The European Journal of Plant Science and Biotechnology ©2010 Global Science Books

Characterization and Potential Uses of Functional Buckwheat Fractions Obtained by Roller Milling of New Canadian Buckwheat Genotypes

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ABSTRACT

Buckwheat is a well-established special crop in Canada, grown primarily in the province of Manitoba, with production ranging from about 13 to 20 thousand metric tonnes per year. In addition to recently released cross-pollinating lines with improved quality characteristics, the latest breeding activities in Manitoba have concentrated on successful crossing *Fagopyrum homotropicum* with common buckwheat (*Fagopyrum esculentum*). This has allowed for the development of new self-pollinating buckwheat as well as for the development of lines with traits absent from common buckwheat, such as enhanced green testa, frost tolerance and nutraceutical components. Buckwheat has gained an excellent reputation for its nutritious qualities in the human diet. In addition to high quality proteins, vitamins and minerals, buckwheat contains also some bioactive components, such as fagopyritols, flavonoids (rutin), and dietary fiber. Buckwheat starch and dietary fibre constituents also exhibit some unique physicochemical and technological properties. The distribution of buckwheat components is not uniform throughout the groat. Roller milling can be used to fractionate buckwheat groats into various streams enriched in specific components and exhibiting distinct functionality. Value-added processing of buckwheat fractions into a variety of noodles, bread and pasta has a tremendous potential to expand on international markets, given the verifiably high demand for a new generation of food products that are convenient, palatable, and deliver health benefits.

Keywords: buckwheat whole flour, dark flour, dietary fibre, morphology, starch, white flour

CONTENTS

INTRODUCTION

Buckwheat has been grown in Canada as a minor crop for many years. Its production peaked in the 1970s to the average of 38,125 tonnes/year, but declined to approximately 10,000 tonnes/year in the recent decade (FAO). Buckwheat is produced mainly in the provinces of Manitoba, Ontario, and Quebec, with Manitoba producing the majority of Canada's buckwheat in a given year (Statistics Canada). Among the first varieties of common buckwheat ((*Fagopyrum esculentum*) developed in Canada was Tokyo, released in 1955 by Agriculture Canada (Ottawa, Ontario) and Tempest, developed in 1971 by Agriculture Canada in Morden (Manitoba). The cultivars presently licensed for production in Canada are Mancan, Manor, AC Manisoba and AC Springfield, all developed at the Agriculture and Agri-Food Canada in Morden, Manitoba. These varieties are high-yielding, have large seeds with increased seed density, desirable flavour and colour, and produce a high percentage of large, whole groats after dehulling. The most current breeding directions in Manitoba, pursued by Kade Research Ltd., have focused on developing new buckwheat varieties with decreased weather-related variability in yields, self-pollinating capability, unique starch properties, and seed colour (Campbell 2003). The recently licensed varieties of buckwheat include large-seeded, high yielding varieties Koban and Koto, with the latter regarded superior for hand-made soba noodles on the Japanese market. Most recently, a successful cross of *Fagopyrum homotropicum* with *F. esculentum* led to the development of the first ever self-pollinating variety Koma. This manuscript summarizes the results of our studies designed to investigate and compare the composition and properties of recently developed and grown buckwheat genotypes in Canada.

MORPHOLOGICAL FEATURES OF GROATS

The mature fruit (achene) of buckwheat is normally covered by a dark coloured fibrous hull (pericarp) (Wijngard and Arendt 2006). The earlier developed genotypes of Canadian

Received: 1 July, 2009. Accepted: 27 February, 2010.

Invited Mini-Review

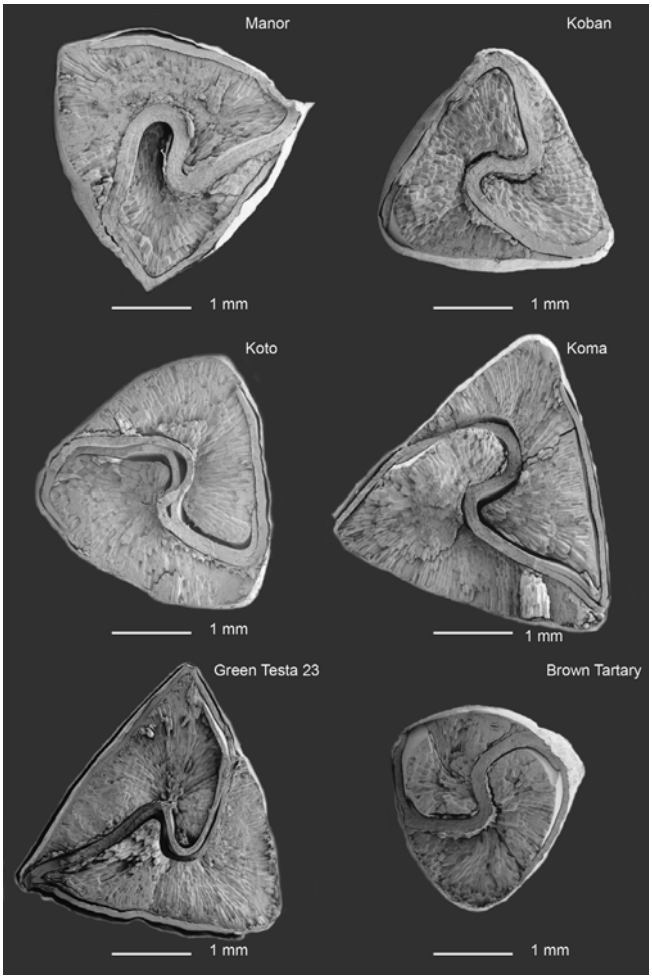

Fig. 1 Scanning electron micrographs of transversely fractured dehulled buckwheat groats. The mounted fractured buckwheat seeds were coated with 50 nm of gold and examined with a JEOL JSM-6400 scanning electron microscope at 10 KV.

buckwheat had dark brown hulls, whereas Koto is the first black hulled variety that has been registered in Canada. The dehulled achenes (groats) of all Canadian cultivars have a triangular shape but differ in size (**Fig. 1**). Groats of the self-pollinating variety Koma and of the green testa lines appeared to be slightly bigger than those of Koto, Koban, and Manor, however variations among groats within each variety have also been observed. Groats of tartary buckwheat were significantly smaller and rounder than those of common buckwheat.

The outer layers (spermoderm) of the buckwheat groat consist of the outer epiderm (testa), spongy parenchyma, and inner epiderm (Pomeranz 1979). In Koto all three spermoderm layers were evident (**Fig. 2A**), whereas in Koma (**Fig. 2B**) and in the green testa line (23) (**Fig. 2C**) the cells of spongy parenchyma and the inner epiderm appeared to be compacted. Staining of the groat sections for proteins (with aniline blue black) (**Fig. 2C**) showed the presence of proteins around the starch granules in the endosperm cells, however, the greatest concentration of proteins was noted in the aleurone and subaleurone layers. The cell walls (CW) of the spermoderm and aleurone cells were much thicker than those of the endosperm cell walls and presence of pectins in the CW was depicted with ruthenium red staining (**Fig. 2A, 2B**).

The scanning electron microscopy (SEM) examination revealed that the tartary genotype exhibited much thinner spermoderm than the common buckwheat lines (**Fig. 3**). Also, the aleurone layer, which thickness in common buckwheat ranged from 10-15 µm, appeared to be only 5-6 µm thick in the tartary buckwheat. Starch granules in buckwheat are contained in the elongated endosperm cells surrounded by relatively thin walls (**Figs. 2, 4-6**). In most genotypes, the endosperm cells located around the embryo and cotyledons were filled rather loosely with starch granules compared to the tightly packed cells in the peripheral portion of the endosperm. As a consequence, the granules originating from the cells of central endosperm were round, compared to the polygonal shapes of granules from the tangential endosperm regions. Starch granules in the tightly packed regions, especially in Koto and tartary buckwheat, appeared to be wholly embedded in a proteinaceous matrix, which presumably strengthens the cell structure. Only remnants of the proteinaceous material were present on the surface of round granules present in the central endosperm of

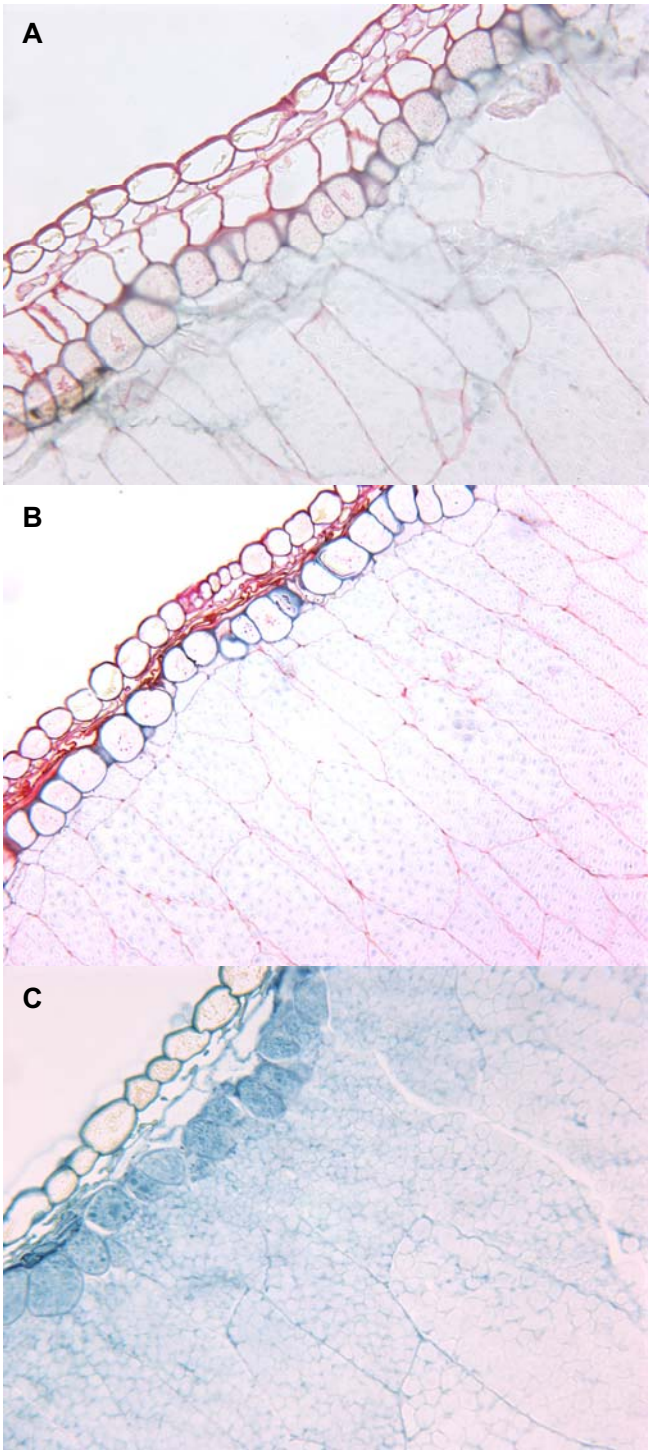

Fig. 2 Light microphotographs of transverse sections (2 µm thick) of groats stained with 0.05% ruthenium red (aqueous) for pectin material (A, B) and 1% aniline blue black in 7% acetic acid for proteins (C). Stained sections were examined with a Wild Leitz Orthoplan light microscope. (**A**) 'Koto', (**B**) 'Koma', (**C**) 'Green Testa'.

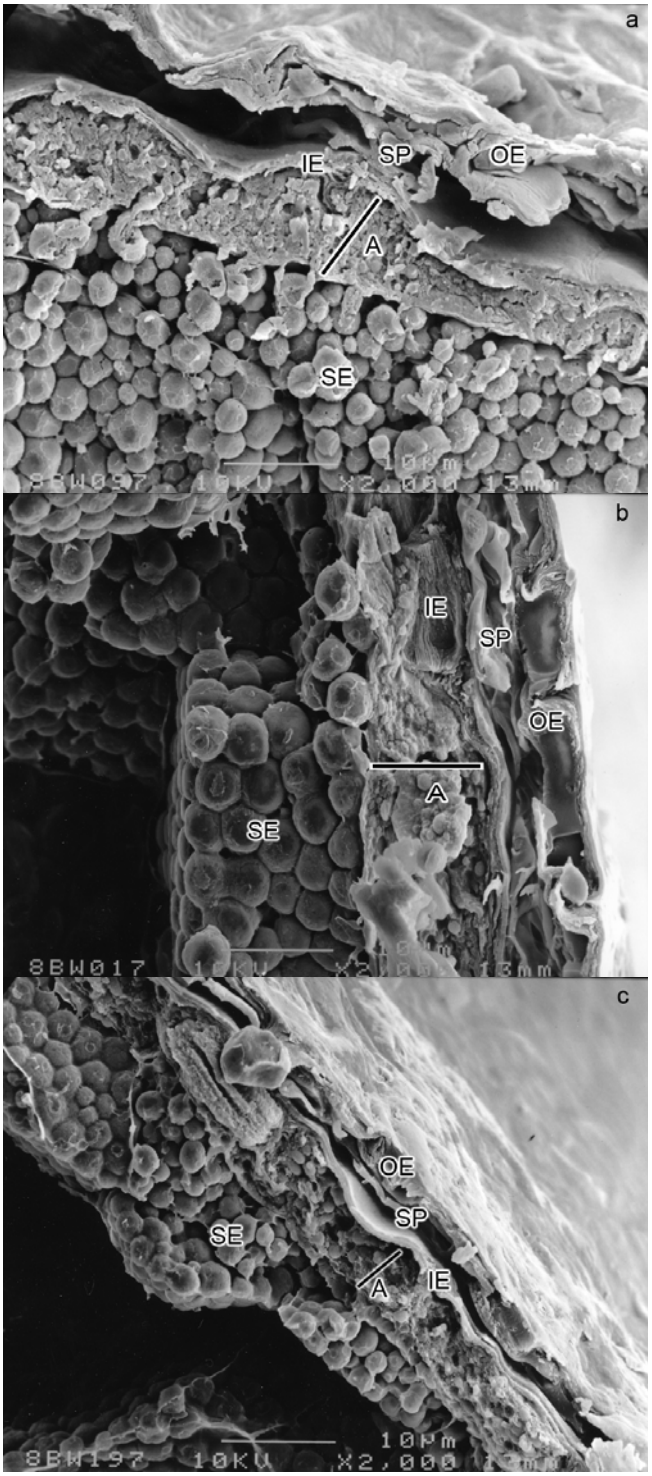

Fig. 3 Scanning electron micrographs of the outer layers of buckwheat groats. OE: outer epiderm; SP: spongy parenchyma; IE: inner epiderm; A: aleurone; SE: starchy endosperm. (**A**) 'Koto', (**B**) 'Green Testa' (**C**) 'Tartary'.

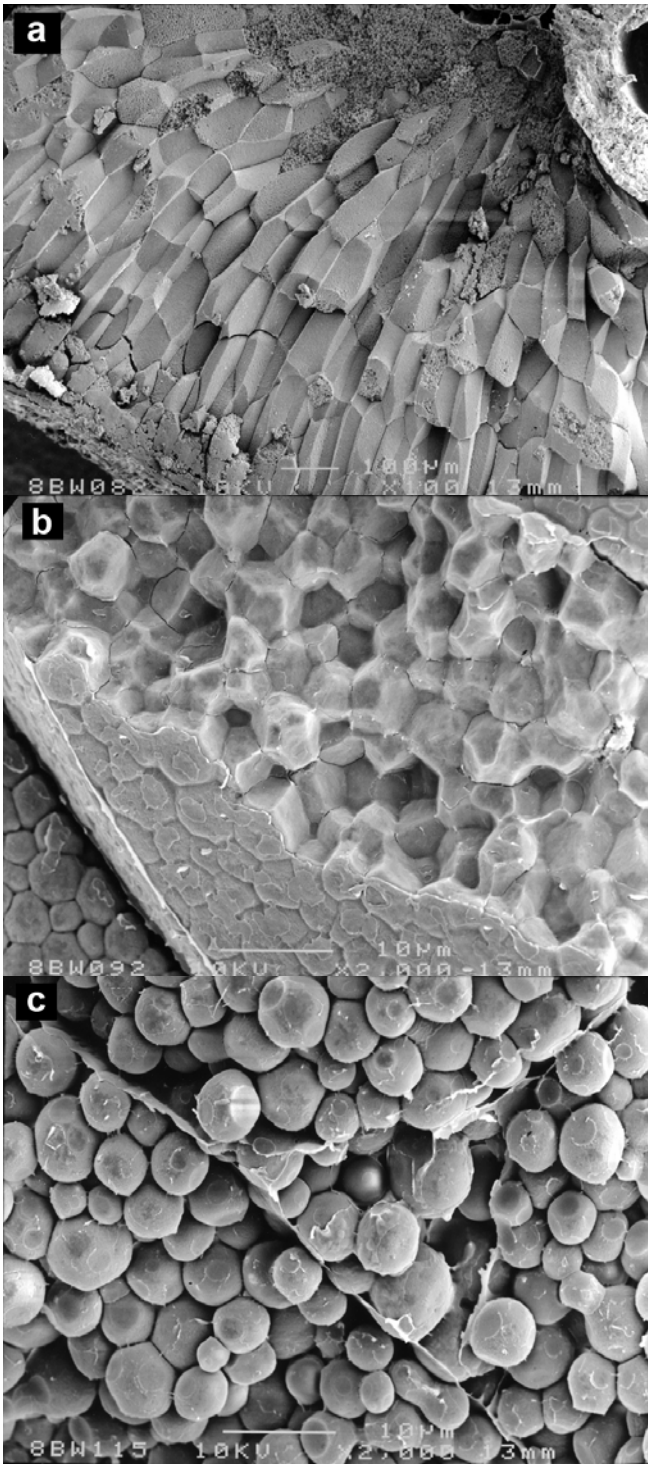

Fig. 4 Scanning electron micrographs of cross-sections of Koto groats (**A**) higher magnification of the peripheral (**B**) and central portions (**C**) of the endosperm.

Koto and Koma (**Figs. 4, 5**). Some differences in the degree of compactness of the endosperm cells and starch granules within the cells were also observed among different genotypes. For instance, Koma exhibited more loosely packed granules in the peripheral endosperm (**Fig. 5B**) than Koto (**Fig. 4B**) and tartary buckwheat (**Fig. 6B**). In contrast, most of the granules in tartary buckwheat were tightly packed within the cells, however some free space between the neighbouring cells were noticeable (**Fig. 6B, 6C**).

MILLING

Dehulled buckwheat was milled on the GRL tandem mill according to the flow shown in **Fig. 7**. Because of relatively soft texture of buckwheat endosperm, the milling flow was substantially shortened compared to the flow used for milling wheat with the same equipment (Martin and Dexter 1991). Groats were conditioned to 14% moisture content and the mill flow consisted of three break passages (instead of four in wheat milling), one sizing passage, and four reduction passages (instead of six). A bran finisher passage was added to reduce the size of bran particles collected after the third breaks. Generally the two common buckwheat cultivars with cross- and self-pollinating characteristics and the experimental green testa lines milled in a very similar

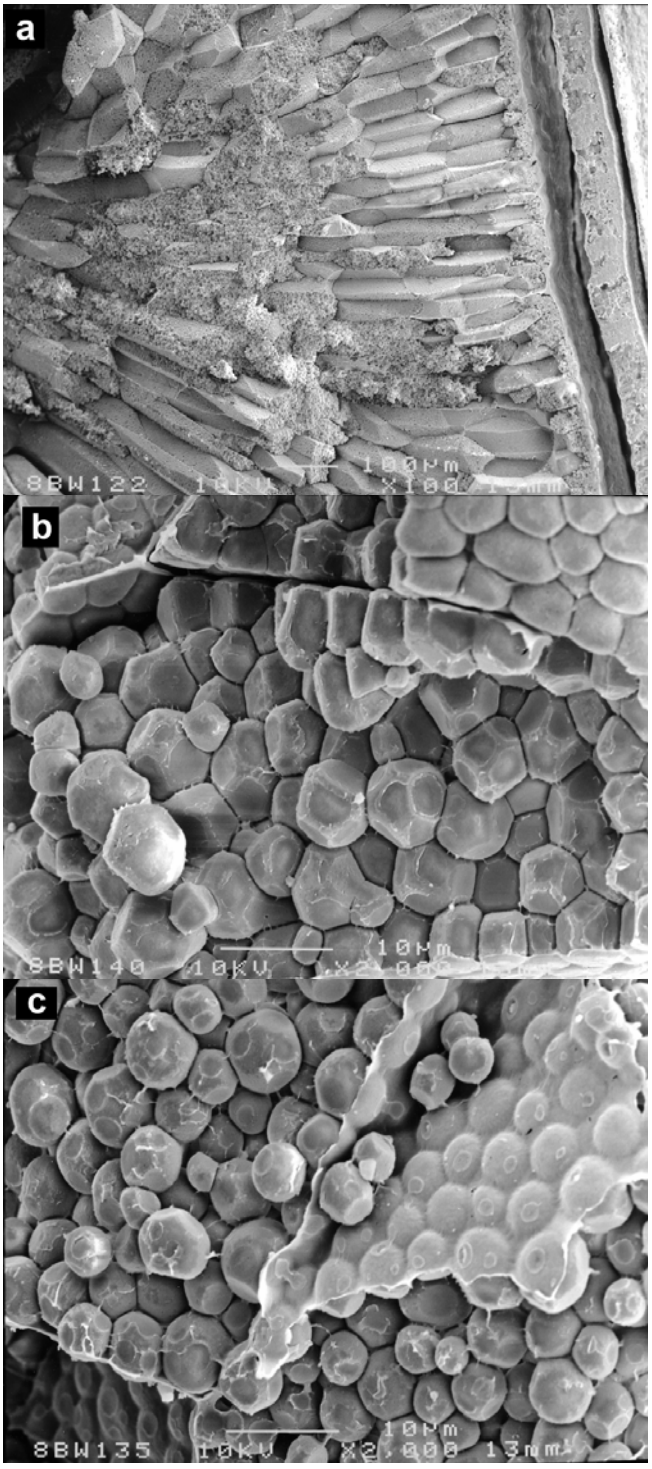

Fig. 5 Scanning electron micrographs of cross-sections of Koma groats (**A**). Higher magnification of the peripheral (**B**) and central portions (**C**) of the endosperm.

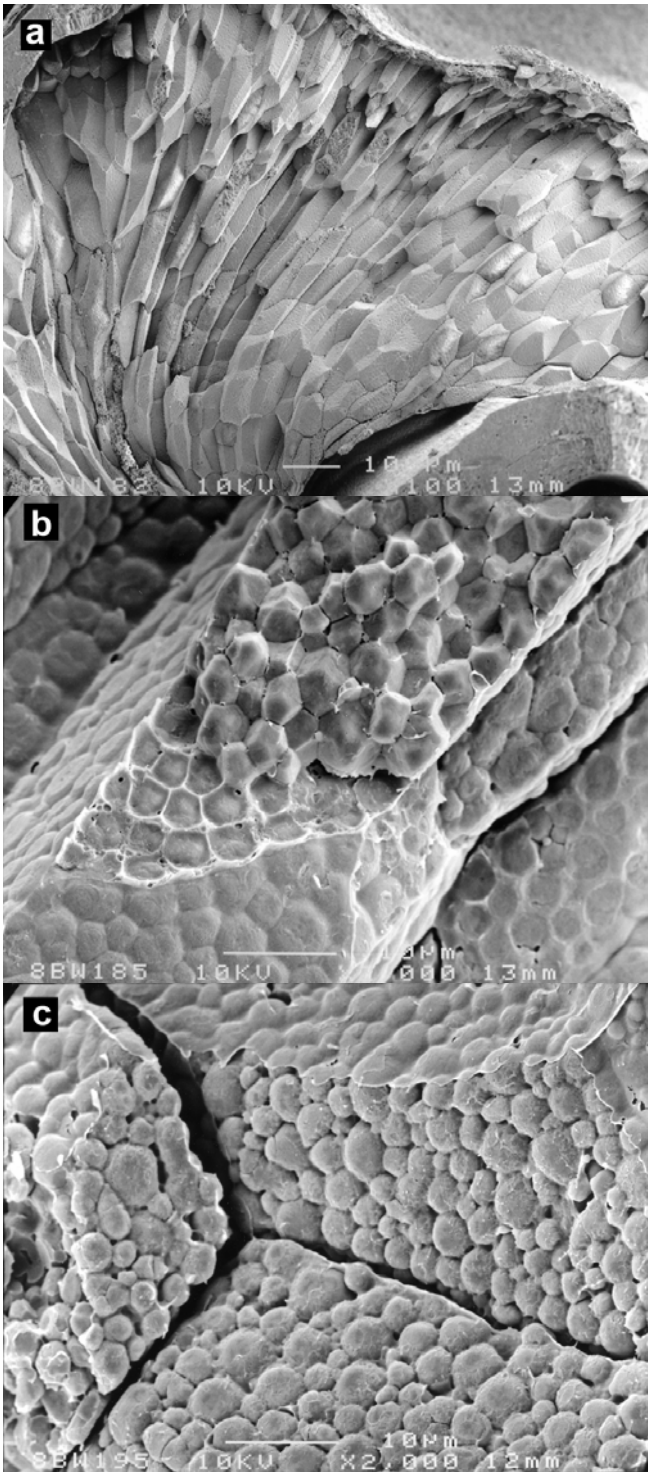

Fig. 6 Scanning electron micrographs of cross-sections of tartary buckwheat groats (**A**). Higher magnification of the peripheral (**B**) and central portions (**C**) of the endosperm.

manner in terms of the yield of individual milling fractions. The yield of total break flour (B1-B3) was very similar for all four lines, ranging from 29.2 to 29.6%; Koto yielded slightly lower amount of sizing (S) flour, but higher amount of bran fractions than Koma and the green testa lines. The tartary buckwheat, on the other hand, yielded substantially more B1-B3 flour and S flour, but lower amount of reduction flour (M1-M4) and bran fractions than the common buckwheat lines. The protein content in individual milling streams showed a specific pattern, with the M2-M4 reduction flours and bran fractions containing 3 to11 times more proteins than B1-B3 break, sizing (S) and M1 reduction flours (**Table 1**). The protein content in break and sizing flours of tartary buckwheat was higher, whereas that in the bran fractions was lower than in the corresponding streams of common buckwheat. The brightness of each milling fractions of tartary buckwheat was lower than of corresponding fractions of common buckwheat. The brightness of all three break flours and all bran fractions of the green testa lines was slightly lower than in corresponding fractions of the other two common buckwheat cultivars, but no differences in the L* values of the sizing and reduction flours were observed among these four lines.

The milling streams were combined based on the protein content and brightness values of individual streams to obtain three ground buckwheat products differing in appearance and composition and yielding a reasonable amount of milled products. Therefore, the white flour was prepared by

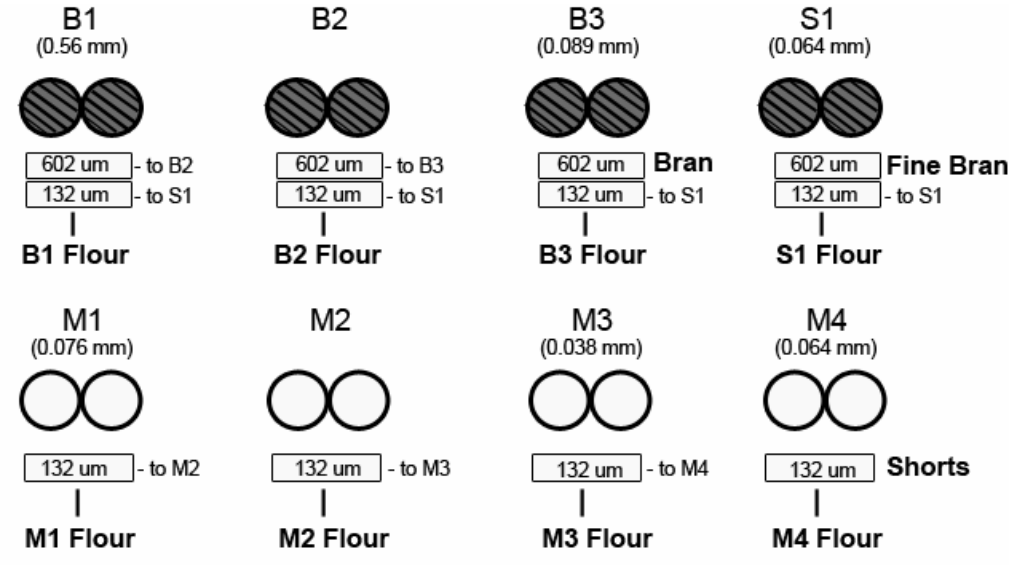

Fig. 7 Roller milling flow for buckwheat groats. B1-B3 break rolls; S1 sizing roll; M1-M4 reduction rolls. Numbers in brackets indicate the roll gap. Numbers in each rectangular indicate openings in sieves.

Table 1 Milling yields and characteristics of individual millings streams obtained after roller milling of different buckwheat lines[d].

Milling Streams/Flours	Green Testa -23			Green Testa -24			Tartary			Koto			Koma		
	Milling Yield[a] (%)	Protein[b] (%)	L*[c]	Milling Yield (%)	Protein (%)	L*	Milling Yield (%)	Protein (%)	L*	Milling Yield (%)	Protein (%)	L*	Milling Yield (%)	Protein (%)	L*
Break1 (B1)	10.6 ± 0.0	4.4 ± 0.0	90.1	10.4 ± 0.1	4.3 ± 0.0	89.6	9.0 ± 0.7	5.6 ± 0.4	87.4	10.4 ± 0.3	4.0 ± 0.0	90.3	10.8 ± 0.0	4.0 ± 0.1	90.4
Break2 B2	16.7 ± 0.2	4.1 ± 0.1	91.0	16.5 ± 0.1	3.9 ± 0.0	90.8	22.3 ± 0.1	5.1 ± 0.0	89.2	16.6 ± 0.2	3.7 ± 0.0	91.6	16.5 ± 0.1	3.7 ± 0.0	91.4
Break3 (B3)	2.3 ± 0.0	5.2 ± 0.0	90.0	2.3 ± 0.1	5.0 ± 0.0	89.8	2.3 ± 0.4	5.6 ± 0.0	88.1	2.2 ± 0.0	4.8 ± 0.1	90.3	2.1 ± 0.0	4.9 ± 0.0	90.3
Total B1-B3	*29.6*			*29.2*			*33.6*			*29.2*			*29.4*		
Sizing (S)	21.9 ± 0.2	5.1 ± 0.1	91.2	22.2 ± 0.7	4.7 ± 0.0	91.1	27.9 ± 0.6	5.5 ± 0.0	88.5	20.6 ± 1.0	4.5 ± 0.0	91.2	22.0 ± 0.6	4.6 ± 0.0	91.5
Reduction1 (M1)	18.3 ± 0.3	7.2 ± 0.0	90.9	18.0 ± 0.5	6.5 ± 0.0	91.0	17.2 ± 0.4	7.4 ± 0.0	85.4	17.6 ± 0.5	6.1 ± 0.0	90.9	17.8 ± 0.8	6.2 ± 0.0	91.3
Reduction2 (M2)	5.1 ± 0.1	18.6 ± 0.0	88.9	5.1 ± 0.1	16.7 ± 0.0	88.6	4.4 ± 0.1	18.3 ± 0.0	78.4	4.5 ± 0.2	15.8 ± 0.1	88.5	4.3 ± 0.4	16.8 ± 0.2	89.0
Reduction3 (M3)	3.8 ± 0.0	36.4 ± 0.0	87.2	3.6 ± 0.0	35.3 ± 0.1	86.6	2.9 ± 0.3	36.6 ± 0.1	74.7	3.4 ± 0.1	32.8 ± 0.2	86.7	3.3 ± 0.0	34.9 ± 0.1	87.0
Reduction4 (M4)	2.7 ± 0.0	45.6 ± 0.1	85.5	2.4 ± 0.0	44.8 ± 0.0	84.9	1.8 ± 0.2	41.8 ± 0.1	73.1	2.4 ± 0.2	43.0 ± 0.1	84.8	2.4 ± 0.1	43.6 ± 0.0	85.2
Total M1-M4	*29.9*			*29.1*			*26.3*			*27.9*			*27.8*		
Bran	5.9 ± 0.1	43.0 ± 0.5	75.2	6.7 ± 0.1	43.0 ± 0.1	75.4	4.5 ± 0.2	39.2 ± 0.2	71.6	6.9 ± 0.4	41.6 ± 0.2	76.7	7.1 ± 0.0	41.5 ± 0.0	75.2
Fine Bran	5.5 ± 0.0	38.3 ± 0.1	77.0	5.8 ± 0.4	39.0 ± 0.0	75.5	4.3 ± 0.0	32.8 ± 0.3	71.9	6.9 ± 0.7	38.1 ± 0.1	78.0	6.0 ± 0.3	37.3 ± 0.1	77.4
Shorts	6.5 ± 0.2	39.4 ± 0.1	78.1	6.4 ± 0.5	39.7 ± 0.2	76.5	3.2 ± 0.0	31.1 ± 0.1	70.7	7.5 ± 0.4	38.8 ± 0.2	79.7	6.5 ± 0.2	39.6 ± 0.1	78.4
Total Bran	*17.9*			*18.9*			*12.0*			*21.3*			*19.6*		

[a]Yields expressed as percentage of total weight of dehulled buckwheat recovered in each stream.
[b]%N x 5.7; dry matter basis.
[c] The colour of buckwheat milling streams was measured in duplicate using a chromameter (CR-410, Konica Minolta, Tokyo, Japan).
[d] All buckwheat genotypes: Koto, Koma (self-pollinating cultivar), two experimental green testa lines (23 and 24), and a tartary line were grown in southern Manitoba in 2007 and obtained from Kade Research Ltd (Morden, MB).

combining the three break flours, sizing flour and first reduction flour. The dark flour comprised remaining three reduction flours, bran (from break 3), fine bran (from sizing) and shorts. The whole-groat flour was obtained by combining all flour streams including bran and shorts. All four common buckwheat lines yielded between 67.4-69.8% of white flour and 29.5-31.6% of dark flour (**Table 2**). The tartary buckwheat yielded substantially higher amount of white flour (78.7%) at the expense of dark flour (21.1%).

Composition of whole groats and milling fractions

The composition of whole buckwheat flour (WBF) reflects that of the whole groats as the milling losses were generally very small (≤1.2%) (**Table 2**). As previously reported (Mazza and Oomah 2005), starch constitutes the major buckwheat component and its content varied very little (65.8-67.9%) among the four common buckwheat lines. The protein and ash contents were also very similar among cultivars, ranging from 14.1-14.6% and from 2.1-2.3%, respectively. The total dietary fibre content in WBF of Koto and Koma was slightly higher than in WBF of the green testa lines (**Table 3**). The total flavonoids and rutin contents, on the other hand were higher in the WBF of green testa lines. The WBF of tartary buckwheat contained substantially more flavonoids, rutin, and starch, but less proteins, ash, and dietary fibre compared to the WBF of common buckwheat cultivars.

The white buckwheat flours (WF), obtained from each cultivar, were similar in composition and contained mostly starch (~85-89%) and very small amounts of other constituents. The starch content in the WF from common buckwheat was about 20% higher than in the WBF. The dark flour was depleted of starch but enriched in other macro- and micronutrients. The dark buckwheat flours consisted of proteins (32-36%), dietary fibre (20-23%), starch (18-26%), and minerals (5-6%). The concentration of minerals, proteins, and dietary fibre in DF was about 2.5-3 times higher than in WBF. The DF of green testa cultivars contained higher amounts of total flavonoids and rutin than DF of Koto and Koma. The DF of tartary buckwheat contained slightly lower amounts of proteins and ash, but higher amounts of starch and significantly higher amount of flavonoids and rutin than DF of all common buckwheat. The composition of white and dark flours in relation to whole buckwheat flour for the cultivars investigated in this study is in general agreement with previous reports on the composition of roller milling fractions from common buckwheat; although the milling streams in this study were combined somewhat differently compared to previous studies (Stead-

Table 2 Yields and physicochemical characteristics of buckwheat flours.

Genotype/ Milling Fraction	Milling yield (%)	Colour[a]			Protein[b] (%)	Starch (%)	Ash (%)
		L*	a*	b*			
Green Testa-23							
WBF[c]	99.3	84.4	-1.4	8.6	14.6 ± 0.0	66.8 ± 1.0	2.2 ± 0.0
WF	69.8	90.8	-1.3	6.3	5.3 ± 0.0	85.9 ± 1.1	0.5 ± 0.0
DF	29.5	79.5	-1.5	11.2	36.5 ± 0.0	21.6 ± 0.4	6.2 ± 0.0
Green Testa-24							
WBF	99.4	84.3	-1.4	8.5	14.4 ± 0.0	67.9 ± 0.0	2.1 ± 0.0
WF	69.4	90.8	-1.3	6.3	4.9 ± 0.0	88.9 ± 0.2	0.4 ± 0.0
DF	30.0	78.7	-1.5	11.4	36.3 ± 0.0	19.3 ± 0.0	6.0 ± 0.0
Tartary							
WBF	99.8	80.0	-1.4	15.2	11.3 ± 0.1	75.1 ± 0.0	1.3 ± 0.1
WF	78.7	87.9	-1.5	9.4	5.8 ± 0.1	88.1 ± 3.1	0.4 ± 0.1
DF	21.1	72.9	-1.3	21.6	32.2 ± 0.0	26.6 ± 0.3	5.0 ± 0.0
Koto							
WBF	99.0	85.1	-0.8	9.3	14.6 ± 0.0	65.8 ± 0.6	2.3 ± 0.1
WF	67.4	90.9	-1.0	6.2	4.7 ± 0.0	85.7 ± 2.0	0.4 ± 0.1
DF	31.6	80.3	-0.7	12.2	35.6 ± 0.0	23.4 ± 0.6	6.4 ± 0.0
Koma							
WBF	98.8	85.4	-1.3	8.7	14.1 ± 0.0	67.5 ± 0.4	2.2 ± 0.1
WF	69.2	91.3	-1.2	6.0	4.7 ± 0.0	88.6 ± 0.4	0.4 ± 0.1
DF	29.6	79.6	-1.3	12.0	36.1 ± 0.0	18.2 ± 0.1	6.4 ± 0.0

[a]Values are means of 3 replicates; L* – brightness, a* – green/red chromaticity, b* – blue/yellow chromaticity measured with a chromameter (CR-410, Konica Minolta, Tokyo, Japan).
[b]Values of protein (%N × 5.7; dry matter basis), starch and ash are means of two replicates. Moisture and ash contents were determined according to the Approved Methods 44-15A and 08-01, respectively (AACC 2003). Protein content (N × 5.7) was determined by combustion nitrogen analysis (FP-248 Leco Dumas CAN analyzer, St. Joseph, USA) calibrated with EDTA according to Approved Method 46-30 (AACC 2003).
[c]WBF: whole buckwheat flour comprised all milling streams B1 – shorts, as indicated in **Table 1**. WF: white flour comprised milling streams B1 - M1. DF: dark flour comprised milling streams M2 - shorts

Table 3 Content of bioactive compounds in buckwheat flours.

Genotype/ Milling Fraction[a]	Total Flavonoids[b] (mg/100 g db)	Rutin[c] (mg/100 g db)	Total Fagopyritols[d] (mg/100 g)	Dietary Fibre[e] (% db)		
				Total	Insoluble	Soluble
Green Testa-23						
WBF	72.20 ± 7.10	24.37	450	7.6 ± 0.1	5.3 ± 0.1	2.3 ± 0.0
WF	9.45 ± 0.03	6.19	nd	2.0 ± 0.2	0.2 ± 0.0	1.8 ± 0.0
DF	234.20 ± 37.5	54.78	1400	20.9 ± 2.1	17.3 ± 2.1	3.6 ± 0.1
Green Testa-24						
WBF	76.35 ± 1.37	25.10	400	8.6 ± 0.3	5.9 ± 0.3	2.8 ± 0.1
WF	11.96 ± 0.24	7.12	nd	2.2 ± 0.1	0.1 ± 0.0	2.2 ± 0.1
DF	248.60 ± 28.7	53.90	1380	23.6 ± 0.1	20.4 ± 2.7	3.2 ± 0.1
Tartary						
WBF	2990.0 ± 6	1448.25	nd	6.7 ± 0.3	4.3 ± 0.2	2.4 ± 0.1
WF	457.9 ± 0.8	187.69	nd	2.6 ± 0.1	0.3 ± 0.0	2.2 ± 0.1
DF	9570.0 ± 344	5029.28	nd	22.1 ± 0.1	18.9 ± 0.1	3.2 ± 0.1
Koto						
WBF	44.73 ± 5.16	15.14	480	8.9 ± 0.9	5.8 ± 0.9	3.2 ± 0.1
WF	9.24 ± 0.50	5.84	100	2.9 ± 0.3	0.1 ± 0.0	2.8 ± 0.2
DF	146.00 ± 25.8	24.83	2200	21.9 ± 0.7	18.5 ± 0.7	3.4 ± 0.1
Koma						
WBF	47.80 ± 5.25	16.75	520	9.1 ± 0.2	6.5 ± 0.2	2.6 ± 0.1
WF	8.18 ± 0.04	6.06	190	3.8 ± 0.2	1.8 ± 0.1	2.0 ± 0.2
DF	161.30 ± 27.9	28.98	1580	21.5 ± 1.2	17.6 ± 1.2	3.9 ± 0.3

[a]WBF: whole buckwheat flour comprised all milling streams B1 – shorts, as indicated in **Table 1**. WF: white flour comprised milling streams B1 - M1. DF: dark flour comprised milling streams M2 - shorts.
[b]Total flavonoids content of buckwheat flour extract (in 80% methanol) was determined according to the method of Oomah and Mazza (1996).
[c]Rutin content in buckwheat flour extract (in 80% methanol) was determined via HPLC analysis. A HPLC system was equipped with 2487 UV detector and Supelco C18 column (330 × 4.8 mm) held at 37°C.
[d]Fagopyritols were extracted from buckwheat flours with ethanol/water (1:1) and analyzed by gas chromatography according to the method of Kawa *et al.* (2003).
[e] Dietary fibre content was determined according to the AACC Approved Method 32-07.

man *et al*. 2000, 2001a, 2001b; Bonafaccia *et al*. 2003; Skrabanja *et al*. 2004).

PHYSICOCHEMICAL PROPERTIES OF BUCKWHEAT FLOURS

Some differences in the colour of whole buckwheat flour, obtained from the genotypes tested in this study, were observed. The whole flours of Koto and Koma were slightly brighter (higher L* values), less green (higher a* values) and more yellow (higher b* values) than whole flours of the two green testa lines (**Table 2**). The whole flour of tartary buckwheat exhibited substantially lower L* but higher b* values than common buckwheat flours.

The SEM of white flour indicated that it contained mostly small clusters of adhering starch granules originating from the central endosperm. As a result the brightness of white flour was generally very high; the L* values of white flour from green testa lines were only slightly lower than of Koto and Koma. The dark flour, on the other hand, contained fragments of the seed coat, embryo, maternal tissues, and starch granules associated mostly with the peripheral tissues or cotyledons. The milling of green testa lines produced dark flour with slightly lower brightnes, higher green

Table 4 Pasting properties[a] of buckwheat flours.

Genotype/ Milling fraction[b]	Peak Viscosity (RVU)	Trough (RVU)	Breakdown (RVU)	Final Viscosity (RVU)	Setback (RVU)	Peak Time (min)
Green Testa-23						
WBF	372.7 ± 3.1	313.9 ± 2.2	58.8 ± 5.3	737.0 ± 3.0	423.0 ± 5.2	5.7 ± 0.1
WF	716.8 ± 3.8	502.7 ± 11.6	214.0 ± 15.4	1037.0 ± 7.0	534.3 ± 4.6	5.9 ± 0.1
DF	58.5 ± 0.6	54.1 ± 2.7	4.4 ± 2.1	93.2 ± 3.7	39.1 ± 1.0	7.0 ± 0.0
Green Testa-24						
WBF	360.5 ± 11.1	298.8 ± 7.5	61.8 ± 3.5	687.6 ± 8.4	388.8 ± 0.8	5.5 ± 0.0
WF	711.0 ± 5.1	516.8 ± 31.4	194.2 ± 26.2	1032.0 ± 11.4	515.3 ± 19.9	5.9 ± 0.2
DF	58.4 ± 0.8	54.8 ± 0.5	3.6 ± 0.2	89.3 ± 4.1	34.5 ± 3.6	6.9 ± 0.1
Tartary						
WBF	469.4 ± 8.4	427.5 ± 12.1	41.9 ± 3.7	1096.1 ± 11.8	668.6 ± 0.2	5.6 ± 0.0
WF	752.5 ± 1.1	512.5 ± 0.2	240.0 ± 1.2	1145.9 ± 4.0	633.4 ± 3.8	5.1 ± 0.0
DF	52.2 ± 1.0	49.3 ± 0.6	2.9 ± 0.4	102.7 ± 1.0	53.4 ± 0.4	6.8 ± 0.2
Koto						
WBF	375.3 ± 1.4	299.7 ± 3.6	75.6 ± 2.2	656.9 ± 7.0	357.2 ± 3.4	5.5 ± 0.0
WF	700.6 ± 14.4	485.5 ± 1.8	215.1 ± 12.6	926.4 ± 3.1	441.0 ± 1.2	5.8 ± 0.0
DF	58.3 ± 2.0	55.6 ± 0.8	2.7 ± 1.2	87.4 ± 1.7	31.8 ± 2.5	7.0 ± 0.0
Koma						
WBF	395.3 ± 8.4	322.9 ± 13.5	72.4 ± 5.1	693.5 ± 4.1	370.6 ± 9.4	5.7 ± 0.0
WF	709.9 ± 5.2	484.0 ± 3.6	225.9 ± 1.6	918.5 ± 10.6	434.6 ± 7.0	5.8 ± 0.0
DF	54.9 ± 1.4	52.8 ± 1.9	2.1 ± 0.5	88.4 ± 0.2	35.7 ± 2.1	7.0 ± 0.0

[a] RVA pasting parameters were obtained using the standard pasting test, 4 g of material (on 14% moisture content basis) and 25 mL of water; values are means of 2 replicates.
[b] WBF: whole buckwheat flour comprised all milling streams B1 – shorts, as indicated in **Table 1**.
WF: white flour comprised milling streams B1 - M1.
DF: dark flour comprised milling streams M2 - shorts.

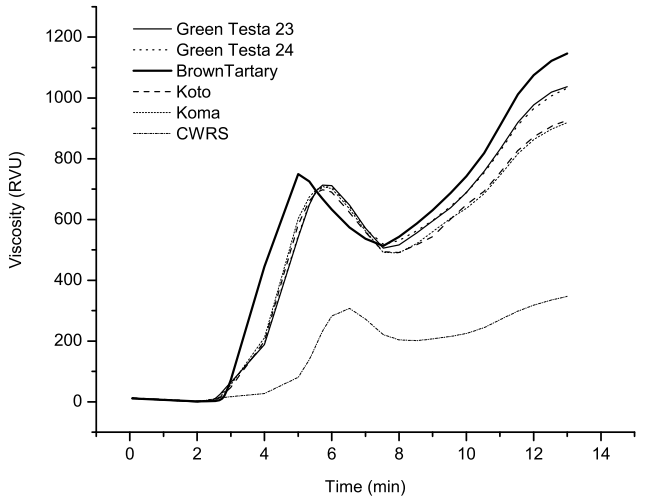

Fig. 8 Rapid Visco™ Analyser (RVA) profiles of white flour fractions from various buckwheat cultivars and wheat flour from Canada Western Red Spring (CWRS) wheat. RVA curves were obtained according to the general pasting test (Method 76-21; AACC 2003) with 4 g of flour (14% moisture content basis) and 25 ml of water.

and lower yellow values than Koto and Koma. The white and dark flours of tartary buckwheat were substantially darker and more yellow than their respective counterparts from the common buckwheat groats.

The pasting profiles for the white flour fractions are presented in **Fig. 8**, and the pasting parameters for all buckwheat samples are shown in **Table 4**. All whole flours and white flour fractions exhibited relatively high peak viscosity, final viscosity and setback values compared to those obtained for the wheat flour. These results confirm the differences in the physicochemical properties between buckwheat and cereal starches and indicate a greater swelling and gelling tendency for buckwheat starch than for wheat starch in agreement with previous reports (Li *et al*. 1997; Yoshimoto *et al*. 2004). High setback and final viscosity values of flours are often associated with firm texture of pasta and noodle products (Bhattacharya and Corke 1996). The differences in the pasting properties between buckwheat whole flour and white flour fractions can be ascribed to the differences in their starch contents (**Table 2**). The dark flour fractions exhibited very low pasting parameters compared to whole and white flours because of substantially lower starch content in the former.

The pasting profiles of whole flours indicated only small differences in pasting properties among the common buckwheat genotypes, with Koma exhibiting slightly higher peak viscosity than other lines, Koto the lowest final viscosity, and one of the green testa line the highest final viscosity. The pasting profiles of white flours from green testa lines showed much higher final viscosity values compared to Koto and Koma. The substantially higher pasting parameters of whole flour of tartary buckwheat can be attributed to about 7-9% higher starch content in the groats of tartary buckwheat compared to common buckwheat. However, despite similar starch content in all white flours, the white tartary flour exhibited higher pasting parameters than the white flours of common buckwheat. These results indicate that the functional properties of white buckwheat flour are governed by the content as well as by the physicochemical properties of starch polymers.

PHYSICOCHEMICAL PROPERTIES OF BUCKWHEAT STARCHES

Isolated and purified buckwheat starch granules were relatively small with majority having diameter ranging from 2 to 12 μm and only a small portion with diameter greater than 12 μm (**Fig. 9**). The granules had round or polygonal shape depending on the location of granules in the endosperm as discussed previously (**Fig. 4-6**). Some differences in the granule size distribution were observed among different cultivars (**Fig. 9**). The volume occupied by the bigger granules (12-28 μm) was greater for starches from Koto and one the green testa line, whereas the volume occupied by the small granules (2-8 μm) was greater for starches from Koma, tartary buckwheat and the second green testa line.

Thermal characteristics of buckwheat starches were determined by differential scanning calorimetry. The first transition, corresponding to melting of crystalline regions of amylopectin in granules, occurred between 55 and 85°C; whereas the second transition attributed to melting of amylose-lipid complexes occurred between 95 and 110°C. The thermal properties of starches isolated from the Canadian buckwheat genotypes were generally similar to those reported for cultivars grown in Japan and China (Li *et al*. 1997; Yoshimoto *et al*. 2004). The onset (To), peak gelatinization

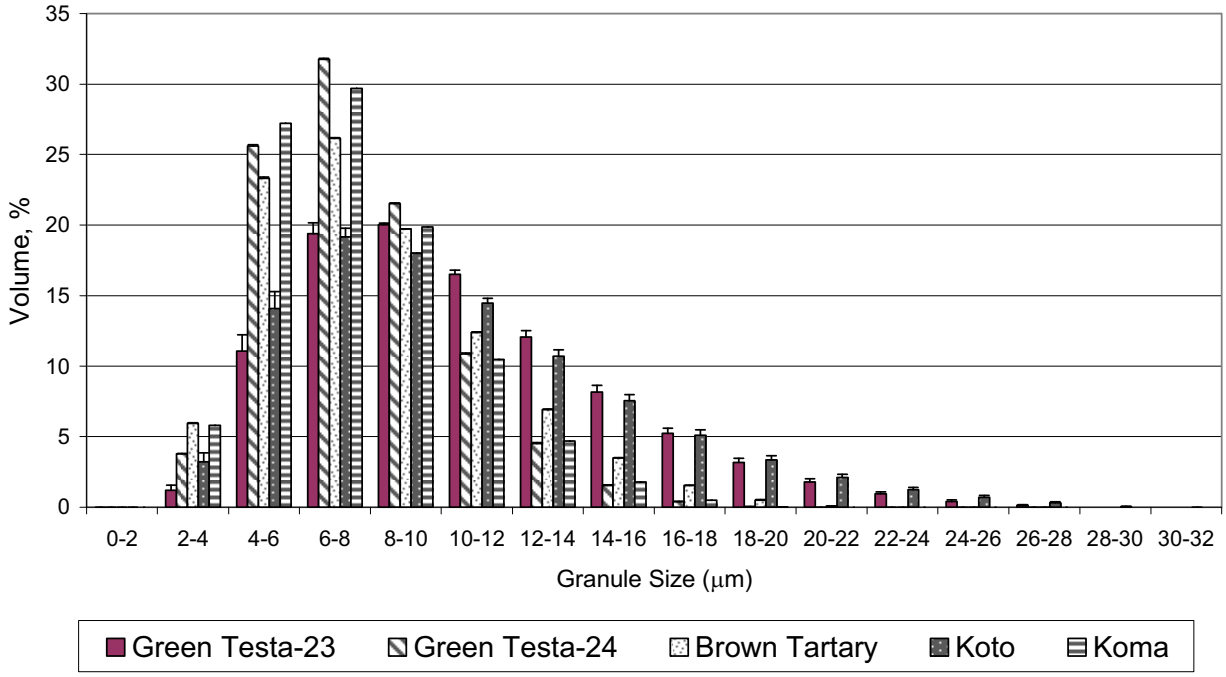

Fig. 9 Histogram of volume distribution of starch granule diameter in purified buckwheat starches. Particle size characteristics of starches were determined by using a laser diffraction sizer, Mastersizer 2000 (Malvern Instruments Ltd., Southborough, MA, USA) with Hydro 2000S attachment.

Table 5 Thermal properties[a] of isolated buckwheat starch.

Starch Source	Amylopectin				Amylose	
	Onset T_o (°C)	Peak T_p (°C)	Conclusion T_c (°C)	ΔH (J/g)	Peak T_p (°C)	ΔH (J/g)
Green Testa-23	54.6 ± 0.2	63.0 ± 0.3	90.7 ± 1.8	14.0 ± 1.2	104.1 ± 0.6	1.2 ± 0.2
Green Testa-24	55.4 ± 0.5	63.3 ± 0.6	91.1 ± 1.4	12.1 ± 2.2	104.9 ± 0.2	1.2 ± 0.1
Tartary	60.1 ± 0.2	66.5 ± 0.1	91.1 ± 1.4	14.1 ± 0.1	103.6 ± 1.7	1.2 ± 0.1
Koto	56.8 ± 0.3	65.0 ± 0.6	92.6 ± 1.7	12.9 ± 1.7	103.7 ± 0.4	0.7 ± 0.1
Koma	57.2 ± 0.5	64.6 ± 0.2	91.5 ± 0.9	14.5 ± 2.4	104.2 ± 0.4	1.2 ± 0.0

[a]The differential scanning calorimetry (DSC) analyses of buckwheat starches isolated from the whole flours were carried with a MDSC 2920 (TA Instruments, New Castle, DE, USA). Buckwheat samples (3.8-4.0 mg) were suspended in water (40% w/w) and hermetically sealed in aluminium pans. The suspensions were heated from 25°C to 130°C with a heating rate of 10°C/min. An empty pan was used as a reference.

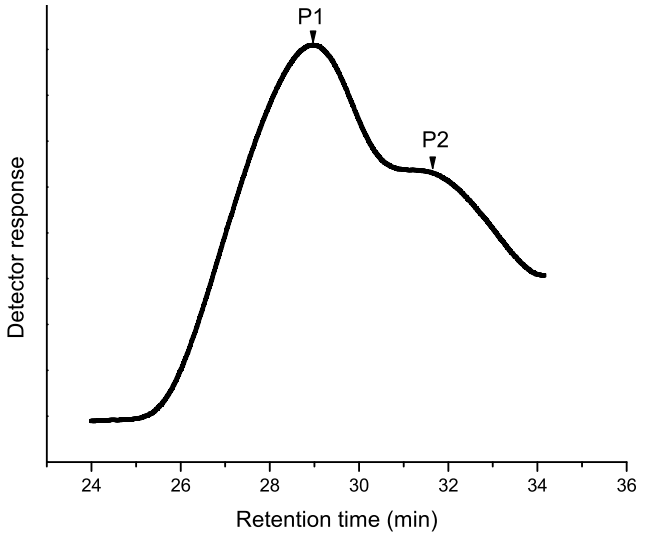

Fig. 10 High performance size exclusion chromatography (HPSEC) profiles of de-branched amylose chains in buckwheat starches.

(Tp), and completion (Tc) temperatures of the first transition were slightly lower for starches from the green testa lines than for starches from Koto and Koma; starch from tartary buckwheat exhibited substantially higher gelatinization temperatures than starches from common buckwheat (**Table 5**). All buckwheat starches exhibited higher gelatinization temperature than wheat starch.

Table 6 Physicochemical properties of amylose polymers after debranching of buckwheat starches with isoamylase.

Starch Source	Amylose, Peak 1		Amylose, Peak 2		Total
	Mw ($x10^{-3}$)	Peak Area (%)	Mw ($x10^{-3}$)	Peak Area (%)	Amylose[a] (%)
Koto	630	15.2	98	9.1	24.3
Koma	592	16.4	93	8.8	25.2
Green Testa 23	580	15.7	98	9.8	25.5
Green Testa 24	604	15.9	94	9.5	25.4
Tartary	463	13.9	90	11.0	24.9

[a] Calculated from the area assigned to amylose from the HPSEC profile of debranched starches as shown in **Fig. 10**.

The content of amylose, as determined by potentiometric titration, was very similar (24-25%) among starches isolated from five Canadian buckwheat genotypes, but lower than in starch isolated from wheat (29%). The distribution of weight average molecular weight (Mw) of amylose chains after debranching of buckwheat starched was achieved by HPSEC with multiangle light scattering detection (MALS). The elution profile showed two populations of polymer chains thus indicating a low degree of branching in buckwheat amylose (**Fig. 10**). The Mw of the first and second population ranged from 463,000 to 630,000 and from 90,000 to 98,000, respectively. The Mw values of both amylose populations were slightly lower for tartary buckwheat starch and the relative proportion of high to low Mw polymers (peak 1/peak 2) was lower than in starches from common buckwheat (**Table 6**).

The distribution of linear chains in amylopectin after debranching was examined by HPAEC and expressed as

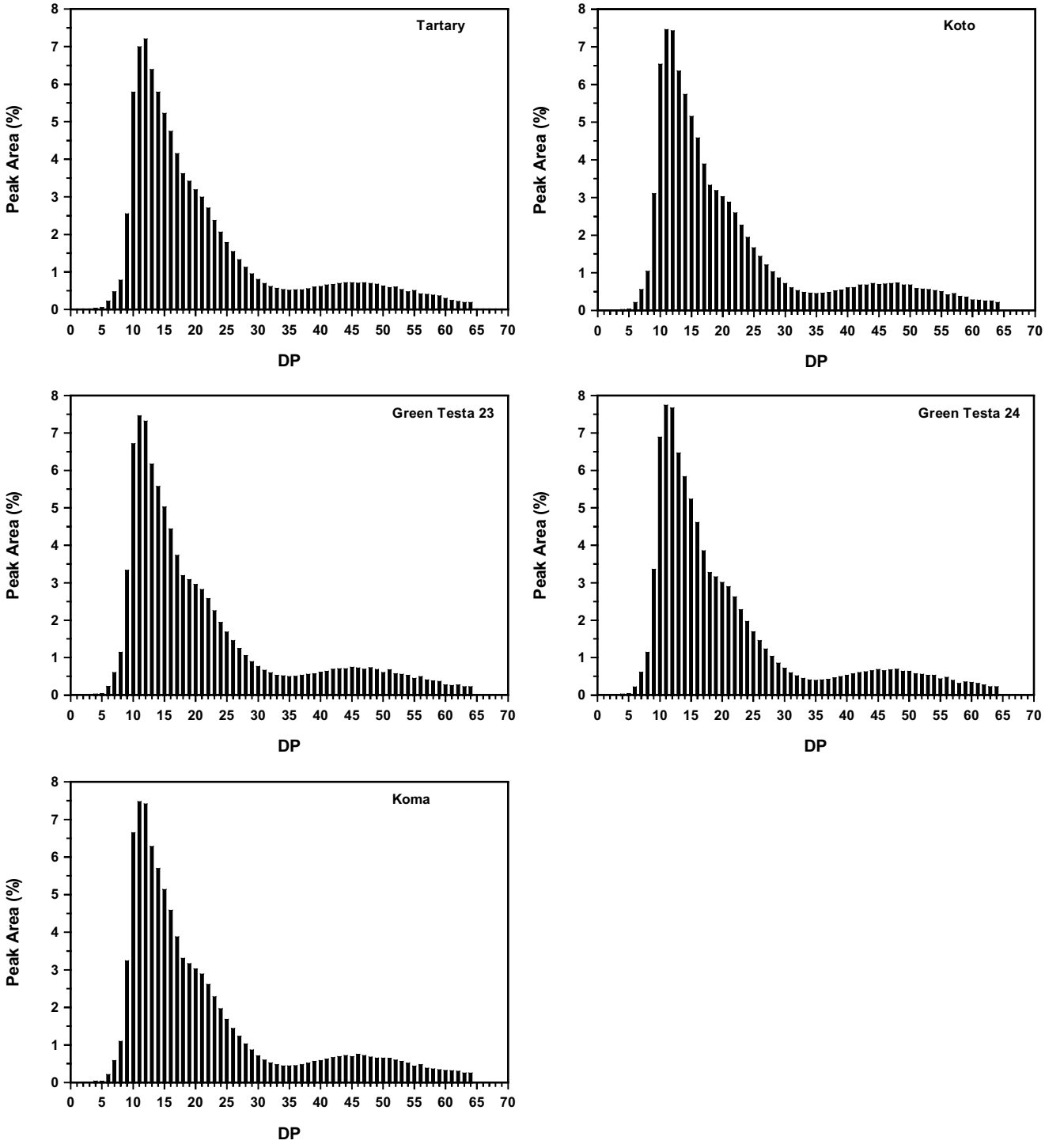

Fig. 11 High performance anion exchange chromatography (HPAEC) profiles of de-branched amylopectin linear chains in buckwheat starches.

relative peak area (**Fig. 11**). All buckwheat starches generally showed similar distribution profiles with the majority of chains having the degree of polymerization (DP) between 6 and 30, and the highest abundance of chains with DP 11 and 12 (**Fig. 11**). Similar profiles were shown for starches from buckwheat grown in Japan and China (Yoshimoto et al 2004). Amylopectin in tartary buckwheat starch contained fewer chains with DP 4-12 (23.9%) compared to the common buckwheat starches (26.3-27.6%). The amount of chains with DP 13-30, on the other hand, was higher in amylopectin of tartary starch (52.2%) than of common buckwheat starch (49.0-50.4%). A relatively large amount (16-18%) of longer chains with DP 31-66, distinguishes buckwheat amylopectin from other cereals. It can also partially explain a strong gelling potential of buckwheat starches. As shown in **Table 7**, at 30% polymer concentration, buckwheat starches formed elastic gels as indicated by high values of the elastic modulus (G') and low values of tan δ. Storage of gels for 24 h at 5°C caused subsequent increases in network rigidity (higher G' values) that have been linked to recrystallization of amylopectin. Among the five buckwheat starches, the tartary buckwheat formed the most rigid gel network after storage, attributed to the most distinctive molecular structure of its amylopectin.

COMPOSITION AND PROPERTIES OF DIETARY FIBRE IN BUCKWHEAT

The amount of total dietary fibre in whole buckwheat groats is usually somewhat lower than in the most common cereal grains such as wheat (12%), barley (17%), oats (11%), although it is comparable to corn (7.4%) and millet (8.5%), and higher than in rice (2-4%) (Cho *et al*. 1999). However, the dark buckwheat flour, obtained by roller milling of vari-

Table 7 Rheological properties of buckwheat starch gels before and after aging.

Starch Source	Fresh gel[a]		Aged gel[a]	
	G' (kPa)[b]	tanδ	G' (kPa)	tanδ
Koto	3.9	0.22	11.7	0.11
Koma	5.5	0.21	11.6	0.11
Green Testa 23	7.0	0.18	19.1	0.10
Green Testa 24	4.6	0.23	8.7	0.13
Tartary	4.5	0.23	30.1	0.10

[a] Starch gels were prepared by boiling starch suspension (30% starch w/v in water) for 15 min in a stainless steel mold (diameter of 7 cm, height 1 mm) and then cooling in water bath at 15°C for 15 min. After cooling, gels were carefully removed from the mold, analyzed fresh and after aging for 16 h at 15°C.
[b] Small strain dynamic rheological tests were performed with a Bohlin Gemini HR^{nano} 200 rheometer (Malvern Instruments Ltd., Southborough, MA, USA) using a parallel plate geometry (0.9 mm gap). The edge of the sample was coated with mineral oil to prevent moisture loss during measurements. Frequency sweep (from 0.02 to 20 Hz at 5% strain) and time sweep (16 hours at 1 Hz and stress of 200 Pa) were performed in duplicate at 15°C. Values of G' and tan δ taken at 0.2 Hz

ous Canadian genotypes, could be considered a reasonable source of dietary fibre since its content in dark flours ranged from 20 to 23%. The majority (~70%) of dietary fibre from whole groats was water insoluble (**Table 3**) and in the dark flour, the proportion of insoluble dietary fibre was even higher; however, in the white flour a large portion of dietary fibre was water soluble. Relatively little is known about the composition and properties of dietary fibre in buckwheat. Asano *et al.* (1970) isolated water soluble non-starch polysaccharides from buckwheat endosperm that consisted of xylose, mannose, galactose, and glucuronic acid. It was postulated that the main chain of this polysaccharide consisted of glucuronic acid, mannose, and galactose.

In order to partially characterize the constituents of dietary fibre in buckwheat, the non-starch polysaccharides from whole, dark, and white buckwheat flours of Koto were isolated with water and purified. The monosaccharide composition of water-extractable non-starch polysaccharides is presented in **Table 8**. The polysaccharides were composed mainly of galactose, xylose, arabinose, and uronic acid residues. Smaller amounts of rhamnose, glucose, mannose, and fucose were also found. The methylation analysis revealed a high proportion of 2-linked Rha, 4-linked GalA, terminal and 5-linked Ara, 4- and 3,4-linked Gal, 4-linked Glc, and terminal Xyl residues, thus indicating typical for dicotyledonous plants, pectic polysaccharides, xyloglucans, and possibly arabinogalactans among the buckwheat dietary fibre constituents. Staining of groat sections for pectins (with ruthenium red) (**Fig. 2A, 2B**) confirmed the highest concentration of these polymers in the cell walls of the outer tissues and their presence in the thin walls of the endosperm cells, but not in the aleurone cell walls. The isolated water soluble non-starch polysaccharides formed very viscous solutions and exhibited shear thinning behaviour with increasing shear rates (**Fig. 12**). At polymer concentration of 4% (w/v), the solutions exhibited a weak gel properties with the elastic modulus G' exceeding the viscous modulus G" (**Fig. 12**). HPSEC indicated the presence of at least two high molecular weight populations in buckwheat NSP. Galacturonic acid residues were found in both populations. The distinctive composition and properties of non-starch polysaccharides in buckwheat, contained in the cell walls of outer tissues and specifically in the dark flour obtained by roller milling of groats, should be explored further as they

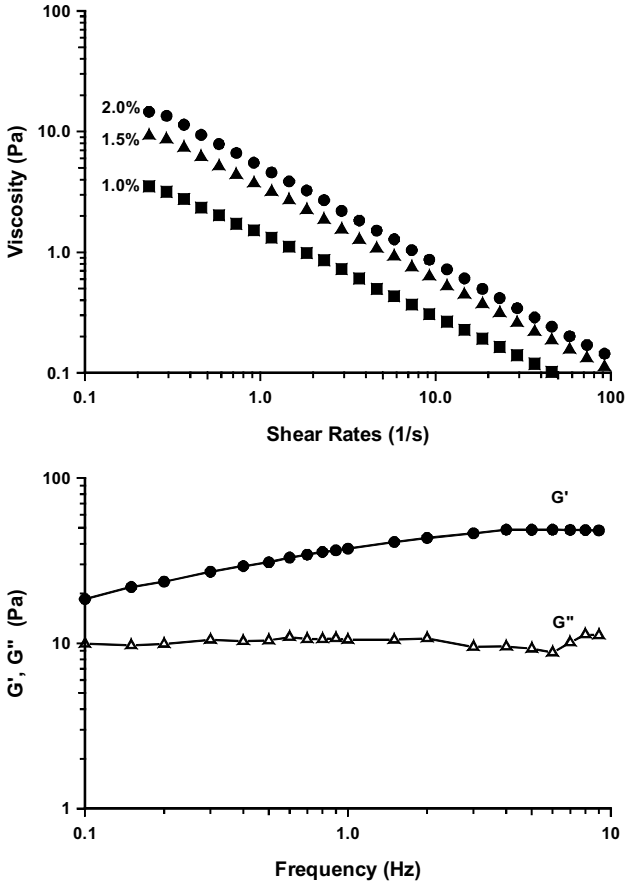

Fig. 12 Effects of polysaccharide concentrations and shear rates on the apparent viscosity of solutions of water-extractable non-starch polysaccharides from dark flour of Koto (top). Mechanical spectrum of 4% (w/v) solution of water-extractable non-starch polysaccharides from dark flour of Koto (bottom). G', elastic modulus; G", viscous modulus.

complement the nature of more widespread cereal dietary fibre constituents.

USES OF BUCKWHEAT MILLING FRACTIONS IN FOOD PRODUCTS

Incorporation of whole buckwheat or buckwheat milling fractions into a variety of wheat-based products such as noodles, bread and pasta has a tremendous potential to expand on international markets, given the verifiably high demand for a new generation of food products that are convenient, palatable, but at the same time deliver specific health benefits. Our preliminary studies indicated that a moderate addition (up to 25% replacement of wheat flour) of buckwheat milling fractions to wheat bread does not pose any technological challenges. Bread with buckwheat fractions was baked using the Canadian short process (CSP) and formula that included wheat flour, whey, shortening, yeast, sugar, salt, and ascorbic acid. The loaf volume of white buckwheat flour-supplemented bread was reduced only by ~10% compared to the wheat flour bread. The addition of the dark or whole buckwheat flour reduced the loaf volume by 20% and 15%, respectively. The crumb structure of the all buckwheat-supplemented bread scored

Table 8 Monosaccharide composition of isolated and purified non-starch polysaccharides from whole buckwheat, white, and dark flour of Koto.

Milling fraction	Monosaccharide composition, % mol[a]					Uronic Acid
	Rha	Ara	Gal	Glc	Xyl	(%)
WBF	4.5	14.1	48.9	4.5	20.1	17.1
WF	2.3	10.0	52.0	4.8	22.5	11.0
DF	3.9	15.9	49.2	4.4	18.9	19.0

[a] Small amounts of Fuc and Man residues were also found. Monosaccharides were determined after acid hydrolysis (1M H_2SO_4, 2 h, 100°C) The hydrolyzates were analyzed by HPLC equipped with a Dionex CarboPac PA1 column and a pulsed amperometric detector (PAD, Dionex Canada Ltd., Etobicoke ON) (Lazaridou *et al*. 2008).

Fig. 13 Bread prepared according to the Canadian short process from CWRS wheat flour (control) and with addition of 20% of whole, white and dark buckwheat flours.

only slightly lower (by visual evaluation) than that of wheat flour bread and generally had excellent appearance, attractive colour, uniform and slightly finer crumb structure than the control white flour bread (**Fig. 13**).

In another study, we tested the performance of different milling fractions (white, dark, and whole flour) obtained from two self-pollinating lines and two cross-pollinating buckwheat varieties in soba noodles (Hatcher *et al*. 2008). The buckwheat flours were blended with wheat flour (Canada Western Red Spring straight grade flour) at 60: 40 ratios. Only small differences were observed in buckwheat noodles derived from the four different buckwheat lines. The flour type, on the other hand, had a strong influence on noodle properties. Significant differences in raw buckwheat noodle colour were very evident depending upon the flour used. The high starch content within the white buckwheat flour yielded the brightest raw noodles while the dark flour yielded the darkest noodles. Dark buckwheat flour consistently yielded the thickest cooked noodles with the largest maximum cutting stress (MCS) and greatest resistance to compression (RTC). Noodles prepared with white buckwheat flour offered the best chewiness, springiness and recovery parameters. White buckwheat flour noodles were significantly firmer as indicated by the stress relaxation tests.

In general, the technological and sensory properties of soba noodles and breads prepared with dark buckwheat flour were compromised to a greater extend than when prepared with whole or white buckwheat flours. However, the products supplemented with the dark buckwheat flour contained considerably higher amounts of minerals, proteins, dietary fibre, and fagopyritols than products prepared with white flour. Since, the bioactivity and usefulness of these constituents in prevention or treatment of certain diseases are becoming evident; the potential health benefits of dark flour buckwheat products may be substantially greater than those prepared with white buckwheat flour.

ACKNOWLEDGEMENTS

The authors would like to acknowledge a research grant from Kade Research Inc. and thank Dr. C. Campbell for providing buckwheat samples and Len Dushnicky for conducting microscopy analyses.

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