

Behavior of *Triticum durum* Desf. Arabinoxylans and Arabinogalactan Peptides during Industrial Pasta Processing

J. A. Ingelbrecht,^{*,†} T. Verwimp,[†] P. J. Grobet,[‡] and J. A. Delcour[†]

Laboratory of Food Chemistry and Centre for Surface Chemistry and Catalysis,
Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, B-3001 Leuven, Belgium

Three industrial pasta processing lines for different products (macaroni, capellini and instant noodles) were sampled at three subsequent stages (semolina, extruded, and dried end products) in the process. Arabinoxylans (AX) and arabinogalactan peptides (AGP) were analyzed. Although very low endoxylanase activities were measured, the level of water-extractable AX (WE-AX) increased, probably because of mechanical forces. No change was observed in the level and structural characteristics of AGP. The WE-AX molecular weight (MW) profiles showed a very small shift toward lower MW profiles; those of AGP revealed no changes as a result of the production process. After separation of WE-AX and AGP, ¹H NMR analysis and gas chromatography of the alditol acetates obtained following hydrolysis, reduction, and acetylation revealed no changes in the arabinose substitution profile of the WE-AX samples during pasta processing. At optimal cooking times, WE-AX losses in the cooking water are small (maximally 5.9%). However, the loss of AGP is more pronounced (maximally 25.0%). Overcooking led to more losses of both components.

Keywords: *Durum wheat (Triticum durum Desf.); spaghetti; arabinoxylan; arabinogalactan peptide*

INTRODUCTION

Semolina, the milling product of durum wheat (*Triticum durum* Desf.), is commonly used for the production of pasta. Apart from starch and gluten, it also contains arabinoxylans (AX) and arabinogalactan peptides (AGP).

AX consist of a backbone of 1,4-linked β -D-xylopyranosyl units partially substituted with α -1-2 and/or α -1-3 L-arabinofuranosyl side chains (1). They can be either water-extractable (WE-AX) or water-unextractable (WU-AX). The reported contents in semolina vary between 0.58 and 3.02% (dry basis) for total AX (2–5) and between 0.30 and 0.43% (dry basis) for WE-AX (3, 5). Durum wheat AX contain a higher proportion of arabinose than *Triticum aestivum* L. AX, indicating a more branched structure (6–9).

The percentage of WE-AX increases during spaghetti production. Although this phenomenon has been ascribed mainly to the action of endogenous endoxylanases (3, 10), recent research (11) indicates that increasing the shear stress results in a significant increase of AX solubilization during mixing of pasta doughs. During bread-making with common wheat flour an analogous solubilization was reported (12, 13). As common wheat flours contain almost no endoxylanase activity (14–16) and a solubilization is not proportional to measured enzymic activities (13), other phenomena must be responsible for the solubilization. Rouau et al. (12) hypothesized that disaggregation of arabinoxylan chains, those which are weakly bound in endosperm cell walls, occurs. It is logical that such release should be favored by temperature increase and mechanical work input.

However, enzymic actions cannot be fully excluded, because AX-hydrolyzing enzymes are present in common wheat flour (17–19).

The impact of AX on pasta quality remains to be clarified. Attempts in the past indicated that AX may have a specific role during the mixing stages (2, 5) and on the quality of the end product (20, 21).

AGP consist of a backbone of β -1,3-linked D-galactopyranosyl residues with a variable amount of β -1,6-linked D-galactopyranosyl units. They are substituted with α -L-furanosyl residues (22). Their carbohydrate structure is covalently linked with a protein moiety rich in hydroxyproline, serine, threonine, and glycine (23). Because of their low molecular weights (MWs), AGP are water-extractable (24).

To the best of our knowledge, AGP have never been quantified in semolina or other durum products, and nothing is known either about their behavior during pasta-making or about their functionality. Reported contents in common wheat flour are 0.24–0.33% (25). Lintas (26) suggested that AGP may be degraded during pasta-making. In contrast, no modification of AGP during the bread-making process with common wheat flour was observed (25). The presence of endogenous cereal AGP-hydrolyzing enzymes has not been documented.

AX are an important source of dietary fiber in refined cereal-based products (27). Dietary fiber consists of the remnants of edible plant cell polysaccharides, lignin, and associated substances resistant to hydrolysis by human alimentary enzymes (28). It follows from this most recent review that AGP are also an important source of soluble dietary fiber. Both soluble dietary fiber components (29–38) and dietary fiber in general (39–45) have beneficial health effects. It is thus of primary importance to retain these components in the final

* Author to whom correspondence should be addressed [telephone (+32)-16-321634; fax (+32)-16-321997; e-mail jeroen.ingelbrecht@agr.kuleuven.ac.be].

[†] Laboratory of Food Chemistry.

[‡] Centre for Surface Chemistry and Catalysis.

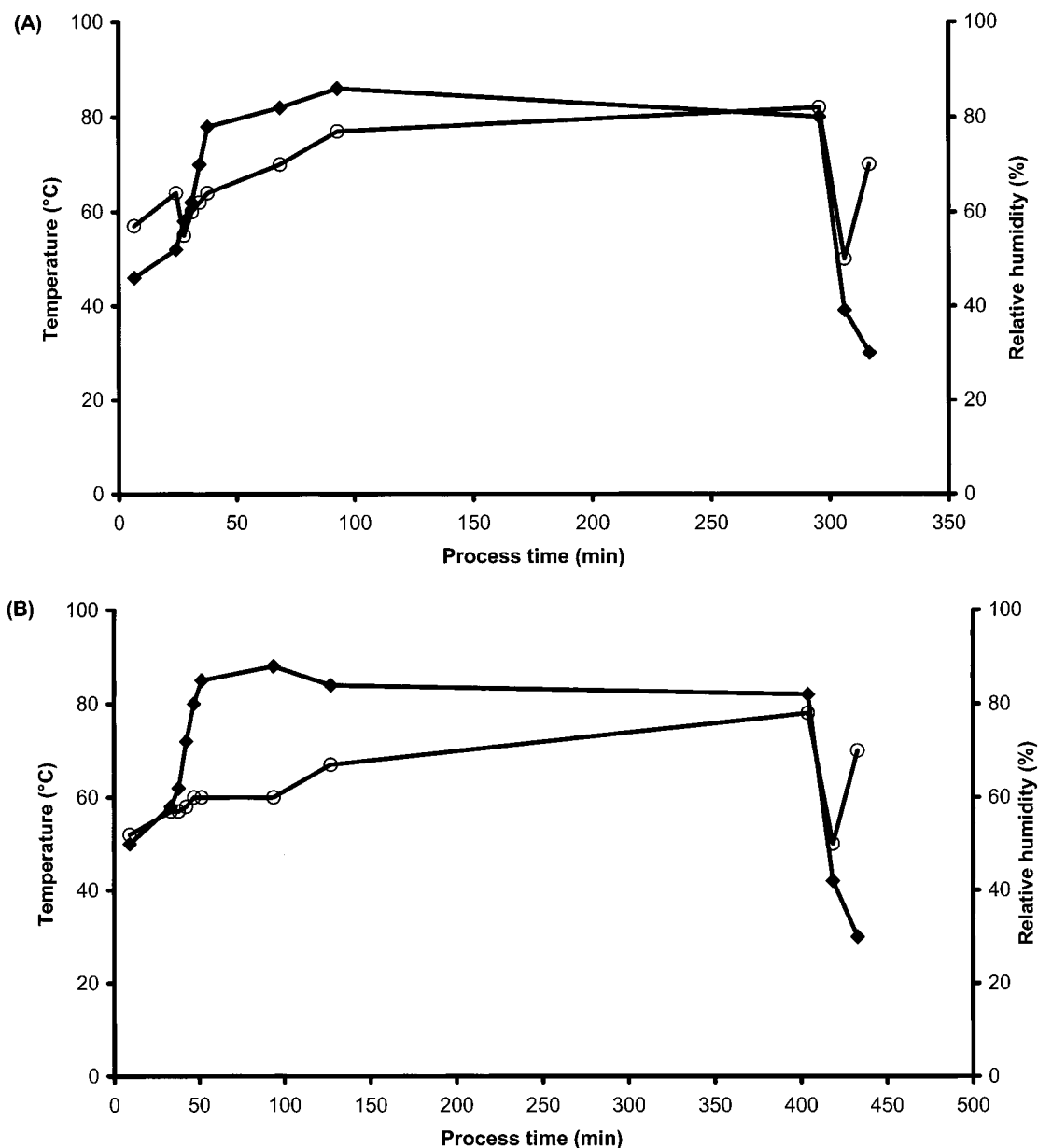


Figure 1. Drying cycle used for capellini (A) and macaroni (B) production: relative humidity (%) (○) and temperature (◆) as a function of process time.

cooked pasta product and not lose them into the cooking water.

The objectives of the present work were to quantify the solubilization of AX and the behavior of AGP during pasta processing. Furthermore, we also characterized cooking losses after optimal and excessive cooking times of the pasta samples.

MATERIALS AND METHODS

Chemicals. All reagents were of at least analytical grade. Substrates used for activity measurements were *p*-nitrophenyl- α -L-arabinofuranoside, *p*-nitrophenyl- β -D-xylopyranoside (Sigma, St. Louis, MO), and azurine-cross-linked xylan (AZCL-xylan) supplied by Megazyme (Dublin, Ireland) as tablets. Sodium acetate and *p*-nitrophenol were from Merck (Darmstadt, Germany); 2[*N*-morpholino]ethanesulfonic acid (MES) and tris-[hydroxymethyl]aminomethane (Trizma base) were obtained from Sigma. Specialty chemicals were heat-stable α -amylase (Thermamyl 120 LS, Novo Nordisk, Bagsvaerd, Denmark) and amyloglucosidase (Boehringer Mannheim, Mannheim, Germany). For both enzymes units were as defined by the

respective supplier. β -D-Allose and clay (montmorillonite K10) were obtained from Sigma and Aldrich (Bornem, Belgium), respectively.

Semolina and Pasta Samples. Pasta samples [capellini (1.22 mm diameter), macaroni (3.80 mm o.d. and 1.6 mm i.d.) and instant noodles (thickness between 0.55 and 2.20 mm and width between 0.25 mm and 0.32 mm)] were withdrawn at three stages during an industrial pasta production (Soubry N.V., Roeselare, Belgium). The evolution of relative humidity and temperature in the dryer during capellini and macaroni production are given in parts A and B, respectively, of Figure 1. Durum wheat semolinas used for the production were from an industrial blend of durum wheats. Protein contents ($N \times 5.7$) were determined according to a Kjeldahl procedure (46) as 12.4, 12.6, and 11.7% (dry basis) for semolinas used for capellini, macaroni, and instant noodle production, respectively. Their ash (dry basis) contents (47) were 0.73, 0.78, and 0.77%, whereas their moisture contents (48) were 12.3, 13.6, and 13.6%, respectively.

Inactivation of Samples. All semolina and extruded and dried pasta samples were boiled in ethanol (under reflux) for 2 h. After cooling, the ethanol was removed by vacuum rotary

evaporation (45 °C), and the material was air-dried. The materials were crushed with a mortar and pestle until they passed a 250 μm sieve. They are further referred to as inactivated material.

Purification of WE-AX and AGP. Inactivated material (80.0 g) was extracted in deionized water (w/v 1:5, 60 min, 4 °C). The suspension was centrifuged (8000g, 15 min, 4 °C), and the supernatant was boiled for 10 min. Following a Thermamyl (3000 units, 30 min, 90 °C) treatment and a centrifugation step (3000g, 15 min, 15 °C), the supernatant was clay treated to adsorb residual proteins as described by Courtin and Delcour (49). The clay and the adsorbed material were removed by centrifugation (8000g, 40 min, 15 °C). Samples were then treated with amyloglucosidase at pH 4.5 (50 units, 12 h, 60 °C) and centrifuged (8000g, 40 min, 15 °C), and the supernatant was boiled (10 min). After a last centrifugation step (8000g, 40 min, 15 °C) to remove the denatured proteins, the supernatant was dialyzed (48 h, 4 °C) and freeze-dried to obtain the nonstarch polysaccharide material.

A further separation between WE-AX and AGP was performed by ethanol precipitation (65%) as in Cleemput et al. (50).

Determination of Carbohydrate Content. For the determination of the water-extractable carbohydrates in inactivated samples, 2.0 g of inactivated material was extracted with 20 mL of deionized water (60 min, 4 °C). After centrifugation (3000g, 15 min, 4 °C), the supernatant (2.5 mL) was hydrolyzed (60 min, 110 °C) with 2.5 mL of 4.0 M trifluoroacetic acid (TFA). Extraction was in fourfold.

For the determination of total carbohydrate content of inactivated materials, 50 mg was hydrolyzed (120 min, 110 °C) with 5.0 mL of TFA (2.0 M). After cooling, the hydrolysate was centrifuged (3000g, 15 min). Purified WE-AX or AGP material (15 mg) was hydrolyzed (60 min, 110 °C) with 5.0 mL of TFA (2.0 M) for carbohydrate analysis. All analyses were done at least in duplicate.

Alditol acetates were prepared according to the method of Englyst and Cummings (51) and were separated on a Supelco SP-2380 (Bellefonte, PA) column (30 m, 0.32 mm i.d., 0.2 μm film thickness) in a Chrompack 9011 chromatograph (Middelburg, The Netherlands) equipped with a flame ionization detector. The carrier gas was He. Separation was at 225 °C, with injection and detection temperatures of 275 °C and β -D-allose as internal standard (1.0 mL added with a concentration of 1.0 mg/mL).

The xylose (xyl), arabinose (ara), and galactose (gal) data led to calculation of the AX and arabinogalactan (AG) contents and the A/X ratio (the arabinose-to-xylose ratio or substitution degree of AX), using the formulas as in Ingelbrecht et al. (5): $\text{AX} = [\% \text{xyl} + (\% \text{ara} - (0.7 \times \% \text{gal})) \times 0.88]$; $\text{AG} = [\% \text{gal} \times 0.90 + (\% \text{gal} \times 0.7) \times 0.88]$, and $\text{A/X} = [\% \text{ara} - (\% \text{gal} \times 0.7)] / \% \text{xyl}$. The A/G ratio (the arabinose substitution degree of AGP) was assumed to be 0.7 (5), which made calculation of ara to be assigned to AGP possible. Conversion factors (0.88 and 0.90) were used for calculation of polymeric material contents, consisting of pentose and/or hexose monomers. AG contents are a good estimation of the content of AGP because it can reasonably (e.g., on the basis of the gel permeation behavior) be assumed that, much as *T. aestivum* L., the peptide component is only a minor proportion of the structure (52).

¹H Nuclear Magnetic Resonance Spectroscopy. ¹H NMR spectra of the purified WE-AX were recorded as outlined before (17). The proportions of unsubstituted (%X₀) and mono- (%X₁) and disubstituted (%X₂) xylose residues were calculated by combining the ¹H NMR spectral data with the gas chromatography results as indicated in Westerlund et al. (53). Chemical shifts were referenced to the internal standard acetone (2.2 ppm).

Gel Permeation Chromatography. Purified WE-AX or AGP material (6.0 mg) was solubilized in 0.3% NaCl (3.0 mL) and centrifuged (10000g, 10 min). The solution was filtered (0.45 μm) and separated on Shodex B-806 HQ (AX) and Shodex B-804 HQ (AGP) (Showa Denko K.K., Tokyo, Japan) GPC columns (300 \times 8 mm) by elution with 0.3% NaCl (0.5 mL/min). The eluate was monitored using a refractive index

detector (VDS Optilab, Berlin, Germany). MW markers were Shodex standard P-82 pullulan standards (Showa Denko K.K.) with MW of 78.8 $\times 10^4$, 40.4 $\times 10^4$, 21.2 $\times 10^4$, 11.2 $\times 10^4$, 4.73 $\times 10^4$, 2.28 $\times 10^4$, 1.18 $\times 10^4$, and 0.59 $\times 10^4$ and made approximate calculations of MW possible.

Enzymic Activities in Samples. *p*-Nitrophenyl- α -L-arabinofuranoside and *p*-nitrophenyl- β -D-xylopyranoside hydrolyzing activities as well as endoxylanase activities were determined at three stages during pasta production, by colorimetric methods as in Cleemput et al. (17) with modifications. As control samples, ethanol-inactivated material, obtained as above, was used.

The release of *p*-nitrophenol from the *p*-nitrophenylglycosides was determined colorimetrically at 410 nm. The activity is expressed as nanokatal (10⁻⁹ mol/s) of *p*-nitrophenol equivalents released under the experimental conditions.

For determination of endoxylanase activity, fine (<250 μm) active and inactivated (control) materials (0.5 g) were extracted (w/v 1:10, 15 min) with a sodium acetate buffer (25 mM, pH 4.7) or a sodium phosphate buffer (25 mM, pH 6.0). After filtration, extract (1.0 mL) was preincubated (5 min, 40 °C), after which an AZCL-xylan tablet was added. After 24 h of incubation at 40 °C, adding 10 mL of a 1% Trizma base solution stopped the reaction. Extinction of the filtrates was measured at 590 nm. Activity is expressed as the difference in absorbance per gram of dry matter between the control and sample. An incubation temperature of 40 °C was chosen to represent pasta production conditions, during which dough temperatures >30 °C are obtained by adding water of 50 °C to semolina (54) and extrusion of pastas is at 38–40 °C (55).

As a second approach for detecting AX-hydrolyzing activities, the method of Courtin et al. (56) was used, with modifications. In this method, the release of xylose and arabinose residues as a result of enzymic action was measured. Fine (<250 μm) active and inactivated semolinas (2.0 g, from their respective sources: capellini, macaroni, and instant noodle production, respectively) were incubated with a sodium phosphate buffer (w/v 1:10, 25mM, pH 6.0, 15% ethanol, 0.02% sodium azide, 40 °C). Various samples were obtained after incubation times varying between 0 and 72 h. After the suspensions had been boiled (15 min) and freeze-dried, the reducing end xylose and arabinose end contents were determined on 800 mg of material. As a control, inactivated samples were used.

In a third AX-hydrolyzing activity assay, purified WE-AX, obtained from the respective semolinas (capellini, macaroni, and instant noodle production) as described above, were incubated with enzyme extracts, as in Cleemput et al. (17) with the modification that extraction and incubation were at pH 4.7, with a sodium acetate buffer (25 mM, 0.02% sodium azide). Again, various samples were obtained after incubation times varying between 0 and 72 h. After boiling (10 min), the samples were examined by gel permeation chromatography as described above.

Determination of Cooking Losses. Pasta (100.0 g) was boiled in 2.0 L of deionized water (with the addition of 1.0 g of salt). Optimal cooking time was determined in a preliminary test by taking five strands out of the boiling water at 30 s intervals and pressing them between two plastic plates and is defined as that at which the white core in the strands is no longer observable (57). Cooking losses were determined at optimal cooking time (*t*) and at *t* + 11 min by freeze-drying the cooking water. The obtained material was then analyzed for moisture, protein, and carbohydrate contents according to the methods described above.

Statistical Analysis. When appropriate, coefficients of variation (CV) were calculated with the following formula: $\text{CV} = \text{standard deviation/mean}$.

RESULTS AND DISCUSSION

Nonstarch Polysaccharide Composition of Pasta Samples. An increase in WE-AX (Table 1) levels was noticed during pasta processing, whereas the level of

Table 1. Nonstarch Polysaccharide Composition (Dry Basis) of Samples (Percent of Raw Material), Purified WE-AX, and AGP

		sample		purified WE-AX					purified AGP	
		%AX ^a	%AG ^b	%AX	A/X ^c	%X ₀ ^d	%X ₁ ^e	%X ₂ ^f	%AG	A/G ^g
capellini										
	total	2.68	0.26	93.0	0.55	69.7	5.6	24.7	66.0	0.69
water extract	semolina	0.46	0.24							
	extruded product	0.61	0.26	96.5	0.56	69.7	4.6	25.7	64.0	0.70
	end product	0.73	0.28	99.3	0.58	69.2	4.7	26.1	63.1	0.70
macaroni										
	total	2.58	0.29							
water extract	semolina	0.49	0.29	97.8	0.57	69.1	5.7	25.2	72.3	0.71
	extruded product	0.69	0.29	97.0	0.58	68.9	5.3	25.8	71.6	0.70
	end product	0.73	0.29	98.5	0.59	68.3	5.5	26.2	69.9	0.71
instant noodles										
	total	2.65	0.25							
water extract	semolina	0.44	0.24	100.5	0.56	nd ⁱ	nd	nd	nd	nd
	laminated product	0.56	0.24	97.8	0.57	nd	nd	nd	nd	nd
	end product	0.54	0.28	96.8	0.56	nd	nd	nd	nd	nd
max CV (%)		7	8	6	6				7	5

^a Arabinoxylans. ^b Arabinogalactans. ^c Arabinose/xylose substitution. ^d Unsubstituted xylose. ^e Monosubstituted xylose. ^f Disubstituted xylose. ^g Arabinose/galactose substitution. ^h Maximal coefficient of variation. ⁱ Not determined.

AG remained constant. During capellini production, 10.1% AX were solubilized [(WE-AX_{endproduct} - WE-AX_{semolina})/TOT-AX], calculated from Table 1]. For macaroni and instant noodles, these values were, respectively, 9.3 and 3.8%.

Lintas and D'Appolonia (3) made similar observations. They obtained higher yields of purified WE-AX and lower yields of purified WU-AX in the end products than in semolina. The degree to which AX are solubilized during pasta dough making depends on extrusion speed and the temperature and hydration level of the pasta dough (11). Higher solubilization levels (up to 75%) can easily be obtained by adding endoxylanases to pasta doughs (5).

Although solubilization of AX mainly took place between the semolina and extruded/laminated product stages, AX solubilization during the drying stage of capellini production was significant (Table 1).

The present results are similar to those that can be seen during bread production with common wheat flour in the absence of exogenous endoxylanases. Reported levels vary between 5.3 and 11.0% (12) and between 13.5 and 18.5% (13).

Structural Characteristics of the Purified WE-AX and AGP. No significant changes in structural characteristics (A/X, %X₀, %X₁, and %X₂) of the purified WE-AX samples were noticed. No change was observed in the A/X ratio of the AX (Table 1). The A/G ratios were highly comparable with those of AGP found in common wheat flour; Izydorczyk et al. (58) and Loosveld et al. (25) found values between 0.66 and 0.75 and between 0.66 and 0.73 for *T. aestivum* L. AGP, respectively.

Activity of Endogenous AX-Hydrolyzing Enzymes. With the procedure of Cleemput et al. (17), very low endogenous endoxylanase activities at pH 4.7 and 6.0 were detected (Table 2) in all samples. A buffer with pH 6.0 was chosen as it represents the conditions in the dough. Preliminary experiments revealed that, at pH 4.7, the "greatest" activities were noted, whereas at all pH values (between 2 and 10) very low activities were seen. With lower incubation times (10 min and 1 h) no significant endoxylanase activities were detected, which necessitated longer incubation times (24 h).

The two other assays used to detect endoxylanase activities also revealed very low activities. Incubation

Table 2. Activities at pH 4.7 or 6.0 of Endogenous AX-Hydrolyzing Enzymes Present in Different Pasta Samples

	endoxylanase ^a		β -D-xylosidase ^b	α -L-arabinofuranosidase ^c	
	pH 6.0	pH 4.7	pH 6.0	pH 6.0	
capellini					
semolina	0.165	0.260	0.015	0.005	
extruded product	0.300	0.380	0.015	0.005	
end product	0.095	0.200	0.010	0.002	
macaroni					
semolina	0.240	0.330	0.015	0.005	
extruded product	0.310	0.390	0.015	0.005	
end product	0.050	0.340	0.005	0.001	
instant noodles					
semolina	0.105	0.300	0.010	0.005	
laminated product	0.215	0.310	0.010	0.005	
end product	0.110	0.215	0.001	0.002	
max CV (%)		12	13	9	10

^a Endoxylanase activity is expressed as absorbance units/g of dry matter. ^b β -D-Xylosidase and ^c α -L-arabinofuranosidase are expressed as nkat/g of dry matter.

of the WE-AX with semolina extracts showed that only after 24 h there was a very small shift in the MW profile of the AX obtained (results not shown).

With a detection limit of 1 μ g of reducing xylose ends (56), no significant amounts were detected in any samples, even in those incubated for 72 h.

The measured α -L-arabinofuranosidase and β -D-xylosidase activities (Table 2) were also much lower than those in *T. aestivum* L. samples (17).

The observed solubilization of AX (Table 1) could not be explained by the low activities of AX-hydrolyzing enzymes (Table 2). However, enzymic actions cannot fully be excluded. In contrast to Lintas and D'Appolonia (3), who believed that great endogenous endoxylanase activities during extrusion and the first phases of drying are possible because of ideal temperatures during these stages, the present results suggest that enzymes have only a limited (if any) impact on the AX during pasta-making. In the case of bread-making, Rouau et al. (12) hypothesized that AX are solubilized by disaggregation of the cell walls, through mechanical actions and high temperatures. Especially during extrusion/lamination, mechanical forces on the pasta doughs are very strong.

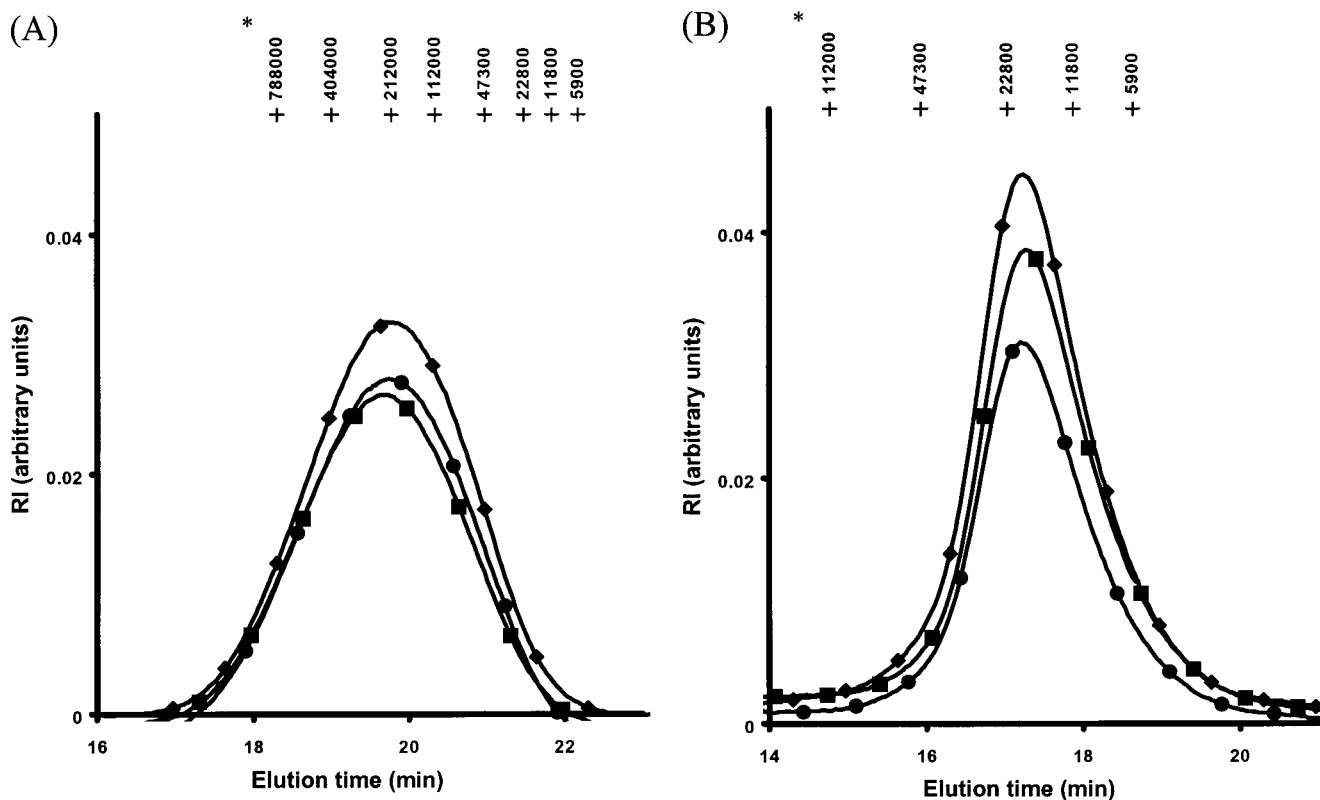


Figure 2. Gel permeation profiles of WE-AX [(A) SB 806 Shodex HPLC column] and AGP [(B) SB804 Shodex HPLC column] purified from the samples at different stages (semolina, ■; extruded product, ●; and end product, ◆) of capellini production. * Molecular weight markers are indicated.

Table 3. (A) Composition of Material Leached out of Pasta Samples Cooked to Optimal Cooking Time and to Optimal Cooking Time plus 11 min and (B) Total Dry Matter, WE-AX, AG, Glucose, Mannose, and Proteins Leached out during Cooking of Pasta Samples

	capellini, cooking time		macaroni, cooking time		instant noodles, cooking time		max CV (%)
	7.30 min	18.30 min	8.30 min	19.30 min	1 min	12 min	
(A) Composition of Leached Material (on Dry Basis)							
% AX	0.45	1.00	0.26	0.65	0.20	1.40	9
% AG	1.09	1.35	1.05	1.65	0.93	0.98	9
% glucose	59.52	66.60	52.36	62.04	55.26	75.36	3
% mannose	0.97	0.64	1.00	0.91	0.71	0.37	9
% proteins	6.98	6.54	6.97	6.69	4.68	5.14	9
(B) Percent of Material in Original Pasta Sample Leached out during Cooking							
% of dry matter leached out	5.85	7.63	4.07	5.68	5.08	18.71	10
% of WE-AX leached out	3.64	10.59	1.48	5.02	1.90	48.47	10
% of AG leached out	24.92	40.00	14.70	32.37	18.81	73.21	9
% of glucose leached out	4.29	6.27	2.62	4.34	3.45	6.41	3
% of mannose leached out	24.98	21.62	21.46	27.37	13.29	17.35	10
% of proteins leached out	3.33	4.07	2.25	3.03	2.03	8.20	9

In addition, Icard-Vernière and Feillet (11) found that during mixing of pasta doughs increasing shear stresses resulted in significant AX solubilization.

Gel Permeation Profiles of WE-AX and AGP.

Only a very small shift was noticed in MW profiles of the WE-AX (Figure 2) purified from the samples withdrawn during the capellini production. This indicates little or no impact of AX-hydrolyzing enzymes. In contrast, in the case of AGP, no MW shift was observed. The MW of AGP (~22000) is perfectly in accordance with those found for common wheat flour AGP (25, 52, 59). Similar profiles were obtained for the samples of both the macaroni and instant noodle production (results not shown). AGP were, therefore, not hydrolyzed during pasta production (Table 1 and Figure 2), in contrast to what was suggested by Lintas (26).

Cooking Losses. Leached material consisted mainly of (polymeric) glucose (Table 3A) and minerals (results

not given). AG and WE-AX were minor components (Table 3A). Overcooking led to a relative increase of WE-AX and AG contents (Table 3). A higher proportion of AG than of WE-AX was leached out (Table 3B). Especially at optimal cooking time, this behavior was obvious. Overcooking led to pasta swelling and promoted leaching of the larger (WE-AX) MW components (Figure 2). Very high losses of WE-AX and AG were obtained by overcooking instant noodles (Table 3A). However, these excessive cooking times resulted in a completely disintegrated product where the pasta structure could no longer be recognized.

Product shape is an important factor in determining cooking losses (60). Pasta products with a high surface/volume ratio lead to higher cooking losses and so to higher losses of WE-AX and AG during cooking. Cooking macaroni, the product with the largest diameter but with contents of WE-AX and AG comparable to those

of capellini, consequently resulted in lower losses of these components (Table 3).

Conclusion. A significant solubilization of AX was observed during pasta processing. No (or only very limited) changes in the structural properties (MW profile and substitution pattern) of the WE-AX could be observed.

Very low endogenous AX-hydrolyzing activities were measured and could not explain the solubilization of the AX. This supports the hypothesis that mechanical forces (during, e.g., extrusion/lamination) are the main influence on the solubilization.

During pasta production, no changes in the contents and the structure (MW profile and A/G) of AGP were noticed.

At optimal cooking times very low losses of WE-AX, as a source of soluble dietary fiber, were noticed. AGP leached out more readily during the pasta cooking process than WE-AX. Excessive cooking times resulted in significantly higher AGP and AX losses.

ABBREVIATIONS USED

AX, arabinoxylans; TOT-AX, total level of arabinoxylans; WE-AX, water-extractable arabinoxylans; WU-AX, water-unextractable arabinoxylans; A/X, arabinose-to-xylose ratio; %X₀, percentage unsubstituted xylose; %X₁, percentage monosubstituted xylose; %X₂, percentage disubstituted xylose; AG, arabinogalactans; AGP, arabinogalactan peptides; A/G, arabinose-to-galactose ratio; AZCL-xylan, azurine-cross-linked xylan; GPC, gel permeation chromatography; MW, molecular weight; TFA, trifluoroacetic acid.

ACKNOWLEDGMENT

J.A.I. acknowledges the receipt of a scholarship from the Vlaams Instituut voor de Bevordering van het Wetenschappelijk-Technologisch Onderzoek in de Industrie (Brussels, Belgium). Etn. Soubry (Roeselare, Belgium) is gratefully acknowledged for providing the pasta samples.

LITERATURE CITED

- Perlin, A. S. Structure of the soluble pentosans of wheat flours. *Cereal Chem.* **1951**, *28*, 382–393.
- Bains, G. S.; Irvine, G. N. The quality of Canadian amber durum wheat grades and the role of pentosan-rich fraction in macaroni dough quality. *J. Sci. Food Agric.* **1965**, *16*, 233–240.
- Lintas, C.; D'Appolonia, B. L. Effect of spaghetti processing on semolina carbohydrates. *Cereal Chem.* **1973**, *50*, 563–570.
- Lempereur, I.; Rouau, X.; Abécassis, J. Genetic and agronomic variation in arabinoxylan and ferulic acid contents of durum wheat (*Triticum durum* L.) grain and its milling fractions. *J. Cereal Sci.* **1997**, *25*, 103–110.
- Ingelbrecht, J. A.; Verwimp, T.; Delcour, J. A. Endoxylanases in durum wheat semolina processing: solubilization of arabinoxylans, action of endogenous inhibitors and effects on rheological properties. *J. Agric. Food Chem.* **2000**, *48*, 2017–2022.
- Medcalf, D. G.; Gilles, K. A. Structural characterization of a pentosan from the water-insoluble portion of durum wheat endosperm. *Cereal Chem.* **1968**, *45*, 550–557.
- Medcalf, D. G.; D'Appolonia, B. L.; Gilles, K. A. Comparison of chemical composition and properties between hard red spring and durum wheat endosperm pentosans. *Cereal Chem.* **1968**, *45*, 539–549.
- Ciaccio, C. F.; D'Appolonia, B. L. Characterization of pentosans from different wheat flour classes and their gelling capacity. *Cereal Chem.* **1982**, *59*, 96–99.
- Roels, S. P.; Collado, M.; Loosveld, A.-M. M.; Grobet, P. J.; Delcour, J. A. Variation in the degree of D-xylose substitution in water-extractable European durum wheat (*Triticum durum* Desf.) semolina arabinoxylans. *J. Agric. Food Chem.* **1999**, *47*, 1813–1816.
- Neukom, H.; Kuendig, W.; Deuel, H. The soluble wheat flour pentosans. *J. Cereal Sci. Today* **1962**, *7*, 112–114.
- Icard-Vernière, C.; Feillet, P. Effects of mixing conditions on pasta dough development and biochemical changes. *Cereal Chem.* **1999**, *76*, 558–565.
- Rouau, X.; El-Hayek, M.-L.; Moreau, D. Effect of an enzyme preparation containing pentosanases on the bread-making quality of flours in relation to changes in pentosan properties. *J. Cereal Sci.* **1994**, *19*, 259–272.
- Cleemput, G.; Booij, C.; Hessing, M.; Gruppen, H.; Delcour, J. A. Solubilisation and changes in molecular weight distribution of arabinoxylans and proteins in wheat flours during breadmaking, and the effect of endogenous arabinoxylan hydrolysing enzymes. *J. Cereal Sci.* **1997**, *26*, 55–66.
- Preece, I. A.; McDougall, M. Enzymic degradation of cereal hemicelluloses II. Pattern of pentosan degradation. *J. Inst. Brew.* **1958**, *64*, 489–500.
- Schmitz, J. F.; McDonald, C. E.; Gilles, K. A.; Medcalf, D. G. Arabinoxylanases and cellulases of wheat. *Cereal Chem.* **1974**, *51*, 809–821.
- Moore, A. M.; Hosney, R. C. Factors affecting the viscosity of flour-water extracts. *Cereal Chem.* **1990**, *67*, 78–80.
- Cleemput, G.; Bleukx, W.; van Oort, M.; Hessing, M.; Delcour, J. A. Evidence for the presence of arabinoxylan hydrolysing enzymes in European wheat flours. *J. Cereal Sci.* **1995**, *22*, 139–145.
- Cleemput, G.; Hessing, M.; van Oort, M.; Deconynck, M.; Delcour, J. A. Purification and characterization of a β -D-xylosidase and an endo-xylanase from wheat flour. *Plant Physiol.* **1997**, *113*, 377–386.
- Cleemput, G.; Van Laere, K.; Hessing, M.; Van Leuven, F.; Torrekens, S.; Delcour, J. A. Identification and characterization of a novel arabinoxylanase from wheat flour. *Plant Physiol.* **1997**, *115*, 1619–1627.
- Sheu, R.-Y.; Medcalf, D. G.; Gilles, K. A.; Sibitt, L. D. Effect of biochemical constituents on macaroni quality. I. Differences between hard red spring and durum wheats. *J. Sci. Food Agric.* **1967**, *18*, 237–239.
- Fardet, A. J.; Baldwin, P. M.; Bertrand, D.; Bouchet, B.; Gallant, D. J.; Barry, J.-L. Textural images analysis of pasta protein networks to determine influence of technological processes. *Cereal Chem.* **1998**, *75*, 699–704.
- Aspinall, G. O. Carbohydrate polymers of plant cell walls. In *Biogenesis of Plant Cell Wall Polysaccharides*; Loewus, F., Ed.; Academic Press: New York, 1973; pp 95–115.
- Fincher, G. B.; Stone, B. A.; Clarke, A. E. Arabinogalactan-proteins: structure, biosynthesis, and function. *Annu. Rev. Plant Physiol.* **1983**, *34*, 47–70.
- Clarke, A. E.; Anderson, R. L.; Stone, B. A. Form and function of arabinogalactans and arabinogalactan-proteins. *Phytochemistry* **1979**, *18*, 512–540.
- Loosveld, A.; Maes, C.; van Casteren, W. H. M.; Schols, H. A.; Grobet, P. J. Structural variation and levels of water-extractable arabinogalactan-peptide in European wheat flours. *Cereal Chem.* **1998**, *75*, 815–819.
- Lintas, C. Carbohydrates of durum wheat. In *Durum Chemistry and Technology*; Fabiani, G., Lintas, C., Eds.; AACC: St. Paul, MN, 1988; pp 121–148.
- Theander, O.; Westerlund, E.; Aman, P. Structure and components of dietary fiber. *Cereal Foods World* **1993**, *38*, 135–141.
- De Vries, J. W.; Prosky, L.; Li, B.; Cho, S. A historical perspective on defining dietary fiber. *Cereal Foods World* **1999**, *44*, 367–369.

- (29) Gatti, E.; Catenazzo, G.; Camisasca, E.; Torri, A.; Denegri, E.; Sirtori, C. R. Effects of guar enriched pasta in the treatment of diabetes and hyperlipidemia. *Ann. Nutr. Metab.* **1984**, *28*, 1–10.
- (30) Briani, G.; Bruttomesso, D.; Bilardo, G.; Giorato, C.; Duner, E.; Iori, E.; Sgnaolin, E.; Pedrini, P.; Tiengo, A. Guar enriched pasta and guar gum in the dietary treatment of type II diabetes. *Phytother. Res.* **1987**, *1*, 177–179.
- (31) Ink, S. L.; Hurt, H. D. Nutritional implications of gums. As sources of water-soluble dietary fiber, gums show unique properties that affect gastrointestinal physiology. *Food Technol.* **1987**, *1*, 77–82.
- (32) Carra, M.; Meshi, F.; Rognetti, F.; Ralzano, F.; Santolli, S.; Silva, F. Blood sugar response to administration of bran or guar added to pasta in children with type I diabetes. *Minerva Pediatr.* **1990**, *42*, 629–640.
- (33) Ripsin, C. M.; Keenan, J. M.; Jacobs, D. R. Oat products and lipid lowering. A meta-analysis. *JAMA* **1992**, *267*, 3317–3325.
- (34) Haskell, W. L.; Spiller, G. A.; Jensen, C. D.; Ellis, B. K.; Gates, J. E. Role of water-soluble dietary fiber in the management of elevated plasma cholesterol in healthy subjects. *Am. J. Cardiol.* **1992**, *69*, 433–439.
- (35) Jenkins, D. J. A.; Wolever, T. M. S.; Venketeshwar Rao, A.; Hegele, R. A.; Mitchell, S. J.; Ransom, T. P. P.; Boctor, D. L.; Spadafora, P. J.; Jenkins, A. L.; Mehling, C.; Katzman Relle, L.; Connelly, P. W.; Story, J. A.; Furumoto, E. J.; Corey, P.; Wüsch, P. Effect on blood lipids of very high intakes of fiber in diets low in saturated fat and cholesterol. *N. Engl. J. Med.* **1993**, *329*, 21–26.
- (36) Nutall, F. Q. Dietary fiber in the management of diabetes. *Diabetes* **1993**, *742*, 503–508.
- (37) Glore, S. R.; Van Treec, D.; Knehans, A. W.; Guild, M. Soluble fiber and serum lipids: a literature review. *J. Am. Diet. Assoc.* **1994**, *94*, 425–436.
- (38) Yokoyama, W. H.; Hodson, C. A.; Knuckles, B. E.; Chiu, M.-C. M.; Sayre, R. N.; Turnlund, J. R.; Schneeman, B. O. Effect of barley β -glucan in durum wheat pasta on human glycemic response. *Cereal Chem.* **1997**, *74*, 293–296.
- (39) Trowell, H. C. Ischemic heart disease and dietary fiber. *Am. J. Clin. Nutr.* **1972**, *25*, 926–932.
- (40) Burkitt, D. P. Some diseases characteristic of modern western civilization. *Br. Med. J.* **1973**, *1*, 274–278.
- (41) Leveille, G. A. Dietary fiber. *Cereal Foods World* **1976**, *21*, 255–258.
- (42) Weber, F. E.; Chaudhary, V. K. Recovery and nutritional evaluation of dietary fiber ingredients from a barley by-product. *Cereal Foods World* **1987**, *32*, 548–550.
- (43) Kahlon, T. S.; Chow, F. I. Hypocholesterolemic effects of oat, rice and barley dietary fibers and fractions. *Cereal Foods World* **1997**, *42*, 86–92.
- (44) Kritchevsky, D. Cereal fiber and lipidemia. *Cereal Foods World* **1997**, *42*, 81–85.
- (45) Meister, K.; Raso, J. A “bran-new” look at dietary fiber. *Priorities Health* **1997**, *9* (1), 7–10.
- (46) American Association of Cereal Chemists. AACC Method 46-11A. *Approved Methods of the AACC*, 8th ed.; AACC: St. Paul, MN, 1983.
- (47) American Association of Cereal Chemists. AACC Method 08-01. *Approved Methods of the AACC*, 8th ed.; AACC: St. Paul, MN, 1983.
- (48) American Association of Cereal Chemists. AACC Method 44-15A. *Approved Methods of the AACC*, 8th ed.; AACC: St. Paul, MN, 1983.
- (49) Courtin, C. M.; Delcour, J. A. Physicochemical and bread-making properties of low molecular weight wheat derived arabinoxylans. *J. Agric. Food Chem.* **1998**, *46*, 4066–4073.
- (50) 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. *Cereal Chem.* **1993**, *70*, 324–329.
- (51) 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.
- (52) Fincher, G. B.; Sawyer, W. H.; Stone, B. A. Chemical and physical properties of an arabinogalactan-peptide from wheat endosperm. *Biochem. J.* **1974**, *139*, 535–545.
- (53) Westerlund, E.; Andersson, R.; Aman, P.; Theander, O. Effects of baking on water-soluble polysaccharides in white bread fractions. *J. Cereal Sci.* **1990**, *12*, 33–42.
- (54) Milatovic, Lj.; Mondelli, G. Processes and unit operations in industrial pasta manufacturing. In *Pasta Technology Today*; Chiriotti Editore: Pinerolo, Italy, 1991; pp 69–95.
- (55) Dalbon, G.; Grivon, D.; Pagani, M. A. Continuous manufacturing process. In *Pasta and Noodle Technology*; Kruger, J. E., Matsuo, R. B., Dick, J. W., Eds.; AACC: St. Paul, MN, 1996; pp 13–58.
- (56) Courtin, C. M.; Van den Broeck, H.; Delcour, J. A. Determination of reducing end sugar residues in oligo- and polysaccharides by gas-liquid chromatography. *J. Chromatogr. A* **2000**, *866* (1), 97–104.
- (57) Abécassis, J.; Abbou, R.; Chaurand, M.; Morel, M.-H.; Vernoux, P. Influence of extrusion conditions on extrusion speed, temperature and pressure in the extruder and on pasta quality. *Cereal Chem.* **1994**, *71*, 247–253.
- (58) Izydorczyk, M. S.; Biliaderis, C. G.; Bushuk, W. Comparison of the structure and composition of water-soluble pentosans from different wheat varieties. *Cereal Chem.* **1991**, *68*, 139–144.
- (59) Neukom, H. Chemistry and properties of the non-starchy polysaccharides (NSP) of wheat flour. *Lebensm.-Wiss.-Technol.* **1976**, *9*, 143–148.
- (60) Holliger, A. Improved method for testing macaroni products. *Cereal Chem.* **1963**, *40*, 231–240.

Received for review July 21, 2000. Revised manuscript received January 9, 2001. Accepted January 11, 2001.

JF0009089