

Composition and Distribution of Pentosans in Millstreams of Different Hard Spring Wheats

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ABSTRACT

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Six commercially grown samples of hard spring wheat were milled using a tandem Buhler laboratory mill. Individual flour streams and branny by-products, as well as whole-grain wheat and straight-grade flour, were characterized in terms of total (TP), water-extractable (WEP), and water-unextractable (WUP) pentosans. One representative cultivar sample was analyzed for its ratio of arabinose to xylose (A/X). TP and WEP of whole grain wheat of the six samples had ranges of 5.45–7.32% and 0.62–0.90% (dm), respectively. Neither TP nor WEP of whole grain was related to ash content variation. There was significant variation in the distribution and composition of pentosans in 16 millstreams of all the wheat samples, including bran and shorts fractions; TP and WEP contents had ranges of 1.69–32.4% and 0.42–1.76% (dm), respectively. When ash contents exceeded $\approx 0.6\%$ (dm), strong positive correlations were obtained between ash and TP contents, and between ash and WUP contents for all

the millstreams. Among bran and shorts fractions, TP and WUP content increased in the order of coarse bran > fine bran > shorts; while WEP, WEP/WUP and A/X showed the opposite pattern of variation of shorts > fine bran > coarse bran. Bran and shorts fractions had pentosan contents several times higher than would be predicted from the relationship between pentosan and ash contents of the flour streams. Pentosans therefore represented a much more sensitive marker of flour refinement compared with ash content. Pentosans of endosperm were substantially different in their extractability and composition from those of bran. On this basis, different functionalities of pentosans of bran and endosperm would be expected. Results demonstrated the importance of milling extraction and millstream blending in the functionality and quality of wheat flour for breadmaking.

The major nonstarch polysaccharides (NSP) of wheat are pentosans, which originate in the cell walls of endosperm and bran. Arabinoxylan (AX), the predominant constituent of pentosans, consists of a β -(1 \rightarrow 4)-linked D-xylopyranose polymer backbone with frequent branching of L-arabinofuranose residues at O-3 (Perlin 1951a and 1951b) or O-2 and O-3 (Gruppen et al 1992). Arabinoxylan polymer also contains the phenolic compound ferulic acid which is esterified to arabinose residues at O-5 (Fausch et al 1963). Ferulic acid is the key component involved in oxidative gelation of pentosans, a cross-linking reaction believed to be unique to the water-extractable pentosan (WEP) fraction (Neukom and Markwalder 1978; Hosney and Faubion 1981). WEP and water-unextractable pentosan (WUP) comprise ≈ 25 and 75%, respectively, of TP present in wheat flour (Meuser and Suckow 1986).

The behavior of pentosans in aqueous solutions relates to the shape and size of the polymers and is largely determined by the complex nature of degree of substitution and contiguity of substitution of AX molecules (Gruppen et al 1993). In general, a higher degree of substitution, i.e., higher ratio of arabinose (A) to xylose (X), is associated with higher solubility of AX in water. A typical average value of A/X of wheat water-soluble AX (WE-AX) is 0.5–0.6 (Cleemput et al 1993) but extreme values of 0.31–1.06 have been reported (Dervilly et al 2000). Average total AX and WE-AX contents in whole common wheat (*Triticum aestivum* L.) are 6.7 and 0.7% (14% mb), respectively (Hashimoto et al 1987).

Similar to mineral and protein, pentosans are not distributed uniformly in the wheat kernel. Limited studies of the histological distribution of wheat AX show a distinct change between endosperm and bran tissues where pentosans are concentrated. Pomeranz (1988) reported TP contents in patent flour, outer pericarp, nucellar epidermis, and aleurone layers of wheat of 2–3%, 29.2–32.6%, 22.2–29.0%, and 21.6–26.5% (14% mb), respectively.

Indirect information about the distribution of AX in the wheat kernel can be obtained from studies of the concentration and structure of AX in mill products. However, this literature is relatively small and incomplete and some results have been contradictory (Stephen et al 1949; D'Appolonia and MacArthur 1975; Ciacco and D'Appolonia 1982; Hartunian-Sowa 1997; Lempereur et al 1997; Delcour et al 1999). Stephen et al (1949) determined total AX of several U.S. hard red winter cultivars and some distinct bran layers and millstreams. They found lower AX contents associated with low ash content fractions, with AX concentrated in the hyaline-aleurone tissues. Also, flour AX content declined when wheat was debranned before milling. D'Appolonia and MacArthur (1975) compared AX of wheat bran and endosperm and reported a higher degree of branching of bran AX compared with that of endosperm. Ciacco and D'Appolonia (1982) studied the concentration and gelling capacity of WE-AX of selected millstreams of a single U.S. hard red spring wheat cultivar. They concluded that AX isolated from flour streams representing primarily the inner layer of the kernel had a higher intrinsic viscosity, were less branched, and in general had higher gelling capacity than those isolated from flour streams containing a greater percentage of the outer layer of the kernel. Hartunian-Sowa (1997) investigated the concentration and structure of NSP of 33 wheat cultivars and millstreams and reported that the range of total AX of whole grain was 5.55–7.51% (14% mb), with hard wheat cultivars exhibiting higher concentrations than soft wheats. Bran and shorts had higher concentrations of total AX and lower ratios of A/X compared with corresponding results for flour streams. Hartunian-Sowa (1997) did not determine WE-AX and WU-AX contents. Milling fractions of durum wheat have also been studied in terms of AX and ferulic acid content (Lempereur et al 1997), but the focus of that research was on genotype-by-environment effects and no A/X results were reported. Delcour et al (1999) studied the distribution and structural variation of AX in a single European wheat sample and reported that the total AX and WE-AX of 19 wheat milling fractions varied at 1.44–30.66% and 0.3–1.38% (dm), respectively; both AX fractions increased with increasing ash content once the latter exceeded 0.6% (dm). A/X range was 0.65–0.39, with the lowest values found for fractions with highest ash content, indicating that the mineral-rich tissues contained more AX that were less branched, a finding that disagreed with that of Ciacco and D'Appolonia (1982).

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Although the content of pentosans in wheat flour is relatively low (2–3%, w/w), these polymers play an important role in flour functionality, with WEP and WUP having different effects on breadmaking. Courtin and Delcour (2002) stated that WE-AX increased the stability of liquid films and thus of the dough foam structure, resulting in higher bread loaf volumes and a finer and more homogeneous crumb grain. In contrast to WE-AX, WU-AX are present in discrete cell wall fragments that can form physical barriers for the gluten network during dough development; thereby lowering dough foam stability and destabilizing dough structure. As a result, lower loaf volumes with coarse crumb and higher initial crumb firmness are obtained.

Apart from pentosan functionality for breadmaking, pentosans represent an important dietary fiber component of wheat, especially wheat bran. Pentosans are relatively poorly studied in terms of health-promoting functions compared with those of β -glucans, which are the main NSP of oats and barley. All forms of dietary fiber are fundamentally functional (Anonymous 2003) and promote beneficial physiological effects such as laxation, blood cholesterol, and blood glucose attenuation. However, there is increasing evidence that pentosans may be particularly advantageous from a health perspective. Wheat bran rich in pentosans ferments differently and more slowly than oat bran rich in β -glucans (Karppinen et al 2000; Wood et al 2002). Also, unlike β -glucans, pentosans of wheat have a distinct prebiotic function (Crittenden et al 2002) and promote the proliferation of beneficial probiotic bacteria (*Bifidobacterium species*) that are related to good colonic health in the fermentation of dietary fiber during food digestion. Moreover, the high antioxidant activities of wheat millfeeds, and high correlations between total phenolics and antioxidant activities of wheat pearling fractions (Beta et al 2005), strongly implicate pentosans and constituent ferulic acid as the source of the antioxidant activity.

More knowledge of the composition and distribution of pentosans in the wheat kernel is required to better understand and exploit this compelling wheat constituent. To this end, this study reports comprehensive information on the distribution and composition of TP, WEP, WUP, and A/X in millstreams of different wheat samples. Analysis of the literature indicates that no complete data on pentosan composition of bran and shorts have been reported. Accordingly, particular attention was paid to the bran and shorts fractions where pentosans are concentrated to examine the relative value of whole wheat, shorts, and different bran fractions as sources of dietary fiber, of which pentosans are the predominant components in wheat.

MATERIALS AND METHODS

Samples

Six Canadian wheat samples grown commercially in western Canada in 2001, each comprising a single cultivar, were supplied by the Canadian Wheat Board and included four genotypes representing three commercial classes: AC Barrie and Superb (Canada Western Red Spring), AC Corinne (Canada Western Extra Strong), and Snowbird (Canada Western Hard White). Superb and Snowbird were grown in two different locations.

Milling

Wheat samples were tempered to a moisture of 16% and milled using a tandem Buhler MLU-202 pneumatic laboratory mill (Martin and Dexter 1991), with minor flow changes. The mill flour sieves were clothed with 132- μ m Nitex cloth, and roll gaps were set to achieve an extraction rate of \approx 80%. Sixteen mill fractions were obtained: flours from four break passages (B1–B4), flour from a sizing passage (S1) that receives relatively pure endosperm middlings from B1 to B3, flour from a quality passage (Q1) that receives branny material from S1 and middlings from B4, and flour from six reduction (middling) passages (M1–M6). Bran flour

(BF) and finished coarse bran were obtained by passing coarse bran from B4 through a bran finisher followed by sieving on a box sifter over Nitex 183- μ m cloth. Fine bran and shorts represented the coarse overtail products from Q1 and M6, respectively.

Various millstreams from each milling were collected, weighed, and analyzed for moisture and ash content in triplicate according to Approved Methods 44-15A and 08-01, respectively (AACC International 2000). Four pairs of flour streams were combined: B1 and B2, B3 and B4, M1 and M2, and M3 and M4. Additionally, all flour streams of each cultivar sample (AC Barrie, AC Corinne, Superb1, and Snowbird2) were blended according to yield proportions to produce straight-grade flour. Millstreams were double-bagged to minimize moisture loss, left at room temperature for four weeks to allow maturing, then stored at -30°C .

Determination of Total Pentosans and Water-Extractable Pentosans

TP of all flour millstreams, excluding bran and shorts fractions, were analyzed for pentosan content using the colorimetric method of Douglas (1981). D-(+)-Xylose was used as a standard to construct calibration curves. TP of a test sample was calculated based on the absorbance differences at 552 and 510 nm using the calibration curve. TP of whole grain wheat, bran, and shorts fractions were determined using the method of Bell (1985) which is similar to Douglas' procedure but implements sample prehydrolysis using 0.5M sulfuric acid, which is necessary to completely solubilize bran particles that would otherwise interfere with subsequent absorbance measurements.

WEP of flour fractions were determined by the method of Lempereur et al (1997) with modifications. Sample (200 mg) was weighed into a Kimax tube (15 mL) and distilled water (10 mL) was added. The mixture was dispersed using a vortex mixer and shaken in a rotary shaker (40 rpm) for 15 min at room temperature. After centrifugation (5 min, $5,000 \times g$), the diluted supernatant (2 mL) was collected and analyzed using the phloroglucinol method of Douglas (1981). WEP of ground wheat, bran, and shorts were determined by extracting the sample (200 mg) with distilled water (10 mL) under continuous stirring (30°C , 2 hr) to completely extract WEP from wheat, bran, and shorts (Hashimoto et al 1987; Delcour et al 1999). After centrifugation (10 min, $8,000 \times g$), the extract (3 mL) was incubated with 1M sulfuric acid (3 mL, 100°C , 30 min). After centrifugation (10 min, $8,000 \times g$), the diluted hydrolyzate (2 mL) was analyzed using the method of Douglas (1981). WUP was calculated as the difference of TP and WEP. Replicates of TP and WEP of test samples were performed on separate days.

Determination of Arabinose-to-Xylose Ratio

The A/X for total AX of the millstreams of one representative cultivar sample (AC Barrie) was determined using the alditol acetates method with inositol as the internal standard (Englyst and Cummings 1984). Bran and shorts fractions were prehydrolyzed with 72% (w/w) sulfuric acid for 1 hr at 30°C followed by further hydrolysis with 1M sulfuric acid for 3 hr at 100°C . Arabinose and xylose were released and analyzed as alditol acetate derivatives. The latter were separated by gas chromatography (GC) using a column (DB-5) 30 m \times 0.25 mm, i.d., in a Varian STAR 3400CX GC operated at 200°C and equipped with a flame-ionization detector set at 250°C . The A/X of the millstreams was calculated as the total arabinose divided by xylose. We made no distinction for the contribution of arabinose from arabinogalactans because the latter are water-soluble (Gruppen 1992) and are therefore included in the WEP fraction.

Statistical Analysis

Statistical analysis of mean differences was performed using statistical software SPSS 8.0 for Windows (SPSS, Chicago, IL);

analysis of variance (ANOVA) was followed by Duncan's multiple comparison for mean difference testing.

RESULTS AND DISCUSSION

Concentration and Composition of Pentosans in Whole Grain Wheat Samples

There were significant variations in wheat pentosan content and composition among the different wheat samples (Table I). TP and WEP in whole grain wheat ranged from 5.45–7.32% and 0.62–0.90% (dm) respectively. These results are similar to those previously reported (Hashimoto et al 1987; Henry 1987; Hartunian-Sowa 1997). Both TP and WEP contents of whole grain wheat were independent of wheat ash content as no correlations between ash content and TP and WEP were found. All pentosan parameters for whole grain wheat, including the WEP/WUP ratio, showed evidence of both genotype and environmental influences. TP and WEP varied by ≈ 25 and 31%, respectively, among cultivar samples. As well, there was a 28% difference in WEP content for the two samples of Superb (Table I) with WEP contents of 0.70 and 0.90%, respectively. While the quantity of WEP in wheat or flour (see below) is relatively low compared with TP or WUP, small variation in WEP may be practically significant, as this fraction is more rheologically reactive than WUP. WEP has a positive effect on breadmaking, in contrast to WUP, which has a negative effect (Jelaca and Hlynka 1972; Hanh and Rasper 1974; Rouau et al 1994; Courtin and Delcour 2002). Therefore, WEP may have a disproportionate effect on pentosan functionality for breadmaking. Very little is known about environmental effects on pentosans and the possible influence on flour functionality. Our results for the cultivar Superb are in agreement with the finding of Lempereur et al (1997), who found high levels of genetic and environment variability in total AX and WE-AX fractions of durum wheat. Research on genetic and environmental effects on wheat pentosans is currently ongoing in our laboratory.

Extractability of pentosans can be characterized by the WEP/WUP ratio (Lempereur et al 1997). For whole grain wheat, it was highest for the Superb1 sample (0.16), while AC Barrie (0.11) and Superb2 (0.11) had the lowest values. No relationship was found

between water extractability of pentosans and pentosan concentration in whole wheat.

Variation in Concentration and Composition of Pentosans in Straight-Grade Flour

The basic purpose of milling for production of refined flour from wheat is to separate endosperm from other kernel tissues as efficiently as possible. Depending on the flour extraction rate, straight-grade flour would be expected to contain a concentration and composition of pentosans very different from that of whole wheat, which is what we found (Table II). There was significant variation in TP content among the four straight-grade flours that were tested. TP ranges were 1.88–2.22% (dm), reflecting a 17% difference between the lowest (AC Corinne) and highest (Superb1) values. WEP contents of straight-grade flours varied by $\approx 20\%$, from 0.49% (AC Barrie) to 0.60% (Superb1) but the differences were not statistically significant. TP and WEP data are in agreement with the previous results (Ciacco and D'Appolonia 1982; Hartunian-Sowa 1997; Delcour et al 1999).

Both TP and WEP contents of straight-grade flour, and ash content as well, were much lower than those in whole wheat, confirming that the aleurone and pericarp layers that are enriched in pentosans (Lempereur et al 1997) were efficiently removed during milling. Averaged over all samples, ash, TP, and WEP contents of flour were 60, 69, and 32% lower, respectively, than corresponding values in whole wheat. However, the WEP/WUP of flour was $>260\%$ higher when compared with whole grain wheat, indicating that flour pentosans are considerably more extractable in water.

Again, we found no apparent correlation between ash content and TP and WEP among the straight-grade flour samples.

The relationship between TP content of whole grain wheat and straight-grade flour ($r = 0.66$) was less strong than that for WEP content ($r = 0.89$). Based on the limited number of four wheat samples that we compared in this way, TP content of straight-grade flour cannot be well predicted from wheat data. In contrast, for WEP content, it appeared that wheat data could provide a reliable indicator of flour WEP concentration. This would be beneficial from a cultivar development perspective (for breeding of genotypes with higher levels of WEP), particularly for screening

TABLE I
Variation in Concentration and Composition of Pentosans in Whole Grain Wheat^a

Sample	Ash (%)	TP ^b (%)	WEP ^c (%)	WEP/WUP ^d
AC Barrie	1.76 ± 0.0bc	6.28 ± 0.06b	0.62 ± 0.03a	0.11
AC Corinne	1.63 ± 0.06a	5.45 ± 0.02a	0.70 ± 0.06a	0.15
Superb1	1.90 ± 0.01d	6.61 ± 0.10c	0.90 ± 0.05b	0.16
Superb2	1.79 ± 0cd	6.91 ± 0.13c	0.70 ± 0.02a	0.12
Snowbird1	1.87 ± 0.05cd	7.32 ± 0.03d	0.87 ± 0.05b	0.13
Snowbird2	1.65 ± 0.01ab	6.72 ± 0.13c	0.87 ± 0.04b	0.15

^a Data are mean values (dm) ± standard deviation. Values followed by different letters in columns indicate significantly different means at $P < 0.05$.

^b Total pentosans.

^c Water-extractable pentosans.

^d Ratio of WEP to water-unextractable pentosans (WUP).

TABLE II
Variation in Concentration and Composition of Pentosans in Straight-Grade Flour^a

Sample	Ash (%)	TP ^b (%)	WEP ^c (%)	WEP/WUP ^d
AC Barrie	0.53 ± 0.05a	1.88 ± 0.04a	0.49 ± 0.02a	0.36
AC Corinne	0.57 ± 0.01a	1.87 ± 0.03a	0.50 ± 0.03a	0.37
Superb1	0.54 ± 0.01a	2.22 ± 0.08b	0.60 ± 0.08a	0.37
Snowbird2	0.51 ± 0.01a	2.04 ± 0.01ab	0.54 ± 0.07a	0.36

^a Data are mean values (dm) ± standard deviation. Values followed by different letters in columns indicate significantly different means at $P < 0.05$.

^b Total pentosans.

^c Water-extractable pentosans.

^d Ratio of WEP to water-unextractable pentosans (WUP).

of early generation material when the amount of available wheat is insufficient for accurate milling.

Variation in Distribution and Composition of Pentosans in Millstreams

To understand how the concentration and composition of pentosans changed during milling in response to varying flour refinement, millstreams, bran, and shorts fractions were evaluated for TP and WEP contents and WEP/WUP ratio (Table III). In addition, the A/X ratios of millstreams of AC Barrie were analyzed to measure dependency of pentosan structure on degree of flour refinement.

There was substantial variation in the distribution of pentosans in millstreams among the six cultivar samples. The collective patterns of variation in TP and WEP contents within and among the three major milling fractions (break flours, reduction flours, and bran and shorts) are shown in Fig. 1. All the samples produced similar pentosan distributions within millstreams; however the uniformity of pentosan composition declined with decreasing flour refinement. This was especially evident in the WEP contents of the tail-end reduction streams M5 and M6 and bran flour (BF) (Fig. 1B). In general, coarse bran, fine bran and shorts were the most variable fractions across cultivar samples for both TP and WEP (Fig. 1) presumably due to their higher TP and WEP concentrations.

The first patent flours (S1, M1, and M2) and low-grade flour streams containing higher ash content (M5, M6, bran flour) typically yielded lower and higher TP contents, respectively, and the highest and lowest WEP/WUP ratios, respectively. TP and WEP ranged widely from 1.69–32.4% and 0.42–1.76% (dm), respectively, across 16 milling fractions including bran and shorts fractions. The efficacy of milling to generate refined flour from wheat through separation of endosperm from bran can be seen clearly in the discontinuity between ash and TP contents for bran and shorts fractions compared with corresponding results for flour streams. For example, whereas there was only a ≈15% difference in mean ash content between the lowest grade flour stream (M6) and the shorts fraction, the latter contained more than three times the pentosan content of M6 (Table III), which clearly shows that the ash gradient in the kernel does not match the TP gradient as tissues cross over from endosperm to aleurone and pericarp. Therefore, shorts and bran fractions have considerably more TP-rich material than M6, though ash content is comparable. Shorts should be particularly rich in aleurone and have higher WEP compared with M6. This would support the conclusion that the higher values in shorts are due to higher aleurone content despite comparable ash content. Lack of sensitivity of ash content as a measure of flour refinement at relatively high extraction rates is underscored by these results.

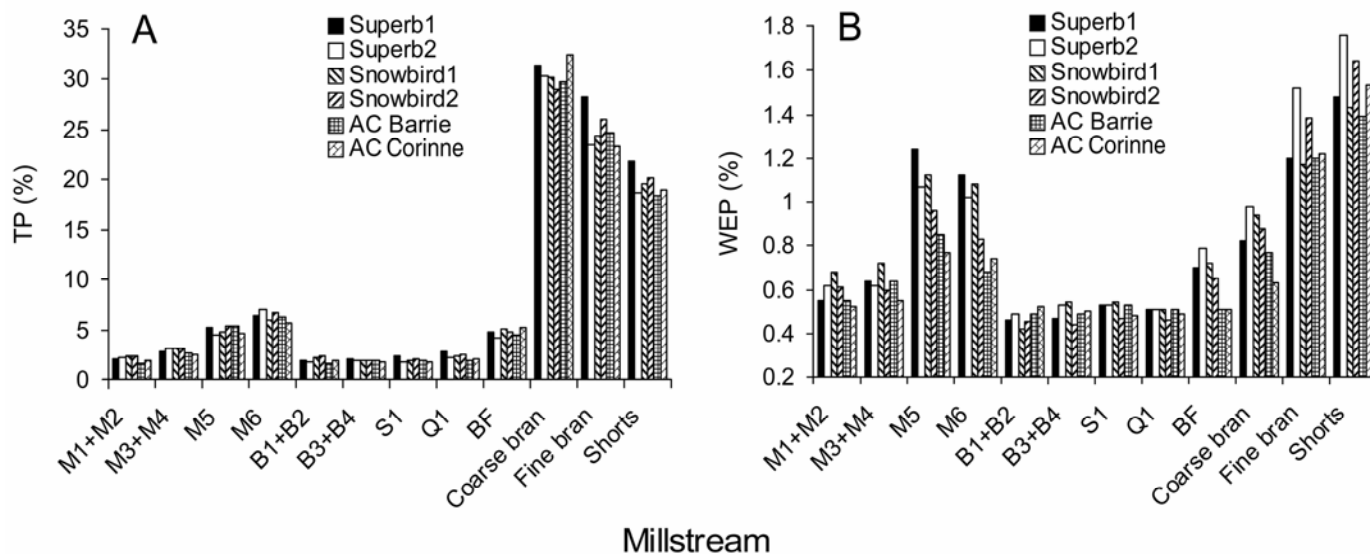


Fig. 1. Total pentosan (TP) (A) and water-extractable pentosan (WEP) (B) contents of flour streams and bran and shorts fractions. Histogram bars from left to right are for samples Superb1, Superb2, Snowbird1, Snowbird2, AC Barrie, and AC Corinne.

TABLE III
Variation in the Distribution and Composition of Pentosans in Millstreams of Six Cultivar Samples^a

Millstreams	Ash (%)		TP ^b (%)		WEP ^c (%)		WEP/WUP ^d	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
M1+M2	0.43	0.37–0.47	2.14	1.69–2.45	0.59	0.52–0.68	0.39	0.33–0.48
M3+M4	0.99	0.87–1.10	2.92	2.72–3.18	0.63	0.55–0.72	0.28	0.23–0.31
M5	2.30	2.02–2.60	5.00	4.42–5.41	1.00	0.85–1.24	0.26	0.19–0.32
M6	3.52	3.08–3.91	6.37	5.63–7.10	0.91	0.68–1.12	0.17	0.12–0.22
B1+B2	0.58	0.49–0.77	1.98	1.71–2.32	0.47	0.42–0.52	0.32	0.23–0.40
B3+B4	0.67	0.57–0.80	1.95	1.93–2.09	0.50	0.44–0.54	0.35	0.29–0.40
S1	0.44	0.44–0.58	2.00	1.81–2.37	0.51	0.47–0.54	0.35	0.28–0.40
Q1	0.80	0.72–0.88	2.33	2.00–2.81	0.50	0.46–0.51	0.28	0.22–0.35
BF	2.90	2.63–3.33	4.79	4.19–5.29	0.65	0.51–0.79	0.16	0.11–0.23
Coarse bran	7.08	6.83–7.48	30.6	29.0–32.4	0.84	0.63–0.98	0.03	0.02–0.03
Fine bran	5.38	4.90–5.62	25.1	23.4–28.3	1.28	1.17–1.52	0.06	0.04–0.07
Shorts	4.15	3.91–4.29	19.6	18.3–21.9	1.54	1.39–1.76	0.09	0.07–0.10

^a Dry basis.

^b Total pentosans.

^c Water-extractable pentosans.

^d Ratio of WEP to water-unextractable pentosans (WUP).

Above $\approx 0.6\%$ (dm) ash, there was a strong positive relationship between ash and TP content of millstreams (Fig. 2A, $R^2 = 0.92$), and ash and WUP content (Fig. 3A, $R^2 = 0.93$). Similarly for bran and shorts fractions, very strong relationships existed between ash and TP contents (Fig. 2B, $R^2 = 0.89$) and ash and WUP contents (Fig. 3B, $R^2 = 0.90$). For bran and shorts fractions, TP and WUP content increased in the order of coarse bran > fine bran > shorts (Figs. 2B and 3B). Absence of correlations between ash and TP, or ash and WUP for millstreams below $\approx 0.6\%$ ash is due partly to the highly refined nature of these flour streams (i.e., minimal aleurone or bran contamination) and likely absence of any significant pentosan gradient in endosperm. These observations confirm the results of Delcour et al (1999), who showed that TP, WEP, and A/X were practically independent of extraction rate up to $\approx 75\%$ for a single European wheat.

No relationship existed between WEP and ash contents across all millstreams (Fig. 4A), although there was a positive relationship between WEP and ash content for high-grade flour streams at 0.6–1.0% (dm) ash. Interestingly, at $\approx 0.60\%$ ash, WEP concentration was at a distinct minimum (Fig. 4A). For all six cultivar samples, this point generally corresponded to millstreams B1+B2 in contrast with M1+M2 streams, which invariably had lower ash contents (≤ 0.47 , Table III).

WEP concentration of bran and shorts fractions (Fig. 4B) showed an opposite pattern of variation compared with that observed for TP (Fig. 2B). WEP content decreased with increasing ash content

($R^2 = 0.84$, Fig. 4B) and showed a different rank order from that of TP and WUP: shorts > fine bran > coarse bran. The results for bran and shorts fractions are consistent with the findings of Delcour et al (1999), Hartunian-Sowa (1997), and Hashimoto et al (1987). According to Delcour et al (1999), a lower WEP in bran than in shorts is probably due to reduced accessibility of the bran fraction to water.

The WEP/WUP of all millstreams among all cultivar samples (Table III) ranged from 0.02 (coarse bran, AC Corinne) to 0.47 (M1+M2, AC Barrie). WEP/WUP decreased with increasing ash content ($R^2 = 0.82$, Fig. 5). The lower WEP/WUP of lower grade flour streams and millfeed fractions confirm the previous results of a lower degree of water extractability of pentosans toward the outer layers of the kernel (Ciacco and D'Appolonia 1982; Hartunian-Sowa 1997; Delcour et al 1999).

The A/X ratio has been widely used to examine structural characteristics of pentosans (Medcalf et al 1968; Ciacco and D'Appolonia 1982; Izydorczyk et al 1991; Hartunian-Sowa 1997; Delcour et al 1999). A higher A/X ratio indicates a greater degree of substitution along the xylan backbone that will prevent aggregation of unsubstituted xylose residues and will result in increased water extractability of pentosans (Andrewartha et al 1979; Vinkx and Delcour 1996; Hartunian-Sowa 1997). For the AC Barrie cultivar sample, the A/X of 14 millstreams varied from 0.39 (coarse bran) to 0.62 (M1+M2) (Fig. 6A and 6B). The result suggests an inverse relationship between A/X and contamination of millstreams with aleurone tissue. According to Mares and Stone (1973), the differences in extractability of pentosans from wheat endosperm cannot be ascribed to the differences in pentosan size or A/X ratio but to chemical interactions with other cell wall components. However, we found a strong negative relationship ($R^2 = 0.77$, Fig. 6A)

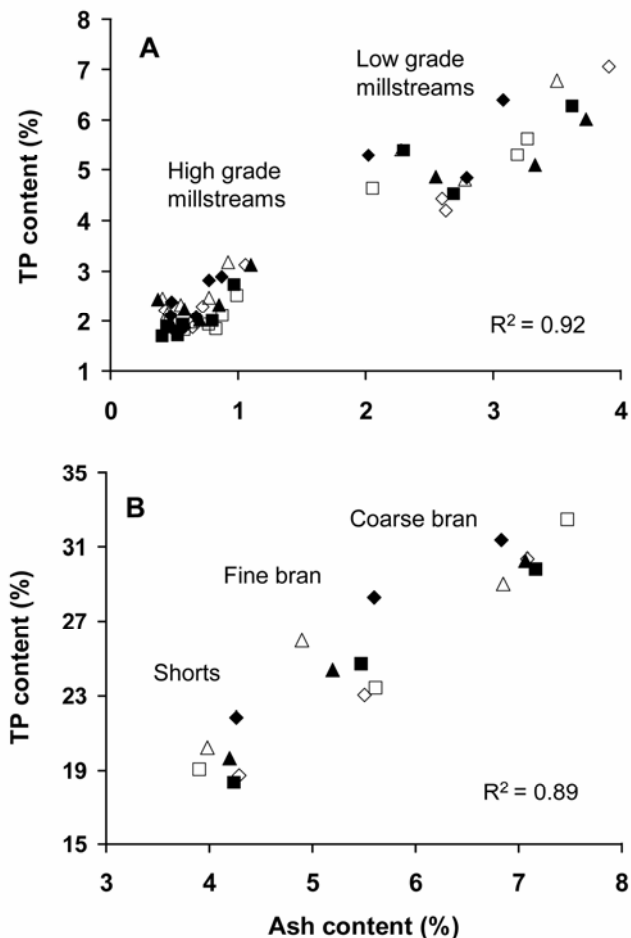


Fig. 2. Total pentosan (TP) content of flour streams (A) and bran and shorts fractions (B) in relation to ash content of different cultivar samples. ■ AC Barrie, □ AC Corinne, ◆ Superb1, ◇ Superb2, ▲ Snowbird1, △ Snowbird2. High- and low-grade millstreams refer to those with relatively low and high ash contents, respectively, as reported in Table III. Low-grade millstreams comprise M5, M6, and bran flour.

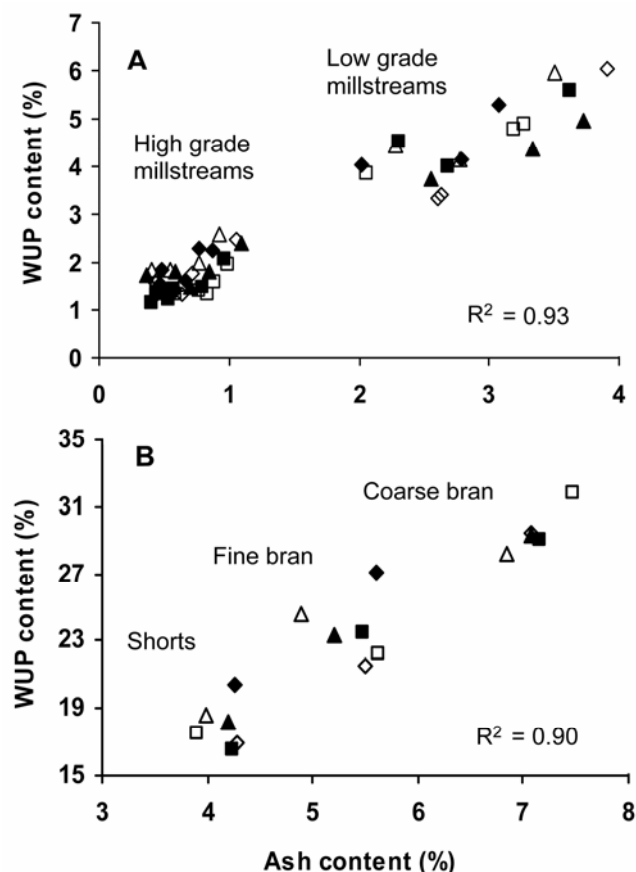


Fig. 3. Water-unextractable pentosan (WUP) content of flour streams (A) and bran and shorts fractions (B) in relation to ash content of different cultivar samples. ■ AC Barrie, □ AC Corinne, ◆ Superb1, ◇ Superb2, ▲ Snowbird1, △ Snowbird2. High- and low-grade millstreams as in Fig. 2.

between A/X and ash content, indicating that A/X decreases from the inner endosperm toward the outer layers of the kernel. This result is opposite to the findings of D'Appolonia and MacArthur (1975) and Ciacco and D'Appolonia (1982), who reported a higher degree of branching for wheat bran arabinoxylans compared with

those of endosperm. However, those results were derived from studies on isolated WEP and therefore relate only to the structures of the particular isolated fractions. In the present study, the A/X was analyzed in different milling fractions and our results are consistent with those of Delcour et al (1999), even though that study was also conducted on isolated WEP. We also confirmed A/X to be highly correlated with pentosan extractability (WEP/WUP, $R^2 = 0.80$, Fig. 6B). This supports our earlier supposition that WEP are concentrated in the inner endosperm. Taken together, our results demonstrate that pentosans of endosperm are clearly different in their extractability and structure from those of bran, therefore, leading to different functionality of pentosans.

CONCLUSIONS

The present study has provided a comprehensive analysis of the content and composition of pentosans in flour streams and bran and shorts fractions for a set of six hard spring wheats. There was significant variation in the concentration and composition of pentosans among different genotypes of hard spring wheat, although

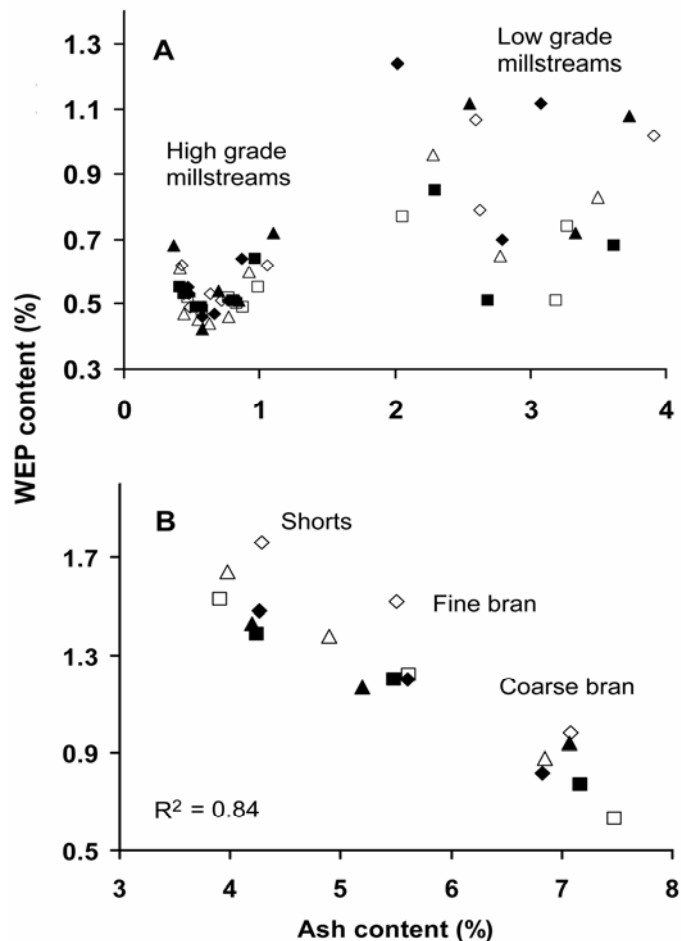


Fig. 4. Water-extractable pentosan (WEP) content of flour streams (A) and bran and shorts fractions (B) in relation to ash content of different cultivar samples. ■ AC Barrie, □ AC Corinne, ◆ Superb1, ◇ Superb2, ▲ Snowbird1, △ Snowbird2. High- and low-grade millstreams as in Fig. 2.

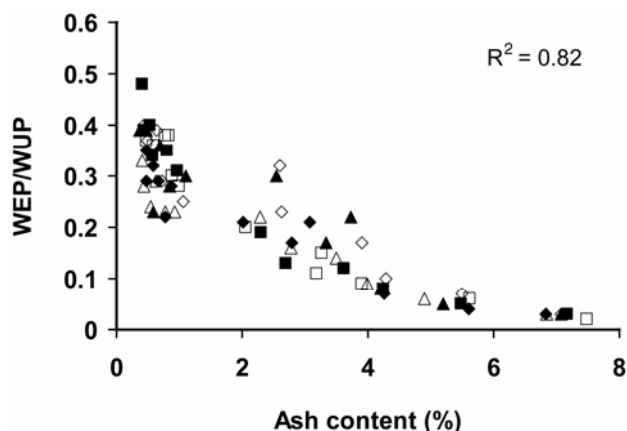


Fig. 5. Ratio of water-extractable pentosan (WEP) to water-unextractable pentosan (WUP) content of millstreams in relation to ash content of different cultivar samples. ■ AC Barrie, □ AC Corinne, ◆ Superb1, ◇ Superb2, ▲ Snowbird1, △ Snowbird2. High- and low-grade millstreams as in Fig. 2.

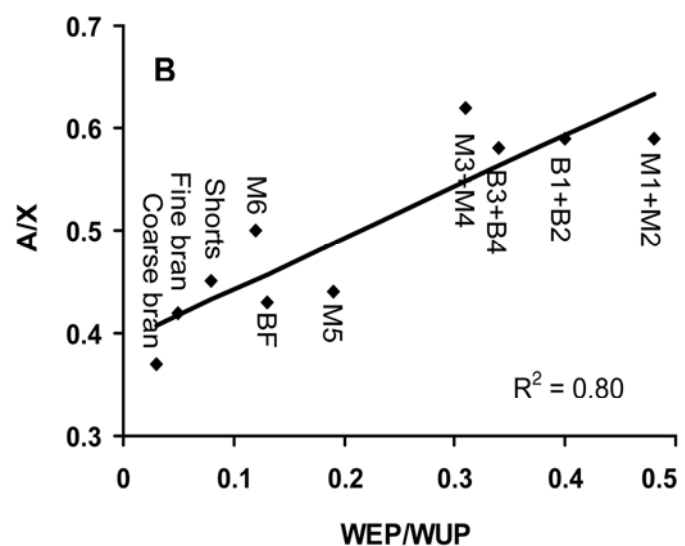
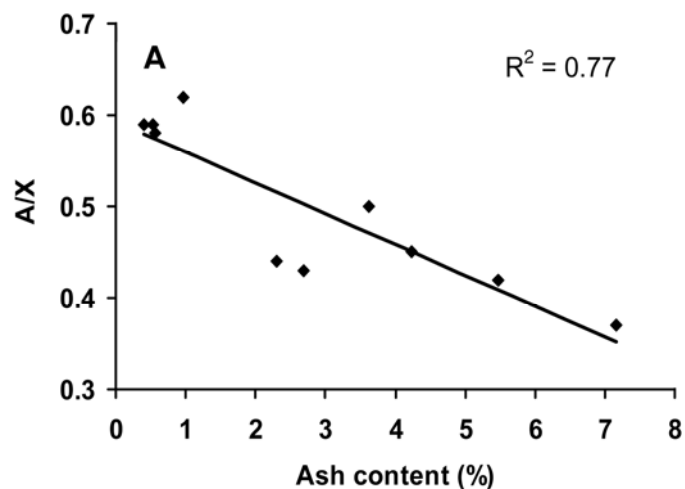


Fig. 6. Ratio of arabinose to xylose (A/X) in millstreams of wheat sample AC Barrie in relation to ash content (A) and the ratio of water-extractable pentosan (WEP) to water-unextractable pentosan (WUP) content. Data corresponds to milling fractions or combinations in order of increasing ash content: M1+M2, B1+B2, B3+B4, M3+M4, M5, bran flour (BF), M6, shorts, fine bran, and coarse bran.

undefined environmental factors may also have contributed significantly to the variation. The analysis of whole grain showed that both TP and WEP were independent of wheat ash content among the different genotypes. TP and WEP content of straight-grade flour were considerably lower than corresponding values in whole grain, and a strong relationship appeared to exist between WEP content of whole grain wheat and flour. This result indicates that flour WEP content could be well predicted from wheat data, an outcome that could be exploited in early generation screening of new cultivars with high WEP contents. Millstream results showed similar patterns of pentosan variation among cultivars. Above $\approx 0.6\%$ (dm) ash, very strong positive correlations were found between flour ash content and TP and WUP for all millstreams, including bran and shorts fractions. For WEP, however, a minimum existed at $\approx 0.60\%$ ash corresponding to the first break flours B1+B2. Compared with TP, no corresponding correlation between WEP and ash content was found across all millstreams, although for millstreams with ash contents of 0.60–1.0%, a positive correlation appeared to exist.

Bran and shorts fractions had considerably higher pentosan content than the lowest grade flour streams, substantially out of proportion with respective ash contents. For example, coarse bran typically had twice the ash level of the M6 flour stream, but TP content was five times higher. Pentosans, therefore, were a much more sensitive marker of flour refinement at high extraction than was ash content. Among bran and shorts fractions, the highest concentrations of TP and WUP were found in coarse bran. On average, $>30\%$ of coarse bran content consisted of pentosans, underscoring the importance of wheat bran as an outstanding source of dietary fiber. Fine bran and the shorts fraction had lower TP and WUP contents. The opposite pattern of variation was found for WEP, WEP/WUP, and A/X in bran and short fractions; shorts had the highest quantities, while fine bran and coarse bran had the lower quantities. In view of the distinctly high ratio of WEP/WUP for shorts, typically more than three times higher than that of coarse bran, the shorts fraction should merit more attention than it has received to date as a candidate for study of potential health benefits.

While the results of this study are pertinent to the six wheat cultivar samples that were tested in the context of the specific mill scheme used, knowledge of pentosan distribution in millstreams can provide millers with important information to optimize the functionality of flour blends for different products and customers. As well, our results clearly affirm the value of wheat bran and shorts as potent sources of dietary fiber for the food industry.

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