1}$. The arabinoxylan content correlated very well with the original gravity. *Conclusion* The amount of malt used in beer production and the grist load seems to be the key factors for the arabinoxylan content of the bottled beer. Only negligible amounts of fructans were found in beer, although fructans were present in wort. Higher arabinoxylan contents did not result in increased viscosity of wort and beer.

Introduction

Today, nutrition worldwide is mainly based on only three cereals, wheat, rice and corn. Together, they contribute over 75% to the worlds starch production (FAO, 2009). At the same time, diseases caused by a wrong or unbalanced diet are becoming a severe problem in Western countries. In this regard, the enrichment of bioactive compounds in the malting process with the objective of providing beneficial health effects for consumers is a possible approach to a healthier nutrition. Water-soluble dietary fibre like arabinoxylans (AX), fructans and β-glucans are such cereal components. They can be delivered to the consumer as breakfast cereals, beer or as a part of malt-based beverages, which can be produced using traditional brewing equipment. With the use of alternative fermentation techniques like lactic acid fermentation or fermentation with *Gluconobacter* spp., new non-alcoholic malt-based beverages can be produced. Such beverages are an excellent source of the so-called 'good carbs' (Bamforth, 2005). A number of countries worldwide have already authorized health claims on products containing soluble dietary fibre originating from cereals (Ames & Rhymer, 2008).

The food industry is directing new product development towards the area of functional foods and functional food ingredients, due to the consumer demand for healthier foods. Cereals can be used as sources of non-digestible carbohydrates, which besides promoting several beneficial physiological effects, can also selectively stimulate the growth of *Lactobacilli* and *Bifidobacteria* present in the colon. These bacteria act as prebiotics (Charalampopoulos *et al.*, 2002).

A high intake of dietary fibre, particularly of the soluble type, improves glycaemic control, decreases hyperinsulinaemia and lowers plasma lipid concentrations in patients with type 2 diabetes (Chandalia *et al.*, 2000). Consumption of soluble fibre fractions reduces low-density lipoprotein cholesterol (Brown *et al.*, 1999; Pins & Kaur, 2006) and is inversely correlated with the risk of coronary heart disease (Pereira *et al.*, 2004).

AXs are a part of natural-occurring dietary fibres in the plant kingdom. The chemical structure of AX is based on a chain of linear β(1-4)-D-xylopyranose units, which can be substituted with α-L-arabinofuranose in the O-2 or the O-3 position or both (Hartmann *et al.*, 2005). AXs in the cell wall are partly cross-linked by diferulic acid bridges and possibly other condensation products of ferulic acid (Vinkx & Delcour, 1996), which may complicate their solubilization (Izydorczyk & Biliaderis, 1992). The solubility of AX increases with a higher degree of arabinose substitution or a shorter chain length of the xylan backbone (Hartmann *et al.*, 2005).

Fructans are β-D-linked polymers of fructose. Approximately 15% of the higher plants store fructans (Karppinen *et al.*, 2003). Fructans can be stored in plants in high concentrations as an alternative to starch. The substrate of fructan biosynthesis is sucrose. Chemically, cereal fructans are linear carbohydrates consisting mainly, if not exclusively, of β(2-1)-fructosyl-fructose linkages. A starting α-D-glucose moiety is mostly present but not necessary (Roberfroid, 2005). Plant fructans generally show a degree of polymerization (DP) < 50, although some have been shown to exceed 200 (Chalmers *et al.*, 2005). Fructans are divided into inulin and fructo-oligosaccharides (FOS). Long-chained polymers with a DP > 30 are referred to as inulin, and FOS have a DP of up to 10 (Korakli *et al.*, 2003). These oligosaccharides are food products with interesting nutritional properties. The extent of resistance to enzymatic reactions occurring in the upper part of the gastrointestinal tract allows fructans to become colonic nutrients, as some bacterial species express specific hydrolases and are able to convert these sugars into short-chain fatty acids (SCFA) and/or gases by fermenting them (Delzenne, 2003).

Among plant carbohydrates, AXs and fructans are non-digestible ingredients, which are not degraded or absorbed in the stomach or in the small intestine and reach the colon intact (Corradini *et al.*, 2004). There they are fermented to a large extent (Glitso *et al.*, 1998) by the large bowel microflora to lactic acid and SCFA. Water-extractable AXs (WEAXs) and FOS appear to be more easily fermented than inulin and due to the increase in the faecal butyrate concentration, have even more favourable effects on colonic health (Grasten *et al.*, 2003). Associated with this is the prebiotic effect of soluble dietary fibre, which has been shown to result in enhanced concentrations of probiotics such as *Lactobacili* and *Bifidobacteria* in the colon lumen (Pool-Zobel, 2005). SCFA like propionate, butyrate or lactate are the products of probiotic carbohydrate fermentation. These can be absorbed and metabolized by the host. They are used as an energy source by the colonic epithelial cells (Grasten *et al.*, 2003), as well as they have a beneficial effect on human liver cells. Butyrate is an especially important factor in maintaining normal functions in colonocytes and a protective agent against colon cancer (Topping & Clifton, 2001). SCFA have been shown to inhibit the growth of tumour cells, induce gluthathione *S*-transferases and protect cells from genotoxic activity of 4-hydroxynonenal (Glei *et al.*, 2006).

By decreasing the pH of the colon, SCFA also prevent the growth of pathogenic bacteria (Grasten *et al.*, 2003). The lower pH in the colon in combination with the SCFA significantly increases mineral absorption, especially of calcium, magnesium and zinc from the gut (Greger, 1999). Calcium absorption decreases when people age. Hence, the relative increase in absorption induced by soluble dietary fibre gets more important for elder population groups (Roberfroid, 2005). This better absorption rate of calcium from food is of course of even more interest for people suffering from osteoporosis.

In the brewing process, WEAXs have been associated with some undesirable effects, such as complicating filtration and lautering (Han, 2000; Sadosky *et al.*, 2002). Additionally, there might also be a contribution of WEAXs to the phenomenon of premature yeast flocculation (Koizumi *et al.*, 2008). In particular, wheat adjuncts decreased filterability and increased wort viscosity in some studies (Sadosky *et al.*, 2002; Lu & Li, 2006). However, this observation could not be made for 40 malted wheat samples harvested from 2006 to 2008. No correlation could be found between WEAXs and the resulting wort viscosity (Burberg *et al.*, 2008).

Materials and methods

Samples

All cereal samples were obtained from commercial seed breeders in Germany and were of good malting quality

according to industrial standard requirements. The germination energy was above 96%. Protein content was 12.8% dry weight base (d.w.b.) in wheat, 10.4% d.w.b. in rye and 10.5% d.w.b. in barley, respectively. The analysed beer samples were purchased in Germany from local bottle stores. Wheat and barley malt for pilot-scale brewing trials were purchased from a commercial supplier (Weyermann, Bamberg, Germany). Rye malt was produced in the pilot-scale malting facility of the institute. Industrial samples from the brewing process were taken from a medium-sized Bavarian brewery. Wort samples were cooled immediately after drawing to stop any ongoing reactions, centrifuged and stored at $-18\,^{\circ}C$ until analysis.

Malting

Malting was carried out in a pilot-scale malting facility. One kilogramme of each sample was steeped 2 days and the final degree of steeping was reached during the third day of germination. Germination occurred in tempered climate chambers from Viessmann (Hof, Germany), which guaranteed a constant air humidity of $> 95\%$ to avoid desiccation of the germinating kernels.

Standard malting parameters were 45% moisture content, a germination temperature of $15\,^{\circ}C$ and a germination period of 6 days. The malting parameters of the barley trial are shown in Table 1. Withering of all malts was performed at $50\,^{\circ}C$ for 14 h, kilning 1 h at $60\,^{\circ}C$, 1 h at $70\,^{\circ}C$ and 1 h at $80\,^{\circ}C$ for wheat and rye and 3 h at $80\,^{\circ}C$ for barley, respectively. Samples from the malting process were collected each day after steeping was finished, freeze-dried and stored at $-18\,^{\circ}C$ until analysis.

Table 1 Malting parameters of the statistical malting trial

Sample	Moisture content (%)	Germination temperature (°C)	Germination time (days)
1	37	15	5
2	45	18	5
3	39	12	5
4	39	18	5
5	39	18	5
6	45	12	5
7	45	12	5
8	39	12	5
9	37	15	7
10	45	18	7
11	45	12	7
12	45	12	7
13	45	18	7
14	42	15	7
15	37	15	8
16	37	18	8
17	42	12	8
18	42	15	8
19	42	15	8
20	39	15	8
21	42	18	8
22	42	15	8

Pilot brewing

The brewing trials were conducted in a 60 L pilot-scale brewing plant. The grist load consisted of 60% wheat malt and 40% barley malt. Barley malt was used to guarantee a sufficient amount of husks for a satisfactory lautering process. After infusion mashing, the mash was separated from spent grain using a lauter tun and boiled for 60 min. After separation of the hot break and subsequent wort cooling, fermentation occurred in cylindroconical fermentation tanks. The initial cell count was 5×10^6 cells of top fermenting yeast (*Saccharomyces cerevisiae*). The fermentation temperature was $21\,^{\circ}C$ and storage occurred at $5\,^{\circ}C$ for 2 weeks.

In the pilot-scale brewing plant, samples could be drawn at any time from the brewing process. In the industrial-scale brewery, sample drawing during mashing was not possible due to technical reasons. To stop any enzymatic or thermal reaction, samples were cooled immediately after drawing in ice water, centrifuged and stored at $-18\,^{\circ}C$ until analysis.

Experimental design and statistical analysis

The experimental design was created using the software for the design of experiments (DoE) DesignExpert™ version 7.0 (StatEase Ltd., Minneapolis, MN, USA). The numeric factors of the response surface methodology applied were germination time, degree of steeping and germination temperature (Zarnkow *et al.*, 2005).

The data obtained were analysed using analysis of variance.

Determination of total AX and WEAX in malt, wort and beer

The analysis of AX and WEAX have been carried out similar to the method presented by Houben *et al.* (1997), with minor modifications. Owing to better separation of the monosaccharides glucose and xylose by the CarboPack PA 10 column from Dionex (Sunnyvale, CA, USA), a treatment with glucose oxidase was not necessary in the modified method. For the determination of the total AX content, the samples were milled in a laboratory hammer mill

(Laboratory Mill 3100, Danfoss, Esslingen, Germany). Then, 0.1 g of the sample was dispersed in 4.0 mL of distilled water and 4.0 mL of 4 M HCl and hydrolysed for 60 min in boiling water in a normal laboratory screw-cap test tube. The samples were cooled to room temperature and 4.0 mL of 4.0 M NaOH was added to neutralize the samples. Subsequently, the concentration of monosaccharides was measured by a high-performance anion-exchange chromatography system with pulsed amperometric detection (HPAEC/PAD).

The amount of WEAX was determined in congress wort, which was produced according to the MEBAK and EBC standard method (MEBAK 3.1.4.2, EBC 4.5.1.) (Eerde, 1998; Anger, 2006). Congress wort was used because it is the most common method for malt analysis. All other parameters analysed in this work were also measured in congress wort. Previous trials (data not shown) had showed no influence of the method of mashing on the resulting content of WEAXs in wort. After cooling and subsequent filtration, 3.0 mL of the wort obtained were hydrolysed with 3.0 mL of 4.0 N HCl in a boiling water bath and neutralized as described above. Before analysis by HPAEC/PAD, the chloride ions were removed using OnGuard II Ag cartridges from Dionex. The contents of AX and WEAX were calculated as the sum of the pentose sugars arabinose and xylose multiplied by 0.88 to correct for anhydromonosaccharides (Houben *et al.*, 1997). All analyses were carried out in duplicate. The coefficient of variation was $< 2\%$.

AX in beer samples measured after the removal of carbon dioxide according to the procedure used for wort.

At the same time, the arabinogalactan peptide (AGP) concentration in wort can be measured by the commonly used method (Courtin *et al.*, 2009). AGP has an arabinose content of 0.7 (Van den Bulck *et al.*, 2005); hence, the AGP content in wort can be calculated by the galactose content of the hydrolysed sample. For AGP, the factors 0.88 (pentose sugar) and 0.9 (hexose sugar) were used to correct for the incorporation of water during hydrolysis. AGP can be calculated as 1.516 times the galactose content. This value slightly underestimates because of the peptide moiety representing approximately 4% of the AGP molecular weight (Courtin *et al.*, 2009). In this study, the arabinose values for the calculation of WEAX were corrected for arabinose formerly bound in AGP.

Determination of fructan

The analysis of the fructan content of the samples was performed according to the method presented by Andersen & Sorensen (1999) with some further modifications. For the extraction of fructan, 0.1 g finely ground grist of each sample were mixed with 1.5 mL of water and stirred at 80 °C for 60 min. Following centrifugation, the resulting amount of monosaccharides was measured.

In the enzymatic step, 0.1 mL of inulinase (EC 3.2.1.7, Novozymes, Bagsvaerd, Denmark) was added to 0.2 mL of the supernatant and stirred at 37 °C for 60 min. Subsequently, the resulting monosaccharides were measured.

The amount of fructan in the sample was calculated by subtracting the amount of fructose and the calculated amount of fructose formerly bound in sucrose measured before the enzymatic treatment from the total fructose analysed after the enzymatic step. In this study, final glucose moieties were not taken into account. Only the amount of fructose polymers in the samples was measured. If the possible presence of final glucose moieties are taken into account, the true fructan values might be higher. All analyses were carried out in duplicate. The coefficient of variation was $< 2\%$.

Carbohydrate analysis

The separation of the carbohydrate monomers arabinose (Roth, Karlsruhe, Germany), fructose, glucose, sucrose and xylose (Sigma-Aldrich, Schnelldorf, Germany) was performed using HPAEC/PAD from Dionex. The analysed samples were injected using an AS 50 autosampler; the pump system used was a GP 40 pump. Separation of monosaccharides was carried out using a CarboPac 10 analytical column and detection by an ED 50 detector, all from Dionex.

Eluent A was 250 mM NaOH (Baker, Deventer, The Netherlands) and eluent B was water. The flow rate was 0.25 mL min^{-1} and the injection volume was 2.5 µL. Monosaccharides were separated by isocratic elution (20 min, 5% A). Adjacent polysaccharides and starch were removed from the column (35 min, 80% A). The column was re-equilibrated subsequently (20 min, 5% A). The potential during the detection of the monosaccharides was programmed from $+0.1$ ($t = 0$–0.4 s) to -2 ($t = 0.41$–0.42 s) to 0.6 ($t = 0.43$–0.44 s) and finally – 0.1 ($t = 0.44$–0.5 s). Integration of the resulting signal was performed from $t = 0.2$ to 0.4 s.

Malt analysis

Malt analysis was performed according to the methods outlined in MEBAK and Analytica – EBC. The malt extract was determined using an Anton Paar Alcolyzer (Anton Paar, Graz, Austria) following the MEBAK method 3.1.4.2.2 (EBC 8.2.2). Water content was analysed by the MEBAK method

3.1.4.1 (EBC 4.2) and protein content by the MEBAK method 3.1.4.5.1.1 (EBC 4.3.1). Wort viscosity was measured using a rolling ball viscosimeter AMWn-Automated Micro Viscometer (Anton Paar) at 20 °C according to the MEBAK method 3.1.4.4.2 (EBC 4.8). The β-glucan content was measured using flow injection analysis with calcofluor in a Skalar analytical system (Breda, the Netherlands) according to the MEBAK method 4.1.4.9.2 (EBC 4.16.2) (Eerde, 1998; Anger, 2006).

Results and discussion

AXs and fructans during the malting process

Total AX and WEAX were measured every day during the malting of wheat (*Triticum aestivum*) and rye (*Secale cereale*). Total AXs were 5.5 g/100 g d.w.b. in wheat and 7.0 g/100 g d.w.b. in rye, respectively. The initial WEAX content was 0.78 g/100 g d.w.b. in the wheat sample and 1.4 g/100 g d.w.b. in the unmalted rye. Figure 1 shows the development of the WEAX content during the malting processes for wheat and rye. In wheat during standard malting, the WEAX content increased during the entire germination process. The final WEAX level was 1.54 g/100 g d.w.b. Withering and kilning had no discernable effect. The strongest increase was observed in the first days of germination. At the same time, the increase in WEAX became less pronounced. The WEAX content increased 97% during the entire malting process. DAXS increased from 14% to 28%. The arabinose/xylose ratio decreased from 0.74 to 0.63 during the malting process of wheat.

In rye during the first days of germination, an increase of 75% to 2.45 g/100 g d.w.b. could be observed. From day 4 until the start of the withering process, no further increase could be seen. The WEAX content even slightly decreased. Preliminary trials had shown a significant influence of withering and kilning on the WEAX content of rye. Because of this observation, additional samples were drawn after withering before the starting of the kilning process. Withering showed a small effect; the WEAX content rose by 0.1 g/100 g d.w.b. Kilning, however, had a remarkable effect as the WEAX content increased by 0.4 resulting in 2.9 g/100 g d.w.b. in the malted rye. This is probably due to a cleaving of diferulic acid bridges present in AXs through heat during the kilning process. Thus, WEAX fragments are liberated from the cell walls. This possibility is supported by the fact that rye malts with very high kilning temperatures show significantly lower viscosities than malts kilned at lower temperatures (Braun, 1998). Standard malting of rye resulted in an increase of the WEAX content of 107%. The final DAXS was 41% compared with 20% before malting. The arabinoyse/xylose ratio in rye WEAX decreased from 0.86 to 0.67 during malting.

Barley was malted according to the statistical malting scheme presented in Table 1. The results of the malt analysis are shown in Table 2. Using response surface methodology, the influence of the malting parameters on the resulting attributes can be calculated. The responses analysed in this work were AX content ($R^2 = 0.788$), β-glucan content ($R^2 = 0.953$) and extract content ($R^2 = 0.723$). In the brewing industry, soluble fibre is often believed to increase wort viscosity and thus to result in prolonged lautering and filtration time (Eyben & Duthoy, 1979; Bamforth, 1982; Edney *et al.*, 1998; Jin *et al.*, 2004a, b). Figure 2 shows the highly significant correlation (statistical significance 99.9%; $R = 0.968$; $n = 25$) between the β-glucan content of congress wort and the resulting wort viscosity. In previously

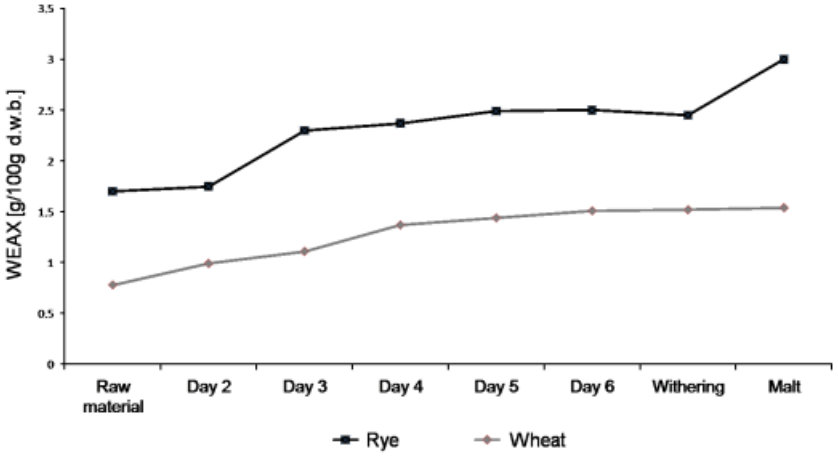

Figure 1 Water-extractable arabinoxylan (WEAX) during the malting of wheat and rye.

published papers, AXs have been associated with the same difficulties in the brewing process as β-glucans (Han & Schwarz, 1996; Li *et al.*, 2005; Lu & Li, 2006). Figure 3 shows the significant negative correlation between WEAX and viscosity (statistical significance 99.9%; $R = 0.812$; $n = 22$). Extract levels in the malted barley samples varied between 81.2% and 82.8% d.w.b. Congress wort viscosity ranged from 1.404 to 1.845 mPa s. The analysed β-glucan levels ranged from 1.787 to 0.043 g L^{-1}. The lowest WEAX content was measured in sample 1 with 0.76 g/100 g d.w.b. and the highest in sample 11 with 1.13 g/100 g d.w.b. Arabinose/xylose ratios of the analysed samples were between 0.59 and 0.65 and thus in the range reported by Debyser *et al.* (1997). The results found in this work strongly support the negative impact of β-glucans on the brewing process. The relationship between WEAX and viscosity published earlier could not be confirmed. The negative correlation found supports the results of Saulnier *et al.* (1995). This is due to the further breakdown of the AX resulting in shorter chain lengths and a lower degree of polymerization in a more intensified malting process (Courtin *et al.*, 2009). Smaller molecules are of less relevance for the resulting wort viscosity. Previous work supports the theory of different effects on viscosity by AXs of different chain lengths and degree of arabinose substitution (Bengtsson *et al.*, 1992). The method used to determine WEAX in this study does not provide information about molecular mass and structure of the WEAX molecules.

Table 2 Results of the malt analysis of the statistical malting trial

Sample	Extract (% d.w.b.)	Viscosity (mPa s)	β-glucan (g L^{-1})	WEAX (g/100 g d.w.b.)
1	81.6	1.769	1.663	0.76
2	82.5	1.411	0.215	0.98
3	81.5	1.845	1.641	0.82
4	81.8	1.554	0.994	0.86
5	82	1.57	0.983	0.83
6	82	1.575	0.990	0.95
7	82.1	1.727	1.546	0.89
8	81.3	1.823	1.787	0.82
9	81.9	1.589	1.148	0.93
10	81.9	1.404	0.089	0.97
11	82.7	1.423	0.369	1.13
12	82.8	1.446	0.318	1.12
13	81.8	1.415	0.043	1.04
14	81.9	1.423	0.269	1.11
15	81.4	1.657	1.231	0.88
16	81.6	1.592	1.058	0.99
17	82.5	1.528	0.886	0.97
18	81.9	1.458	0.516	0.99
19	82.2	1.46	0.513	1.06
20	81.4	1.541	0.964	0.88
21	81.2	1.437	0.291	1.02
22	82.5	1.45	0.473	1.06

d.w.b., dry weight base; WEAX, water-extractable arabinoxylan.

The differing effects of the two soluble dietary fibre fractions β-glucan and WEAX can be explained by the different methods of analysis. The method used for quantification of AXs in this work is measuring all of the AX polymers present in the sample. The degrees of polymerization, molecular size or weight are of no importance for this method. In contrast, flow injection analysis with calcofluor only detects β-glucan molecules with a molecular weight of $> 10^4$ kDa (Jorgensen, 1988; Ullrich *et al.*, 1991). Thus, only the fractions of relevance for the resulting wort viscosity are measured. Smaller degradation products of β-glucan are not detected.

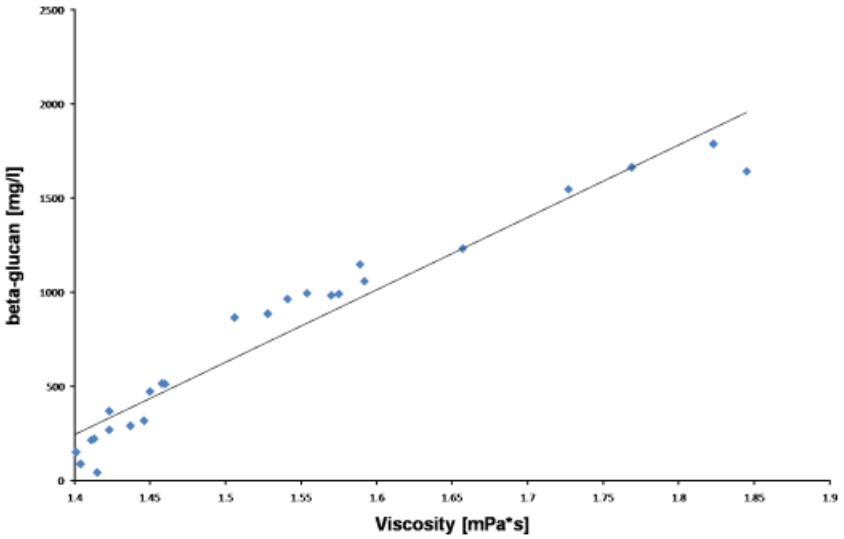

Figure 2 Correlation between β-glucan and viscosity.

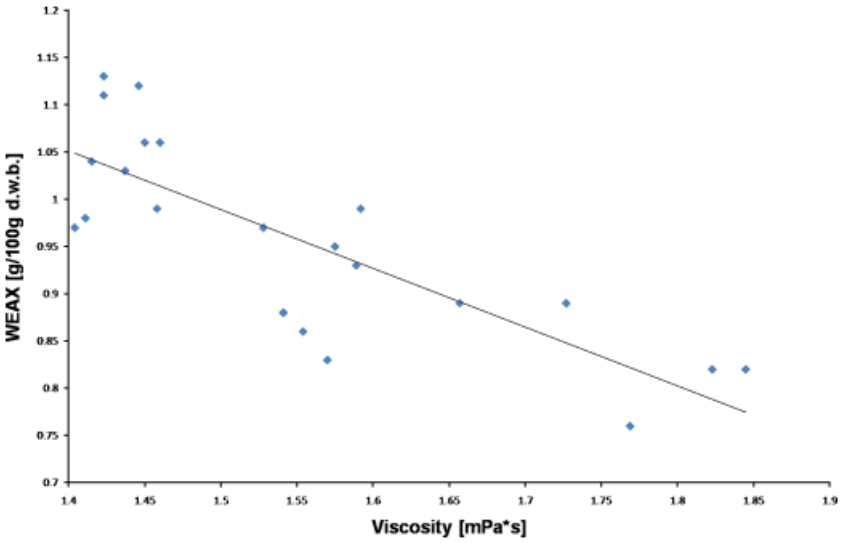

Figure 3 Correlation between water-extractable arabinoxylan (WEAX) and viscosity.

The model used was significant. *P*-values for the three analysed responses were 0.0001 or lower. Terms showing a *P*-value higher then 0.1 were removed by the use of backward elimination. According to the model, the extract content of malted barley is mainly influenced by moisture content and germination time. Germination temperature was of less importance. The β-glucan levels are strongly influenced by germination temperature and germination time but the moisture content also had a significant but lower impact. This supports the thesis that a more intensive germination always results in lower β-glucan levels (Narziss, 1999). In barley, only moisture content and germination time showed a significant impact on the resulting WEAX content. In the model used, the germination temperature did not influence the resulting WEAX levels in malt.

The fructan content in the analysed samples measured after hot water extraction showed no impact of the malting process or of a variation of the malting parameters. The wheat sample contained 0.98 g/100 g d.w.b., the rye sample 3.0 g/100 g d.w.b. and the barley sample 0.75 g/100 g d.w.b., respectively. This observation can be explained by the fact that fructans in contrast to β-glucans and AX are not a part of the cereal cell walls but reserve carbohydrates. In harsh environmental conditions, fructans are used by plants and are associated with freezing tolerance (Crafts-Brandner, 2005). The conditions of the malting process are supposed to be good growing conditions for the embryo; hence, starch is being degraded for the necessary energy supply. As no major changes in the fructan were observed, the authors believe the method used measuring only the fructose polymers in the samples and thus estimating the real amount of fructan as suitable.

AXs and fructans during the brewing process

To determine the influence of the brewing process on the AX content, the parameters original gravity and AX content were analysed during mashing (pilot scale), lautering, wort boiling (pilot and industry scale), fermentation, storage and bottling (industry scale). In order to describe the changes during the process, the quotient between WEAX and original gravity was used. The results are shown in Table 3. At the beginning of the mashing process, the WEAX content is increasing fast. After the sample drawn during the 52 °C rest, no further changes can be seen. Maximum WEAX levels were reached a long time before original gravity reached maximum values. During lautering and wort boiling, WEAX levels are directly linked to original gravity. The quotient is constant. Only after second sparging is the quotient getting lower. Hence, the lixiviation is more pronounced for extract than WEAX, which seems to be entirely in solution. The same observation was made during fermentation, storage, centrifugation, flash pasteurization and bottling.

In analysed beer samples, only traces of fructan were found although cooled wort produced from fructan-rich malts contained up to 2 g L^{-1} of fructose polymers. In order to determine the fate of fructan, enriched wort was fermented. During fermentation $> 90\%$ of the fructans present in the wort were fermented by the yeast (data not shown).

Table 3 WEAX during the brewing process

Process step	WEAX (g L^{-1})	Original gravity (°P)	WEAX/ original gravity
Mashing in 45 °C	2.16	4.77	0.45
52 °C hold	2.40	5.66	0.42
62 °C hold	2.40	13.54	0.18
68 °C hold	2.38	18.42	0.13
72 °C hold	2.37	19.2	0.12
Final mash pumping	2.40	20.4	0.12
End of pilot scale brewing			
Trub wort	2.01	15.08	0.13
First wort	2.44	18.48	0.13
First sparging	2.25	17.02	0.13
Second sparging	0.53	4.07	0.13
Last running	0.22	2.08	0.11
Start of wort boiling	1.53	12.03	0.13
Mid of wort boiling	1.56	12.36	0.13
End of wort boiling	1.58	12.68	0.13
After whirlpool	1.45	12.55	0.13
Fermentation	1.49	12.55	0.13
Storage	1.50	12.55	0.13
Centrifugation	1.51	12.55	0.13
Flash pasteurization	1.49	12.55	0.13
Bottled beer	1.50	12.55	0.13

WEAX, water-extractable arabinoxylan.

AX content of commercial beers

Table 4 shows the results of the analysis of 40 commercially available wheat beers from Germany. In order to guarantee a wide spectrum of different brews, all kinds of wheat beers were chosen. Non-alcoholic, light, pale and dark as well as strong beers were analysed with regard to original gravity, alcohol content and AX content. Original gravity ranged from 6.17 to 16.65°P, alcohol content from 0.43% to 7.07% alcohol by volume and AXs from 0.87 to 2.88 g L^{-1}. Arabinose/xylose ratios in the analysed beer samples were between 0.69 and 0.80. Figure 4 shows the positive correlation between original gravity and AX content of the analysed beers (statistical significance 99.9%; $R = 0.810$; $n = 40$). This correlation supports the findings recently published by Courtin *et al.* (2009).

Conclusions

It can be concluded that the AX content in beer is only influenced by the choice of raw materials and not by the mashing or brewing process or the brewing equipment used. No changes in the AX content could be observed after the end of the malting process. The malting process has a significant influence on the amount of WEAXs in malt, and thus in beer and malt-based beverages made of it. By varying the malting parameters moisture content and germination time, it is possible to influence the WEAX content of barley malts. As WEAX and viscosity were correlated negatively, there is no reason to use malts with low WEAX content. Especially in the production of alternative fermented beverages, soluble dietary fibre might be a valuable health-beneficial bioactive compound. Fructans are present to the same extent in malt as in un-malted cereals but are fermented by the yeast. However, they are potential functional components present in novel malt-based drinks.

Table 4 Results of the analysis of 40 commercial German wheat beers

Sample	WEAX (g L^{-1})	Original gravity (°P)	Alcohol content (% ABV)
1	1.62	12.86	5.33
2	1.12	8.98	3.61
3	1.36	12.82	5.47
4	1.16	12.34	5.61
5	1.54	12.72	5.43
6	1.44	12.69	5.62
7	1.66	12.67	5.54
8	0.87	7.52	3.16
9	1.70	12.55	5.14
10	1.21	11.62	5.11
11	1.71	12.97	5.51
12	1.66	12.74	5.34
13	2.14	16.65	7.07
14	1.13	7.93	3.27
15	1.76	12.99	5.62
16	1.76	12.78	5.61
17	1.20	7.74	3.24
18	1.89	12.68	5.57
19	1.46	12.28	5.29
20	1.39	12.28	5.06
21	1.74	12.82	5.50
22	1.83	12.74	5.58
23	1.12	7.62	3.19
24	1.66	11.90	5.13
25	1.82	11.94	5.30
26	1.69	12.04	5.26
27	1.78	12.20	5.29
28	1.87	11.38	4.91
29	1.14	7.50	3.13
30	1.62	11.84	5.13
31	1.81	12.60	5.39
32	1.10	6.17	0.43
33	1.71	11.63	5.07
34	1.00	7.49	3.14
35	1.84	12.73	5.56
36	1.74	11.99	5.17
37	1.78	12.36	5.32
38	2.15	12.54	5.29
39	1.58	12.62	5.60
40	2.88	16.35	6.27

WEAX, water-extractable arabinoxylan; ABV, alcohol by volume.

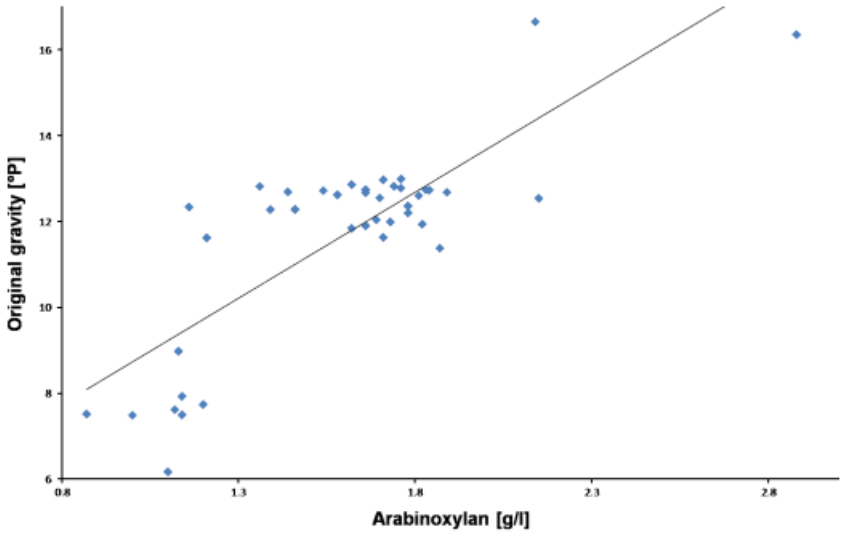

Figure 4 Correlation between original gravity and arabinoxylan in commercial beer samples.

Acknowledgement

This work was supported by the Fond InBev-Baillet Latour.

References

Ames N.P., Rhymer C.R. (2008) Issues surrounding health claims for barley. *Journal of Nutrition*, **138**, 1237s–1243s.

Andersen R., Sorensen A. (1999) An enzymatic method for the determination of fructans in foods and food products – comparison of the results by high performance anion exchange chromatography with pulsed amperemetric detection. *European Food Research and Technology*, **210**, 148–152.

Anger H.-M. (2006). *Brautechnische Analysenmethoden*. Freising, Selbstverlag der MEBAK.

Bamforth C.W. (1982) Barley beta-Glucans – their role in malting and brewing. *Brewers Digest*, **57**, 22–35.

Bamforth C.W. (2005) Beer, carbohydrates and diet. *Journal of the Institute of Brewing*, **111**, 259–264.

Bengtsson S., Andersson R., Westerlund E., Aman P. (1992) Content, structure and viscosity of soluble arabinoxylans in rye grain from several countries. *Journal of the Science of Food and Agriculture*, **58**, 331–337.

Braun F. (1998) *Mälzungs- und Maischversuche zu Möglichkeiten der technologischen Einflussnahme auf ungünstige Fließeigenschaften bei Roggenmalzwürzen unter besonderer Berücksichtigung des Reinheitsgebotes*. Diploma thesis, TU München.

Brown L., Rosner B., Willett W.W., Sacks F.M. (1999) Cholesterol-lowering effects of dietary fiber: a meta-analysis. *American Journal of Clinical Nutrition*, **69**, 30–42.

Burberg F., Hartmann K., Gastl M., Zarnkow M., Krahl M., Back W. (2008) Qualitätsbrauweizen – Ergebnisse der Kleinmälzung der Sortenbetrachtung 2007. *Brauwelt*, **148**, 1030–1034.

Chalmers J., Lidgett A., Cummings N., Cao Y.Y., Forster J., Spangenberg G. (2005) Molecular genetics of fructan metabolism in perennial ryegrass. *Plant Biotechnology Journal*, **3**, 459–474.

Chandalia M., Garg A., Lutjohann D., Von Bergmann K., Grundy S.M., Brinkley L.J. (2000) Beneficial effects of high dietary fiber intake in patients with type 2 diabetes mellitus. *New England Journal of Medicine*, **342**, 1392–1398.

Charalampopoulos D., Wang R., Pandiella S.S., Webb C. (2002) Application of cereals and cereal components in functional foods: a review. *International Journal of Food Microbiology*, **79**, 131–141.

Corradini C., Bianchi F., Matteuzzi D., Amoretti A., Rossi M., Zanoni S. (2004) High-performance anion-exchange chromatography coupled with pulsed amperometric detection and capillary zone electrophoresis with indirect ultra violet detection as powerful tools to evaluate prebiotic properties of fructooligosaccharides and inulin. *Journal of Chromatography A*, **1054**, 165–173.

Courtin C.M., Broekaert W.F., Swennen K., Aerts G., Van Craeyveld V., Delcour J.A. (2009) Occurrence of Arabinoxylo-oligosaccharides and Arabinogalactan Peptides in Beer. *Journal of the American Society of Brewing Chemists*, **67**, 112–117.

Crafts-Brandner S.J. (2005) Fructans and freezing tolerance. *New Phytologist*, **166**, 708–709.

Debyser W., Derdelinckx G., Delcour J.A. (1997) Arabinoxylan and arabinoxylan hydrolysing activities in barley malts and worts derived from them. *Journal of Cereal Science*, **26**, 67–74.

Delzenne N.M. (2003) Oligosaccharides: state of the art. *Proceedings of the Nutrition Society*, **62**, 177–182.

Edney M.J., Laberge D.E., Langrell D.E. (1998) Relationships among the beta-glucan contents of barley, malt, malt congress extract, and beer. *Journal of the American Society of Brewing Chemists*, **56**, 164–168.

Eerde P.V. (1998). *Analytica-EBC*. Nürnberg, Fachverlag Hans Carl.

Eyben D., Duthoy J. (1979) The filterability of wort and beer. *MBAA Technical Quarterly*, **16**, 135–141.

FAO. (2009) Top production – world – 2007. 14 August 2009. Avaialble at http://faostat.fao.org/site/339/default.aspx.

Glei M., Hofmann T., Kuster K., Hollmann J., Lindhauer M.G., Pool-Zobel B.L. (2006) Both wheat (*Triticum aestivum*) bran arabinoxylans and gut flora-mediated fermentation products protect human colon cells from genotoxic activities of 4-hydroxynonenal and hydrogen peroxide. *Journal of Agricultural and Food Chemistry*, **54**, 2088–2095.

Glitso L.V., Brunsgaard G., Hojsgaard S., Sandstrom B., Knudsen K.E.B. (1998) Intestinal degradation in pigs of rye dietary fibre with different structural characteristics. *British Journal of Nutrition*, **80**, 457–468.

Grasten S., Liukkonen K.H., Chrevatidis A., El-Nezami H., Poutanen K., Mykkanen H. (2003) Effects of wheat pentosan and inulin on the metabolic activity of fecal microbiota and on bowel function in healthy humans. *Nutrition Research*, **23**, 1503–1514.

Greger J.L. (1999) Nondigestible carbohydrates and mineral bioavailability. *Journal of Nutrition*, **129**, 1434S–1435S.

Han J.Y. (2000) Structural characteristics of arabinoxylan in barley, malt, and beer. *Food Chemistry*, **70**, 131–138.

Han J.Y., Schwarz P.B. (1996) Arabinoxylan composition in barley, malt, and beer. *Journal of the American Society of Brewing Chemists*, **54**, 216–220.

Hartmann G., Piber M., Koehler P. (2005) Isolation and chemical characterisation of water-extractable arabinoxylans from wheat and rye during breadmaking. *European Food Research and Technology*, **221**, 487–492.

Houben R., Deruijter C.F., Brunt K. (1997) Determination of the pentosan content of wheat products by hydrolysis, glucose oxidase treatment and analysis by HPAEC/PAD. *Journal of Cereal Science*, **26**, 37–46.

Izydorczyk M.S., Biliaderis C.G. (1992) Influence of Structure on the Physicochemical Properties of Wheat Arabinoxylan. *Carbohydrate Polymers*, **17**, 237–247.

Jin Y.L., Speers R.A., Paulson A.T., Stewart R.J. (2004a) Effect of beta-glucans and process conditions on the membrane filtration performance of beer. *Journal of the American Society of Brewing Chemists*, **62**, 117–124.

Jin Y.L., Speers R.A., Paulson A.T., Stewart R.J. (2004b) Effects of beta-glucans, shearing, and environmental factors on wort filtration performance. *Journal of the American Society of Brewing Chemists*, **62**, 155–162.

Jorgensen K.G. (1988) Quantification of high molecular-weight (1-]3)(1-]4)-beta-D-glucan Using Calcofluor complex-formation and flow-injection analysis .1. Analytical principle and its standardization. *Carlsberg Research Communications*, **53**, 277–285.

Karppinen S., Myllymaki O., Forssell P., Poutanen K. (2003) Fructan content of rye and rye products. *Cereal Chemistry*, **80**, 168–171.

Koizumi H., Kato Y., Ogawa T. (2008) Barley malt polysaccharides inducing premature yeast flocculation and their possible mechanism. *Journal of the American Society of Brewing Chemists*, **66**, 137–142.

Korakli M., Hinrichs C., Ehrmann M.A., Vogel R.F. (2003) Enzymatic determination of inulin and fructooligosaccharides in food. *European Food Research and Technology*, **217**, 530–534.

Li Y., Lu H., Gu G.X., Shi Z.P., Mao Z.G. (2005) Studies on water-extractable arabinoxylans during malting and brewing. *Food Chemistry*, **93**, 33–38.

Lu J., Li Y. (2006) Effects of arabinoxylan solubilization on wort viscosity and filtration when mashing with grist containing wheat and wheat malt. *Food Chemistry*, **98**, 164–170.

Narziss L. (1999). *Die Technologie der Malzbereitung*. Ferdinand Enke Verlag, Stuttgart.

Pereira M.A., O'reilly E., Augustsson K., Fraser G.E., Goldbourt U., Heitmann B.L., Hallmans G., Knekt P., Liu S.M., Pietinen P., Spiegelman D., Stevens J., Virtamo J., Willett W.C., Ascherio A. (2004) Dietary fiber and risk of coronary heart disease – A pooled analysis of cohort studies. *Archives of Internal Medicine*, **164**, 370–376.

Pins J.J., Kaur H. (2006) A review of the effects of barley beta-glucan on cardiovascular and diabetic risk. *Cereal Foods World*, **51**, 8–11.

Pool-Zobel B.L. (2005) Inulin-type fructans and reduction in colon cancer risk: review of experimental and human data. *British Journal of Nutrition*, **93**, S73–S90.

Roberfroid M.B. (2005) Introducing inulin-type fructans. *British Journal of Nutrition*, **93**, S13–S25.

Sadosky P., Schwarz P.B., Horsley R.D. (2002) Effect of arabinoxylans, beta-glucans, and dextrins on the viscosity and membrane filterability of a beer model solution. *Journal of the American Society of Brewing Chemists*, **60**, 153–162.

Saulnier L., Peneau N., Thibault J.F. (1995) Variability in grain extract viscosity and water-soluble arabinoxylan content in wheat. *Journal of Cereal Science*, **22**, 259–264.

Topping D.L., Clifton P.M. (2001) Short-chain fatty acids and human colonic function: roles of resistant starch and nonstarch polysaccharides. *Physiological Reviews*, **81**, 1031–1064.

Ullrich S., Clancy J., Cuti J., Tompkins C. (1991) Analysis of beta-glucans in barley and malt: a comparison of four methods. *Journal of the American Society of Brewing Chemists*, **49**, 110–115.

Van Den Bulck K., Swennen K., Loosveld A.M.A., Courtin C.M., Brijs K., Proost P., Van Damme J., Van Campenhout S., Mort A., Delcour J.A. (2005) Isolation of cereal arabinogalactan-peptides and structural comparison of their carbohydrate and peptide moieties. *Journal of Cereal Science*, **41**, 59–67.

Vinkx C.J.A., Delcour J.A. (1996) Rye (*Secale cereale* L.) arabinoxylans: a critical review. *Journal of Cereal Science*, **24**, 1–14.

Zarnkow M., Kessler M., Burberg F., Kreisz S., Back W. (2005) Gluten free beer from malted cereals and pseudocereals. *Proceedings of the Congress – European Brewery Convention* 1041–1048.

