

Genotypic Variation in Color and Discoloration Potential of Barley-Based Food Products

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ABSTRACT

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Barley has a variety of potential food uses. However, the dark gray color of the final products negatively affects consumer acceptability. We determined the discoloration potential of barley from different classes and genotypes, and evaluated the relationship of barley composition, total polyphenol content, and polyphenol oxidase (PPO) activity with discoloration potential of barley. Barley grains were abraded, milled into flour, and analyzed for composition, total polyphenol content, and PPO activity. Total polyphenol content of abraded barley, expressed as gallic acid %, was lowest in hulled proanthocyanidin-free barley (0.02–0.04%), followed by hulled proanthocyanidin-containing barley (0.11–0.18%), and hull-less barley (0.19–0.26%). PPO activity of abraded kernels ranged from 62.1 units/g in hulled proanthocyanidin-containing Baron-

esse to 116.5 units/g in hulled proanthocyanidin-free CA803803. Dough sheet brightness (L^* value) was the best indicator of discoloration potential of barley. Large variation in L^* value of dough sheets was observed among different classes and among genotypes within classes. Brightness of dough sheets measured at 24 hr were significantly higher in hulled (65.3–78.1) than in hull-less (59.0–63.9) barley, and within hulled barley, higher in proanthocyanidin-free (72.2–78.1) than in proanthocyanidin-containing (65.3–69.6) barley. Total polyphenol content significantly correlated with the discoloration potential of barley. Protein content and ash content also had a significant negative correlation with discoloration of dough sheets. The results indicated that polyphenol compounds may play a major role in discoloration potential of barley-based products.

Barley is one of the earliest cultivated cereal grains in the world and is gaining renewed interest for food use due to its hypocholesterolemic effect and other desirable nutritional and functional characteristics (Newman and Newman 1991). Barley contains β -glucans, tocopherol, and tocotrienols (Newman and Newman 1991; Wang et al 1993; Bhatti 1999), which are believed to be the components responsible for the reduction of serum cholesterol (Newman et al 1989). Hypoglycemic and anticarcinogenic effects have also been attributed to barley consumption (Bhatti 1999).

Abraded barley and its milling fractions can be used in a variety of food products. Abraded barley kernels are used as a rice extender or substitute. Barley flour can be incorporated into wheat flour for making bread, noodles, pasta, muffins, biscuits, pastries, and flat bread (McNeil et al 1988; Swanson and Penfield 1988; Newman et al 1990; Berglund et al 1992; Baik and Czuchajowska 1997; Başman and Kösel 1999; Marconi et al 2000). Barley flour may also be blended with rice flour for making extruded ready-to-eat cereal (Berglund et al 1994). By-products of barley pearling can be used to supplement wheat products such as pasta and bread to increase fiber content (Knuckles et al 1997; Marconi et al 2000). Despite numerous health benefits of eating barley and great potential for its use in various food products, food use of barley is extremely low in many Western countries compared with other cereal grains. The limited food use of barley is probably due to cultural eating practices as well as undesirable color and unfamiliar flavor of barley-based food products.

Gray color development of barley in food products may be nonenzymatic or enzymatic. Nonenzymatic browning results from polymerization of endogenous phenolic compounds and from the Maillard reaction. The Maillard reaction occurs when mixtures of amino acids and reducing sugars are heated. Enzymatic browning is the discoloration that is caused mainly by PPO. Oxidation of phenolic compounds to *o*-quinones, which condense and react with other phenolic compounds and amino acids, produces discoloration (McEvily et al 1992; Sapers 1993).

Barley grains contain numerous polyphenols, phenolic acids, proanthocyanidins, and catechins in the hull, seed coat, and aleurone layer (Jende-Strid 1981; Nordkvist et al 1984). Both PPO and peroxidase are present in barley and may be related to browning reactions during malting and brewing (Jerumanis et al 1976; Clarkson et al 1992). The role of polyphenols in brewing, especially their implication in beer haze formation, has been reviewed by several authors (Gramshaw 1970; Gardner and McGuinness 1977; Bendelow and LaBerge 1979). To prevent beer haze formation, scientists identified proanthocyanidin-free barley mutants that do not contain proanthocyanidins and catechins (Wettstein et al 1980). Theuer (2002) reported that iron-fortified barley cereal has a tendency to turn gray during processing and that proanthocyanidin-free barley preparations do not develop the gray color when an iron compound is added. The objectives of this study were to determine the discoloration potential of barley of different classes and genotypes, and to evaluate the relationship between discoloration potential of barley and chemical composition, polyphenol content, and PPO activity.

MATERIALS AND METHODS

Twenty-two genotypes of barley including 14 hulled and eight hull-less genotypes were evaluated. Hulled barley included 10 proanthocyanidin-containing genotypes (Gallantin, Baronesse, Farmington, Harrington, Crest, Steptoe, Morex, Kamiak, Hundred, and Kold) and four proanthocyanidin-free genotypes (Radiant, CA803803, WA18009-94, and WA13217-97). Hull-less barley included five regular starch genotypes (Condor, Bear, CDC McGwire, Lou Guang Mai, and WA11414-97) and three waxy genotypes (CDC Alamo, CDC Candle, and SH97110). Hull-less barleys were all proanthocyanidin-containing. The barley genotypes were grown in Pullman, WA, in 2000. To obtain comparably pearled grains, hulled and hull-less barleys were abraded with a tangential abrasive dehulling device (TADD, Venables Machine Works, Ltd., Saskatoon, Canada). The pearling process removed 15 and 30% of the kernels by weight for hull-less and hulled barley, respectively. Both whole and abraded barley were ground with a cyclone sample mill (Udy Corp., Fort Collins, CO) fitted with a 0.5-mm opening and subjected to chemical composition analysis. For color measurements, abraded kernels were ground with a hammer mill (Weber Bros. & White Metal Works, Chicago, IL) with a 0.6-mm opening. Whole and abraded barley kernels and the flours were stored at 4°C until analyzed.

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Chemical Composition

Moisture content of barley flours was determined according to Approved Method 44-15A (AACC 2000). Protein (N × 6.25) was determined using a nitrogen analyzer (Leco Corporation, St. Joseph, MI), according to Approved Method 46-30 (AACC 2000). Ash content was determined according to Approved Method 08-01 (AACC 2000). β-Glucan content was determined using a mixed-linkage β-glucan assay kit (Megazyme Int., Ireland) according to Approved Method 32-23 (AACC 2000). Free lipid content of abraded barley was determined according to Approved Method 30-25 (AACC 2000). Reducing sugar content was determined by a colorimetric method using dinitrosalicylic reagent (Bernfeld 1955). Flour of abraded barley (1 g) was dry-combusted for 16 hr at 580°C, digested for 30 min in 2 mL of concentrated HCl, diluted to 25 mL with distilled water, and analyzed with an atomic absorption spectrophotometer (model 2380, Perkin-Elmer, Norwalk, CT) for copper and iron content. All analyses were performed at least in duplicate, and mean results of all analyses reported on a moisture-free basis.

Total Polyphenol Content

Total polyphenol content was determined according to Bendelow (1977) with modifications. Barley flour (1 g) was extracted with 30% (v/v) dimethylformamide (10 mL) for 45 min at 20 ± 2°C using a gyrotory shaker (model S-3, New Brunswick Scientific Co., New Brunswick, NJ) at speed 8, and centrifuged at 5,000 × g for 10 min. The supernatant (0.5 mL) was placed into a test tube and 15% (w/v) NH₄OH (1 mL), 2% (w/v) 4-aminoantipyrine (0.5 mL), 2% (w/v) K₃Fe(CN)₆ (0.5 mL), and water (7.5 mL) were added. After thoroughly mixing the contents of the tube and

allowing the mixture to stand for 30 min, absorbance at 505 nm was measured. A calibration curve was constructed using solutions of gallic acid, and the results were expressed as gallic acid %. The test for total polyphenol content was performed at least in duplicate and reported on a moisture-free basis.

PPO Activity

PPO activity of barley was determined spectrophotometrically according to Okot-Kotber et al (2001) with modifications. Barley flour (1 g, 14% mb) was soaked overnight in 50 mM potassium phosphate buffer pH 6.5 (10 mL) in a 50-mL centrifuge tube at 4°C. After homogenization (Polytron, Kinematica GmbH, Switzerland) at speed 5 for 1 min with the tube immersed in an ice water bath, the tube was shaken in a gyrotory shaker at speed 8 (model S-3, New Brunswick Scientific) at 4°C for 3 hr and centrifuged at 40,000 × g for 30 min. The clear supernatant (0.5 mL) was added to a cuvette containing 10 mM L-dopa (1 mL) in 50 mM potassium phosphate buffer (pH 6.5) and the contents were mixed immediately by inversion. To obtain the change of absorbance per minute, the absorbance of the solution was measured at 480 nm using a spectrophotometer (Ultrospec 4000, Pharmacia Biotech, England) every 10 sec over a 5-min period at 37°C. The change in absorbance/min was corrected for substrate autoxidation by subtracting the absorbance/min of blank without PPO extract added and without substrate added. Assay conditions were verified using a standard preparation of mushroom PPO (Sigma Chemical Co., St. Louis, MO). One unit of PPO activity was defined as the amount of the enzyme giving a change in absorbance of 0.001/min. PPO activity determination of barley flour was performed at least in triplicate and expressed as units/g of flour.

TABLE I
Composition of Whole and Abraded Grains of Different Genotypes of Barley

Class and Genotype	Whole Barley			Abraded Barley						
	Protein (%)	Ash (%)	β-Glucans (%)	Protein (%)	Free Lipids (%)	β-Glucans (%)	Reducing Sugars (%)	Ash (%)	Cu (mg/100 g)	Fe (mg/100 g)
Hulled										
Proanthocyanidin-containing										
Gallantini	13.6	2.40	4.6	10.6	1.07	5.2	0.31	0.74	0.18	2.54
Baronesse	11.8	2.47	3.8	9.9	1.09	4.4	0.24	0.88	0.32	2.95
Farmington	13.2	2.36	5.6	10.0	1.24	6.3	0.23	0.77	0.28	3.14
Harrington	10.9	2.28	4.2	10.6	1.25	5.0	0.25	0.91	0.37	3.18
Crest	13.5	2.41	4.7	10.7	1.12	5.6	0.22	0.84	0.14	2.71
Steptoe	10.9	2.34	3.9	8.9	1.21	5.2	0.25	0.96	0.31	1.98
Morex	13.5	2.26	4.1	11.1	1.12	5.5	0.29	0.87	0.06	1.93
Kamiak	10.3	2.44	5.6	8.0	1.05	5.3	0.19	0.84	0.69	1.86
Hundred	11.2	2.55	4.0	9.3	1.19	5.1	0.29	0.90	0.36	2.99
Kold	11.5	2.24	5.5	9.0	1.02	5.3	0.20	0.82	0.38	2.31
Average (n = 10) ^a	12.0b	2.38a	4.6bc	9.8b	1.14c	5.3bc	0.25bc	0.85c	0.31a	2.56a
Proanthocyanidin-free										
Radiant	12.0	2.32	4.2	9.6	1.01	5.1	0.22	0.99	0.29	2.35
CA803803	11.2	2.26	4.8	9.5	1.23	5.0	0.20	0.88	0.42	2.84
WA18009-94	11.1	2.24	4.3	8.8	1.33	4.6	0.13	0.84	0.20	1.60
WA13217-97	11.9	2.27	4.3	10.1	1.42	5.2	0.24	0.98	0.15	2.56
Average (n = 4)	11.6b	2.28a	4.4c	9.5b	1.25c	5.0c	0.20c	0.93bc	0.26a	2.34a
Hull-less										
Regular										
Condor	13.9	1.49	5.3	11.5	1.56	6.3	0.27	0.90	0.22	2.43
Bear	13.7	1.58	4.7	11.3	1.41	5.2	0.31	0.99	0.30	3.12
CDC McGwire	14.1	1.54	4.8	11.6	1.61	5.5	0.38	0.85	0.39	2.97
Lou Guang Mai	16.7	1.74	5.7	15.0	1.71	6.9	0.38	1.16	0.42	2.99
WA11414-97	12.9	1.60	5.6	10.4	1.40	6.2	0.31	1.13	0.39	2.84
Average (n = 5)	14.3a	1.59b	5.2b	12.0a	1.54b	6.0b	0.33b	1.01ab	0.34a	2.87a
Waxy										
CDC Alamo	15.5	1.87	8.8	13.1	1.95	8.5	0.63	1.15	0.39	3.11
CDC Candle	14.2	1.63	8.4	11.7	1.78	10.0	0.37	0.99	0.17	2.88
SH97110	14.1	1.59	8.5	11.9	1.96	9.8	0.47	1.02	0.22	2.34
Average (n = 3)	14.6a	1.70b	8.5a	12.2a	1.90a	9.5a	0.49a	1.05a	0.26a	2.78a
LSD ^b	0.1	0.04	0.3	0.1	0.10	0.2	0.02	0.05	0.09	0.54

^a Average of each class. Values in the same column with different letters are significantly different ($P < 0.05$).

^b Least significant difference ($P < 0.05$). Differences between two means exceeding this value are significant.

Color Evaluation

To evaluate the discoloration potential of barley, two replicates of cooked abraded kernels, gels, and dough sheets were prepared. Brightness was determined using a spectrophotometer (CM-2002, Minolta Camera Co., Ltd., Chuo-Ku, Osaka, Japan) and expressed by CIE-Lab L^* . The higher the L^* value, the brighter the barley.

Cooked abraded barley was prepared according to Klaczynski et al (1998). Abraded kernels (10 g) were simmered in boiling water (30 mL) for 30 min. After cooking, the kernels were removed, cooled for 30 min at $20 \pm 2^\circ\text{C}$, and transferred into a petri dish (clear polystyrene, 35×10 mm), covered with a lid and inverted. Color of the cooked kernels was measured through the inverted petri dish.

To prepare gel, barley flour (10 g, 14% mb) was dispersed in water (90 mL). The slurry was heated and boiled for 5 min. After cooking, the hot paste was poured into a petri dish (clear polystyrene, 35×10 mm), cooled for 30 min at $20 \pm 2^\circ\text{C}$, covered with a lid and inverted. Color of the resulting gel was measured through the inverted petri dish, immediately (0 hr) and after 24 hr of storage at $20 \pm 2^\circ\text{C}$.

Dough sheets were prepared by mixing flour (10 g, 14% mb) with water (6.4 mL) in a 10-g mixograph (National Mfg., Lincoln, NE) for 1 min and sheeting on a cookie sheet to a 5-mm thickness using a rolling pin. Dough sheets were placed in plastic bags and kept at $20 \pm 2^\circ\text{C}$. Color of dough sheets was determined at 0, 1, 2, 4, 6, and 24 hr after preparation.

Brightness of abraded kernels was determined using a glass cup (4 cm height \times 4.5 cm diameter) filled level to the top with abraded kernels and covered with plastic wrap. Color was measured through the plastic wrap on duplicate samples.

Statistical Analysis

Analysis of data was performed using statistical software (SAS Institute, Cary, NC) with analysis of variance (ANOVA), Fisher's least significant difference (LSD), and Pearson's correlation coefficient. Differences were considered significant at $P < 0.05$, unless otherwise specified.

RESULTS AND DISCUSSION

Chemical Composition of Whole and Abraded Barley

Protein, ash, and total β -glucan contents of whole and abraded barley kernels are summarized in Table I. In whole kernels, protein content was significantly higher in hull-less barley (12.9–16.7%) than in hulled barley (10.3–13.6%). Ash content of whole kernels was significantly higher in hulled barley (2.24–2.55%) than in hull-less barley (1.49–1.87%). Similar results were previously reported for protein (Bhatty and Rosnagel 1981) and ash (Cheigh et al 1975; Bhatty and Rosnagel 1981). Total β -glucan content of whole kernels was significantly higher in waxy hull-less barley (8.4–8.8%) than in regular hull-less and hulled barley (3.8–5.7%), which was also reported by Bhatty (1999), Faunaught et al (1996), Xue et al (1997), and Newman and Newman (1991).

The first step in processing barley for human consumption is abrasion. Compared with whole kernels, protein and ash contents of abraded kernels significantly decreased, which is in agreement with reports by Summer et al (1985), Bhatty and Rosnagel (1998), Marconi et al (2000), and Yeung and Vasanthan (2001). In hulled and hull-less abraded kernels, protein content decreased by 1.7–3.2%, except for Harrington, which exhibited a 0.3% decrease. Ash content decreased 1.29–1.66% in hulled and 0.46–0.72% in

TABLE II
Total Polyphenol Content and Polyphenol Oxidase (PPO) Activity of Whole and Abraded Grains of Different Genotypes of Barley

Class and Genotype	Total Polyphenol Content (gallic acid %)		PPO Activity (units/g)	
	Whole Barley	Abraded Barley	Whole Barley	Abraded Barley
Hulled				
Proanthocyanidin-containing				
Gallantin	0.37	0.14	187.7	94.7
Baronesse	0.43	0.18	98.5	62.1
Farmington	0.35	0.12	215.6	88.6
Harrington	0.38	0.16	94.6	71.0
Crest	0.40	0.18	115.5	74.5
Steptoe	0.47	0.18	95.8	66.3
Morex	0.36	0.15	105.8	62.2
Kamiak	0.43	0.12	85.5	67.7
Hundred	0.44	0.15	106.5	65.9
Kold	0.44	0.11	94.9	66.0
Average ($n = 10$) ^a	0.41b	0.15b	120.ab	71.9b
Proanthocyanidin-free				
Radiant	0.08	0.04	141.4	88.0
CA803803	0.10	0.03	171.4	116.5
WA18009-94	0.10	0.02	137.5	84.1
WA13217-97	0.13	0.03	162.7	88.0
Average ($n = 4$)	0.10c	0.03c	153.3a	94.2a
Hull-less				
Regular				
Condor	0.43	0.23	99.7	88.6
Bear	0.42	0.22	96.1	78.4
CDC McGwire	0.45	0.22	69.5	63.1
Lou Guang Mai	0.36	0.22	185.7	106.6
WA11414-97	0.51	0.26	92.0	63.5
Average ($n = 5$)	0.43ab	0.23a	108.6ab	80.1ab
Waxy				
CDC Alamo	0.60	0.25	94.8	68.7
CDC Candle	0.44	0.19	113.8	79.9
SH97110	0.45	0.20	81.4	71.5
Average ($n = 3$)	0.50a	0.21a	96.7b	73.4b
LSD ^b	0.02	0.01	7.3	4.5

^a Average of each class. Values in the same column with different letters are significantly different ($P < 0.05$).

^b Least significant difference ($P < 0.05$). Differences between two means exceeding this value are significant.

hull-less barley by abrasion. Changes in total β -glucan content by pearling were dependent on the cultivar. Total β -glucan content of barley kernels generally increased by abrasion, except in Kamiak, Kold, WA18009-94, and CDC Alamo, which exhibited no significant changes in β -glucan content. Similar observations were reported by Klamczynski et al (1998). In abraded barley, protein, free lipids, total β -glucans, reducing sugars, and ash were generally higher in hull-less than in hulled barley (Table I). Protein content in abraded kernels was 8.0–11.1% for hulled and 10.4–15.0% for hull-less barley. Free lipids of abraded kernels were 1.01–1.42% in hulled and 1.40–1.96% in hull-less barley. Total β -glucan content of abraded kernels was 4.4–6.3% in hulled and 5.2–10.0% in hull-less barley. Reducing sugar content was 0.13–0.31% in hulled abraded barley and 0.27–0.63% in hull-less abraded barley. Ash content was 0.74–0.99% in hulled abraded and 0.85–1.16% in hull-less abraded barley. Hulled proanthocyanidin-containing and proanthocyanidin-free abraded barley exhibited similar protein, free lipids, total β -glucans, reducing sugars, and ash contents. On the other hand, hull-less waxy abraded barley had a higher content of free lipids, total β -glucans, and reducing sugars than regular abraded barley. Although there were no differences in copper and iron contents between hull-less and hulled abraded kernels, there was significant genotypic variation. Copper content of abraded barley was 0.06–0.69 mg/100 g and iron content was 1.60–3.18 mg/100 g.

Total Polyphenol Content and PPO Activity

Polyphenols may autopolymerize or undergo an oxidative polymerization catalyzed by inorganic ions (Jerumanis et al 1976) and thus contribute to the discoloration of barley-based food products. Table II shows the total polyphenol content of various classes of

barley. Total polyphenol content of whole kernels was significantly lower in proanthocyanidin-free hulled barley (0.08–0.13%) than in proanthocyanidin-containing hulled and hull-less barley (0.35–0.60%). Among proanthocyanidin-containing barleys, hulled and hull-less genotypes were similar in total polyphenol content, except for CDC Alamo, which exhibited much higher content (0.60%) than other genotypes.

The total polyphenol content of barley kernels significantly decreased by abrasion (Table II). Total polyphenol content decreased 0.21–0.33% in hulled proanthocyanidin-containing barley and 0.04–0.09% in hulled proanthocyanidin-free barley. Within hull-less barley, total polyphenol content decreased 0.15–0.24% in regular and 0.24–0.34% in waxy barley.

Total polyphenol content of abraded barley kernels was lowest in hulled proanthocyanidin-free barley (0.02–0.04%). Hulled proanthocyanidin-containing abraded barley had lower total polyphenol content (0.11–0.18%) than hull-less abraded barley (0.19–0.26%). Although proanthocyanidin-containing barleys were abraded 30% for hulled and 15% for hull-less genotypes, abrasion does not necessarily remove the same layers or components of the kernel because of differences in thickness of outer layers, kernel size, and shape among genotypes.

Discoloration in barley-based products may also occur by oxidative polymerization of phenolic compounds catalyzed by PPO. In whole barley grains, PPO activity varied among genotypes, while differences in PPO activity between barley classes were not evident. Farmington (215.6 units/g) exhibited the highest PPO activity. Other genotypes with relatively high PPO activity were WA18009-94, Radiant, WA13217-97, CA803804, Lou Guang Mai, and Gallantin (132.7–187.7 units/g). Genotypes with moderately low PPO activity were WA11414-97, Harrington, CDC Alamo,

TABLE III
Brightness^a of Abraded Kernels, Cooked Abraded Kernels, and Gels of Barley

Class and Genotype	Abraded Kernels	Cooked Abraded Kernels	0 hr Gels	24 hr Gels
Hulled				
Proanthocyanidin-containing				
Gallantin	70.7	57.8	55.7	57.0
Baronesse	70.3	57.3	54.5	54.8
Farmington	69.2	57.0	52.8	54.1
Harrington	72.6	57.0	54.8	56.1
Crest	69.2	57.1	54.4	54.9
Steptoe	72.7	57.9	55.3	55.9
Morex	71.7	59.4	55.1	55.9
Kamiak	68.5	55.3	54.8	55.8
Hundred	66.7	56.6	56.7	56.5
Kold	67.9	58.8	56.7	57.1
Average (<i>n</i> = 10) ^b	70.0bc	57.4b	55.1b	55.8b
Proanthocyanidin-free				
Radiant	72.0	59.2	58.9	61.1
CA803803	74.3	58.2	58.1	60.2
WA18009-94	74.8	60.8	59.8	61.6
WA13217-97	71.3	59.2	59.5	60.7
Average (<i>n</i> = 4)	73.1a	59.4a	59.1a	60.9a
Hull-less				
Regular				
Condor	67.6	57.1	54.2	53.9
Bear	68.5	56.9	53.4	53.9
CDC McGwire	68.5	58.8	56.5	55.4
Lou Guang Mai	63.5	56.9	57.9	58.0
WA11414-97	69.4	56.6	55.7	54.3
Average (<i>n</i> = 5)	67.5c	57.3b	55.5b	55.1b
Waxy				
CDC Alamo	70.8	57.9	51.4	50.4
CDC Candle	70.8	58.2	53.5	52.2
SH97110	70.8	58.5	53.3	51.0
Average (<i>n</i> = 3)	70.8ab	58.2ab	52.7c	51.2c
LSD ^c	1.9	1.4	2.9	1.4

^a CIE-Lab *L** value.

^b Average of each class. Values in the same column with different letters are significantly different (*P* < 0.05).

^c Least significance difference (*P* < 0.05). Differences between two means exceeding this value are significant.

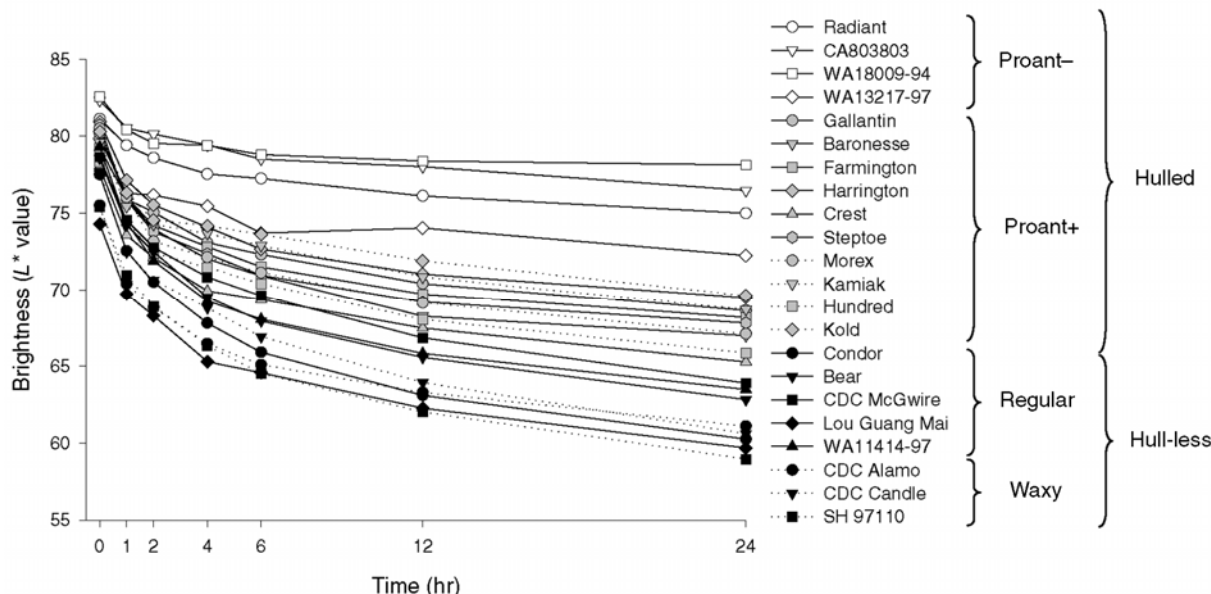


Fig. 1. Brightness of dough sheets measured over time stored at 20°C. Proant- and Proant+ indicate with and without proanthocyanidin, respectively.

Kold, Steptoe, Bear, Baronesse, Condor, Morex, Hundred, CDC Candle, and Crest (92.0–115.5 units/g). Genotypes with low PPO activity were SH97110 and Kamiak (81.4–85.5 units/g). CDC McGwire (69.5 units/g) had the lowest PPO activity.

Abrasion significantly decreased PPO activity in both hulled and hull-less barley, except in SH97110 (Table II). With 30% abrasion, PPO activity in hulled barley decreased by 17.8–127.0 units/g. With 15% abrasion, PPO activity in hull-less barley decreased by 6.4–79.1 units/g in regular and by 9.9–33.8 units/g in waxy barley.

Abraded barleys with relatively high PPO activity were Gallantin, Lou Guang Mai, and CA803803 (94.7–116.5 units/g). Genotypes with moderately low activity were Harrington, SH97110, Crest, Bear, CDC Candle, WA18009-94, Radiant, WA13217-97, Condor, and Farmington (71.0–88.6 units/g). Genotypes with low activity were Baronesse, Morex, CDC McGwire, WA11414-97, Hundred, Kold, Steptoe, Kamiak, and CDC Alamo (62.1–68.7 units/g).

Brightness of Abraded and Cooked Barley Kernels and of Gels and Dough Sheets

The L^* value of abraded kernels did not exhibit clear differences among classes of barley, but significant differences were observed among genotypes (Table III). L^* value of abraded kernels ranged from 66.7 in Hundred to 74.8 in WA18009-94 and was lowest in Lou Guang Mai (63.5). The L^* value of abraded kernels decreased significantly by cooking. Similarly to abraded kernels, the L^* value of cooked abraded kernels did not show significant differences among classes of barley, but genotypic differences were observed. The L^* value of cooked abraded kernels varied from 55.3 in Kamiak to 60.8 in WA18009-94.

There were significant differences in L^* value of gels among barley classes (Table III). The L^* value of gels immediately after preparation (0 hr) was brightest in proanthocyanidin-free genotypes (>58.1), darker in hulled proanthocyanidin-containing and hull-less regular genotypes (52.8–57.9), and darkest in hull-less waxy genotypes (<53.5). The L^* value of barley gels exhibited no significant changes during 24 hr of storage, even though there were slight increases in L^* value in the majority of the hulled and hull-less regular genotypes, and slight decreases in hull-less waxy barley genotypes. This result indicated absence of oxidative polymerization of polyphenols catalyzed by PPO or of autopolymerization of polyphenol compounds in gels during storage. The L^* values of dough sheets measured over time are shown in Fig. 1. Immediately after preparation, L^* value of dough sheets exhibited

relatively small differences between classes and genotypes of barley. During storage, the L^* value decreased rapidly in the first 2–4 hr and then at a slower rate at 6–24 hr. The rate of L^* value decrease during storage was highest in hull-less barley genotypes, lower in hulled proanthocyanidin-containing genotypes, and lowest in hulled proanthocyanidin-free genotypes. Accordingly, differences in L^* values of the dough sheets among barley classes and individual genotypes were much more evident at 24 hr after preparation than immediately after preparation. Hulled proanthocyanidin-free barley exhibited the highest L^* values (72.2–78.1), followed by hulled proanthocyanidin-containing barley (65.3–69.6), and hull-less barley (59.0–63.9). There were also large variations in L^* values among genotypes of the same barley class, indicating the complexity of discoloration in processed barley.

The measurement of brightness of abraded and cooked kernels was probably affected not only by the color of the kernels, but also by the uneven surface of the grains, which in turn affects the accuracy and reliability of the determination. Gels present much smoother surfaces, while the differences in brightness among barley classes and genotypes were relatively small, perhaps due to the dilute nature of the gels. Dough sheets had the smoothest surface and showed the largest differences among barley genotypes. This indicates that the L^* values of dough sheets are the best indicator of discoloration potential of barley in food products.

Relationships Between Composition and Discoloration Potential of Barley

Correlation coefficients between the composition of barley kernels and L^* values of abraded and cooked barley kernels, gels, and dough sheets are summarized in Table IV. Total polyphenol content significantly correlated with the L^* values of abraded kernels, cooked abraded kernels, gels, and dough sheets. While for hulled and hull-less proanthocyanidin-containing barley ($n = 18$), total polyphenol content was significantly correlated with the L^* values of dough sheets. For hulled proanthocyanidin-free barley ($n = 4$), this correlation was not significant (Fig. 2), probably due to differences in the number of barley genotypes tested (20 vs. 4). Within hulled ($n = 10$) or hull-less ($n = 8$) proanthocyanidin-containing barleys, however, no significant relationships were observed between total polyphenol content and brightness of dough sheets (Fig. 2). A large variation in L^* values of dough sheets among barley genotypes (Fig. 1) of similar total polyphenol content (Table II) may indicate that other factors, in addition

TABLE IV
Simple Pearson Correlation Coefficients (r) Between Composition and Discoloration Potential of Barley

Sample	Brightness (L^* value)			
	Abraded Kernels	Cooked Abraded Kernels	Gel	Dough
Overall ($n = 22$)				
Total polyphenols	-0.522 ^a	-0.506 [*]	-0.699 ^{**}	-0.910 ^{***}
Polyphenol oxidase activity	0.051	0.092	0.387	0.270
Protein	-0.441 [*]	-0.061	-0.295	-0.714 ^{**}
Ash	-0.198	-0.099	-0.080	-0.469 [*]
Proanthocyanidin-containing ($n = 18$)				
Total polyphenols	-0.092	-0.010	-0.202	-0.772 ^{**}
Polyphenol oxidase activity	-0.465	-0.211	0.078	-0.310
Protein	-0.308	0.239	-0.071	-0.766 ^{**}
Ash	-0.166	-0.079	-0.100	-0.703 ^{**}
Proanthocyanidin-free ($n = 4$)				
Total polyphenols	-0.900	-0.536	-0.250	-0.790
Polyphenol oxidase activity	0.358	-0.793	-0.906	0.173
Protein	-0.866	-0.648	-0.224	-0.955 [*]
Ash	-0.970 [*]	-0.374	-0.034	-0.861

^a *, **, *** = significant at $P < 0.05$, $P < 0.01$, $P < 0.001$, respectively.

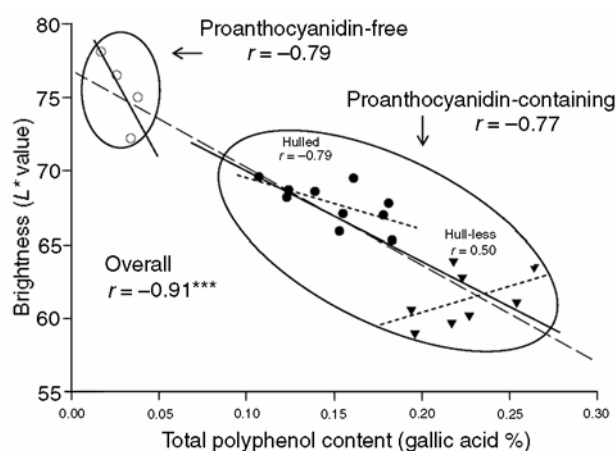


Fig. 2. Relationship between total polyphenol content and brightness of dough sheets.

to polyphenols, including PPO activity and metal ions, may contribute to the discoloration of dough sheets.

Relationships between PPO activity and L^* values of dough sheets were not significant. However, protein content and ash content exhibited significant negative correlations with L^* values of barley dough sheets in overall barley genotypes ($n = 22$). Protein content also showed a significant negative relationship with L^* value of abraded kernels for all barley genotypes ($n = 22$). Within hulled and hull-less proanthocyanidin-containing ($n = 18$) and hulled proanthocyanidin-free barley ($n = 4$), protein content had a significant correlation with L^* value of dough sheets. Significant relationship between protein content of wheat flour and L^* value of noodle dough sheets was reported by Baik et al (1994). It has been suggested that protein is involved indirectly in discoloration of dough for oriental noodles made with wheat flour. Protein content may be correlated with an unknown component that affects hardness or the rate of water binding during dough processing. Ash content correlated negatively with L^* value of dough sheets in hulled and hull-less proanthocyanidin-containing barley ($n = 18$). Highly negative correlation between wheat ash content and spaghetti brightness was also reported by Matsuo et al (1982).

CONCLUSIONS

Discoloration potential of barley in food products was dependent on the class and genotype of barley. The extent of discoloration of barley was also dependent of the food system being

evaluated. Brightness of dough sheets appeared to be the best indicator of the discoloration potential of barley-based food products. Brightness of dough sheets was greater in hulled barley than in hull-less barley. Within hulled barley, proanthocyanidin-free barley exhibited less discoloration of dough sheets than proanthocyanidin-containing barley. Total polyphenol content had a highly significant relationship with the discoloration potential of barley, indicating that polymerization of polyphenol compounds through autoxidation or catalyzed by PPO may play a major role in discoloration potential of barley-based products.

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