REVIEW

The Potential of Hull-less Barley

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ABSTRACT

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Hull-less barley (HB) has been investigated in many countries for use in feed, food, and industry since the publication of the last review in 1986. Literature published since 1990 on various aspects of HB utilization, other than in monogastric feeds, has been reviewed. Several HB cultivars containing low or high β-glucan, low or high extract viscosity, and waxy (0–5% amylose) or normal starch are now available. Interest in HB utilization in the food industry developed largely due to its high β-glucan content, particularly in the waxy cultivars. β-Glucan is a major component of soluble fiber implicated in hypocholesterolemia, hypoglycemia, and in reducing incidence of chemically induced colon cancer in experimental animals. However, large-scale clinical trials using human subjects are needed to corroborate these effects. The zero amylose HB starch had low syneresis or a high freeze-thaw stability suitable for use in frozen foods. Single- or double-modified waxy HB starch may replace corn starch in some food applications, and cationized HB starch can replace corn and potato starches in the pulp and paper industry. HB may be milled using conventional wheat milling equipment to yield bran and flour for multiple food uses. Hull-less barley may also be used as a feed stock for fuel alcohol production, for the preparation of food malt with low or high enzyme activities, and for brewer's and distiller's malts.

The first comprehensive review on hull-less barley (HB) was published more than a decade ago (Bhatty 1986). Later an American Association of Cereal Chemists monograph on barley (MacGregor and Bhatty 1993) included a chapter on nonmalting uses of barley in feed, food, and industry that had been reported mostly before 1990 (Bhatty 1993c). This review has been restricted to information published on HB since 1990, except its utilization in monogastric feeds. This aspect of HB utilization has been covered in several recent publications (Bell and Keith 1994; Aherne et al 1995; Darroch et al 1996; Alberta Barley Commission 1995, 1997). Since the first review was published (Bhatty 1986), a whole new industry has developed around uses of HB in swine and poultry feeds that has become the mainstay of HB production in Canada. HB is not yet used in monogastric feeds in other countries for a variety of reasons, although it evokes a great deal of scientific curiousity.

HB production in Canada is the highest in the world and is estimated to be between 300,000 and 350,000 ha, with an estimated grain production of ≈800,000 t in 1998. The United States, Australia, and Japan, and probably some other countries have HB breeding programs but production is low. In Japan, the 1997 production was 17,000 t (Nakashima 1998). Production in the United States probably does not exceed 5,000 t. Estimates for other countries are not available. Canada thus remains the leading producer and the major source of published information on HB.

HB has been investigated for several potential new applications as a whole grain or for its value-added products. The whole grain can be ground, pearled, steamed, boiled, baked, extruded, roasted, flaked, or cut into grits for use in Western foods. Japanese applications include barley tea, the alcoholic beverage *sochu*, *miso*, and finely pearled barley as a rice extender. Similarly, there are a variety of food applications of HB in India, China (Tibet), and the West Asia-North Africa region. Value-added products include milling of HB for the production of bran and flour for multiple food applications (Bhatty 1995a, 1997), extraction and enrichment of β-glucan (Knuckles et al 1992; Bhatty 1993b, 1995b; Sundberg et al 1995b; Yoon et al 1995; Temelli 1997), production of ethanol (Ingledew et al 1995, Thomas et al 1995), preparation of native and modified starches (Vasanthan and Bhatty 1995, 1996; Vasanthan et al 1997; Bhatty and Rossnagel 1997; Zheng et al 1998, 1999), production of food (Bhatty 1996a), and brewer's and distiller's malts. The latter use of HB will be revolutionary, transcending a thousand years of history.

DEVELOPMENT

HB was rediscovered in western Canada in the early 1970s at the University of Saskatchewan, SK, during investigations of nutritional quality of barley germ plasm (Bhatty et al 1975). This study showed that hull content of barley had major influence on digestible energy in swine and poultry feeding. This and subsequent findings led to the registration of several HB cultivars (five alone in 1999) in Canada (Table I). These cultivars include 2- or 6-rowed, low or high β-glucan, low or high acid-extract viscosity, and waxy or normal starch. Others have relatively low protein and high starch (CDC Gainer) or few attached hulls (CDC Freedom). Registered HB cultivars with normal starch include Bear, Shonkin, Nubet, and Robust with waxy starch Azhul, Waxbar, Merlin, and an isoline of Compana, Prowashonupana in the United States; Waxiro in Australia; and Taiga in Germany, among others. Two-rowed cultivars predominate because of their plump kernel, white aleurone, and soft endosperm, all desirable in food and industrial applications of HB. As far as is known, no other country has yet registered HB cultivars, although several have HB development programs. In Canada, the emphasis now is to extend use of HB in food and industry, including the malting and brewing industries.

COMPOSITION OF HULL-LESS BARLEY

Comparative composition of hulled and HB, taken from two studies conducted in the United States and Sweden, showed HB generally contained more protein and starch, its two major components, and total and soluble β-glucan (Table II). This was due to removal of fibrous hull which has a dilution effect on these components. HB contained more total dietary fiber (TDF), pentosans, largely found in the hull, and TDF components. The latter include Klason lignin, cellulose, enzyme resistant starch, and uronic acid. Composition of HB varies considerably and is influenced by environment and adhering hulls. Ideally, HB should have <5% adhering hulls. In one study (Edney et al 1992), grain protein varied from 13 to 17% in Condor HB (free of adhering hulls) grown at 11 locations in central Alberta. HB had higher concentrations of limiting amino acids, lysine, and threonine than wheat or hulled barley (Edney et al 1992, Boros et al 1996). The com-

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position of 457 samples of HB grown from 1995 to 1997 in the Prairie Provinces of Canada contained, on average, 14% protein (N × 6.25) and 0.5% lysine on a dry weight basis (Edney and Tipples 1997). Hull adherence varied from 4 to 18%. The 1997 samples (*n* = 89) contained 4% adhering hull; protein and lysine contents were 14 and 0.5%, respectively. Physicochemical analysis of 12 HB, which included nine registered Canadian HB cultivars, was reported by Bhatty and Rossnagel (1998). There were significant intracultivar variations in grain hardness, color, chemical composition, TDF, and soluble fiber (SF). The ranges in chemical composition were protein (13–18%), starch (60–74%), β-glucan (4–8%), TDF (12–17%), and SF (3–6%). Particularly noteworthy was the large range in acid-extract viscosity due to waxy HB cultivar CDC Candle.

CARBOHYDRATES OF HB

Components of HB carbohydrates include starch, cell-wall polysaccharides, (1→3),(1→4)-β-D-glucans (β-glucans), (1→3)-β-glucans, and arabinoxylans (pentosans), cellulose, and a number of simple sugars and oligosaccharides. Their concentration, physicochemical properties, structure, and functionality in barley were reviewed by MacGregor and Fincher (1993). More recent studies on barley carbohydrates have been reported by Bornet (1993), Saulnier et al (1994), Izydorczyk and Biliaderis (1995), Gomez et al (1997), Beer et al (1997), Knuckles et al (1997a), and BeMiller (1997).

Starch, β-glucan, tocopherols, and tocotrienols are discussed in greater detail because of their potential contributions to more healthful foods and other applications in foods and industry.

STARCH

Starch is the most abundant single component of HB, accounting for 60–75% of grain on a dry weight basis. Normal HB starch contains 25–30% amylose, the rest is amylopectin. However, waxy cultivars containing 0–5% amylose, or 95–100% amylopectin, have been reported in Canadian and U.S. barleys (Lorenz 1995, Bhatty and Rossnagel 1997). At the other end, Glacier barley has been reported to contain 35–45% amylose. Hull-less barley starch contained a mixture of large lenticular granules 12–26 µm in diameter and small granules 2–10 µm in diameter (Vasanthan and Bhatty 1996). Granule size had a larger range (2–30 µm) in waxy HB than in waxy corn (2–20 µm). HB starch showed A-type X-ray diffraction patterns typical of cereal starches, indicating semicrystalline structure. Amylopectin is responsible for crystallinity of starch. Starch in HB showed inter- and intracultivar variability, largely due to inverse correlation with protein. Edney et al (1992) reported that Condor HB grown at 11 locations showed a range of 60–66% starch that was negatively correlated with protein ($r = 0.91$, $P < 0.01$). The starch content of six Swedish HB cultivars was 49–66% (Oscarsson et al 1996). Twelve Canadian HB cultivars grown at the same location contained 62–75% starch (Bhatty and Rossnagel 1998).

TABLE I
Registered Cultivars of Hull-less Barley in Canada

Barley	Year Registered
2-Rowed	
Scout[a]	1982
Condor	1988
CDC Richard[a]	1990
Phoenix	1993
CDC Candle[b]	1994
CDC Dawn	1995
Merlin[b]	1995
HB803[b]	1995
Tercel	1996
CDC Gainer	1997
CDC Freedom	1998
CDC McGwire	1999
HB 340[c]	1999
HB 343	1999
HB 805	1999
6-Rowed	
Tupper[a]	1982
CDC Buck[a]	1990
Falcon	1993
CDC Silky	1994
Jaeger	1998
Peregrine	1999

[a] Deregistered.
[b] Waxy or low amylose starch.
[c] Zero amylose starch.

Extraction

Wet extraction of starch from HB presents difficulties. β-Glucan present in high concentrations in waxy and high-amylose HB produces high viscosities in aqueous solutions. Furthermore, small starch granules are lost during the extraction and purification procedures. Zheng and Bhatty (1998) used a commercial enzyme cocktail (Roxazyme-G) in wet extraction of starch from four HB cultivars with acid-extract viscosity variation of 8–634 cps. The multienzyme cocktail contained cellulase, endo (1→3),(1→4)-β-D-glucanase, and xylanase. Compared to the conventional procedure, the enzyme-assisted wet extraction reduced slurry viscosity by 50–99% and water use by 30–60%. The starch yield was, on average, 50% compared with 46% in the conventional extraction procedure, with a starch purity of 98%. As expected, the enzyme-assisted extraction largely destroyed β-glucan.

Pin Milling and Air Classification

Starch has also been partially purified from HB by pin milling and air classification (Vasanthan and Bhatty 1995, 1996; Vasanthan et al 1997). HB cultivars containing waxy (CDC Candle), normal (Condor), and high-amylose (Glacier) starch were pin-milled and air-classified into coarse (C) and fine (F) fractions. The coarse (C3) fraction from the three HB cultivars contained 15–36% starch, 12–15% protein, and 13–24% β-glucan. In contrast, the F3 fraction contained 77–78% starch, 8-9% protein, and 6–8% β-glucan. The starch yield in the three F3 fractions was 46–63%. Scanning electron microscopy (Fig. 1) showed that starch in the F3 fraction was large-granule prime starch where at least 75% of the granules had a diameter of 12–26 µm. Physicochemical properties of small and large granule starches isolated from the three barleys were reported (Vasanthan and Bhatty 1996). Knuckles and Chiu (1995) reported partial purification of starch by air classification and sieving from Steptoe, Crystal (pearled), and Waxbar (cleaned waxy) barleys. The five fractions (A–D) contained 78–90% starch, except fractions C and D in Waxbar HB, which contained 47–66% starch.

TABLE II
Effect of Hull-less Gene on Composition of Barley Genotypes

Component (% db)	Hulled[a] (*n* = 10)	Hull-less[a] (*n* = 6)	Hulled[b] (*n* = 12)	Hull-less[b] (*n* = 24)
Protein	12.2	15.1	15.9	16.5
Ether extract	2.5	2.7	2.2	2.3
Ash	2.1	1.6	2.8	2.1
Starch	57.7	60.7	53.7	59.7
Total β-glucan	4.8	5.7	5.2	5.6
Soluble β-glucan	2.3	2.9	3.0	3.1
Pentosans	7.9	5.7	6.5	4.5
Cellulose	4.8	2.9	4.1	2.0
Klason lignin	1.3	0.7	2.0	0.9
Uronic acid	0.8	0.6	· · ·	· · ·
Total dietary fiber	20.6	16.6	18.6	13.8

[a] Waxy, normal and high-amylose starch barleys (Oscarsson et al 1997).
[b] Isotypes of Betzes (CI 6598) and Compana (CI 5438) barleys (Xue et al 1997).

Zero Amylose HB Starch

Waxy lines of HB completely devoid of amylose were reported by Bhatty and Rossnagel (1997). Earlier, Ishikawa et al (1995) had reported zero amylose in sodium azide-treated mutants of barley. Amylose content of the two HB lines is given in Table III. The zero amylose starch from line SB94794 had only 4% syneresis after four freeze-thaw cycles compared with 21% for CDC Candle starch containing 5% amylose (Bhatty and Rossnagel 1997). Physicochemical properties of zero amylose starch were reported by Zheng et al (1998). Zero amylose HB and corn starches showed a similar pasting behavior. The starches gave high peak viscosities (greater in zero amylose HB starch) as a result of rapid starch granule swelling, followed by a rapid breakdown of viscosity (Fig. 2a). Little setback was observed in both starches during the cooling period. CDC Candle HB starch behaved quite differently than zero amylose HB or waxy corn starches. It had lower peak but higher setback viscosities. Its pasting curve showed an initial slow swelling unlike in the other two starches (Fig. 2a). The slow swelling of CDC Candle HB starch granule at an early stage of pasting was confirmed by its swelling power. As temperature increased from 60–70°C, the swelling power increased three- to fourfold in zero amylose HB and corn starches but only 1.4 times in CDC Candle starch (Zheng et al 1998). Another noteworthy characteristic of zero amylose HB starch was its high paste clarity (Fig. 3) as compared to corn and potato starches. A 4% solution of zero amylose HB starch was still clear after one freeze-thaw cycle. These properties of swelling power and high paste clarity made zero amylose HB starch uniquely suitable for use in frozen foods.

TABLE III
Amylose Content (%) of Barleys and Isolated Starches[a]

Product	SB94792	SB94794	CDC Candle	CDC Richard
Ground barley	0	0	3.9	24.6
Starch	0	0	4.3	26.8
Defatted starch	0	0	6.2	30.1

[a] Bhatty and Rossnagel (1997).

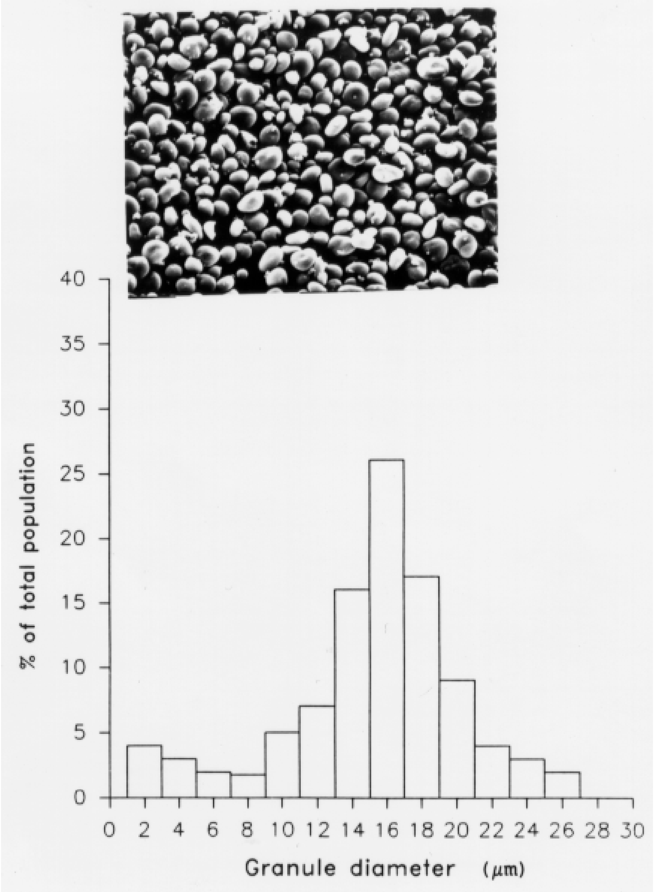

Fig. 1. Granule size distribution in Condor hull-less barley starch purified from the fine 3 fraction. Reprinted from Vasanthan and Bhatty 1995.

Modification of HB Starches

Cationic corn and potato starches are widely used as wet-end additives in the pulp and paper industry to enhance starch and filler retention during paper making. To assess the suitability of HB starch for use in paper making, prime starches isolated from regular (Condor), waxy (SB89528), and high-amylose (Glacier) barleys were cationized using an alkaline alcoholic semiaqueous procedure described by Kweon et al (1996). The degree of substitution (DS) was ≈1 cross-linked group for every 3,600 anhydroglucose units. The strength characteristics of papers containing cationic barley starch were superior to those containing Cato-15, a commercial cationic corn starch, or a laboratory-modified corn starch. Cationic HB starches may therefore be substituted for cationic corn starch in paper making. Cationized waxy, normal, or high-amylose HB starches were equally suitable for paper coating (Vasanathan et al 1997).

Cross-Linking

The narrow range in which zero amylose HB starch developed and lost its viscosity (Fig. 2a) is undesirable in some food applications. However, cross-linked HB starches (single or double modifi-

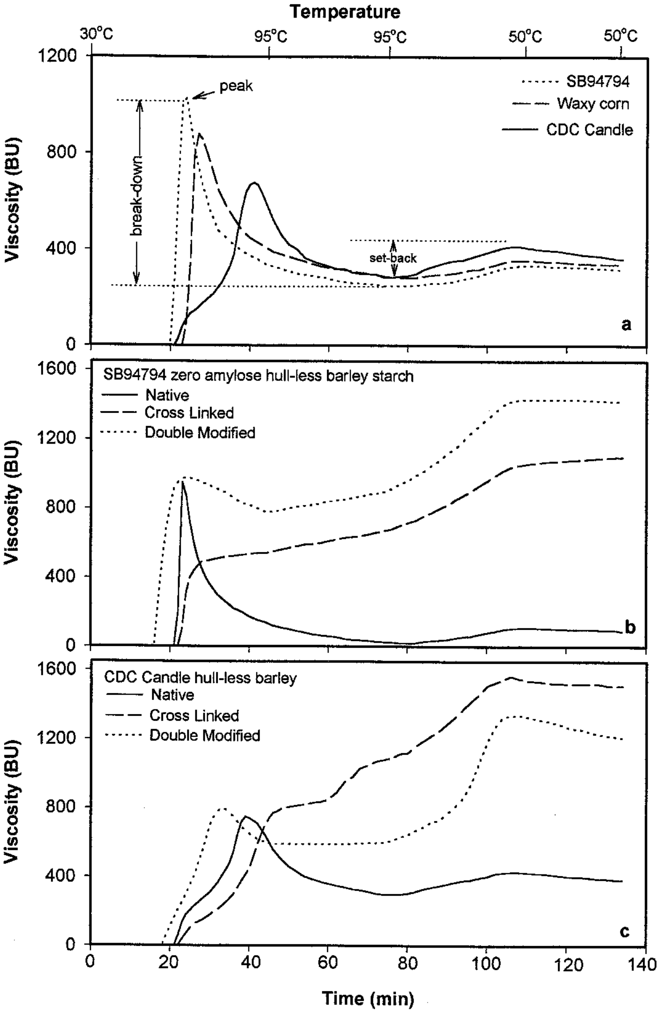

Fig. 2. Amylograph pasting patterns of native (**a**) and modified waxy hull-less barleys and waxy corn starches (**b** and **c**). Reprinted from Zheng et al 1998, 1999.

cation) showed improved pasting properties of zero amylose and CDC Candle HB starches (Fig. 2b and c). Furthermore, cross-linked waxy HB starches were more tolerant to freeze-thaw, shear cooking, autoclaving, and acid treatment than similarly cross-linked waxy corn starch. Hydroxypropylation used in double modification further improved freeze-thaw stability and paste clarity of the cross-linked waxy HB starches.

β-GLUCAN

HB, like oats, contains high concentrations of β-glucan, a major component of TDF and SF, as shown in Table IV. β-Glucan formed 22 and 38% of TDF and SF of bran and 20 and 27% of flour, respectively. Table IV also gives other components of TDF and SF of HB bran and flour. β-Glucan in 10 cultivars of Canadian HB was positively correlated with TDF ($r = 0.81$, $P < 0.01$) and SF ($r = 0.86$, $P < 0.01$) (Fig. 4). The low-amylose (waxy) and high-amylose starch (Glacier) HB contained more β-glucan and therefore more TDF and SF than normal amylose HB (Bhatty 1995a). A similar relationship between β-glucan and TDF and SF in waxy HB has been reported in other studies (Table V). One sample of Prowashonupana, a U.S. waxy HB, contained 17.4% β-glucan. Its TDF and SF were 25.2 and 9.3%, respectively (R. S. Bhatty, *unpublished data*).

A large range exists in β-glucan content of barleys. Bhatty and Rossnagel (1998) reported a range of 4–6% in normal starch and 6–8% in waxy HB starch. Fastnaught et al (1996) reported that seven waxy HB starches contained 6–8% and five regular HB starches contained 4–6% β-glucan. In two other studies, β-glucan content of regular HB starch varied from 4–6% and β-glucan content of waxy HB was >6% (Oscarsson et al 1996, Lee et al 1997). β-Glucan content of barley was influenced by cultivar and growth environments (Fastnaught et al 1996, Perez-Vendrell et al 1996, Lee et al 1997). In dry years, β-glucan and viscosity levels are enhanced, probably due to their enhanced synthesis. Wet and rainy years have a negative effect on β-glucan and acid-extract viscosity. In addition, method of β-glucan determination may influence results. The most common method of β-glucan determination is that of McCleary and Glennie-Holmes (1985), Approved Method 32-23 (AACC 1995). Other methods include the Calcofluor-FIA system which is the recommended method of the European Brewery Convention for determination of β-glucan in barley and malt. Manzanares and Sendra (1996) reported an improved extraction of β-glucan from barley and malt with dilute aqueous nitric acid solution.

Cell-wall thickness in low (3.9%), medium (4.9%), and high (5.4%) β-glucan genotypes of hulled and HB was related to β-glucan concentration (Bhatty et al 1991). Cell walls appeared thicker in the subaleurone layers as well, suggesting higher β-glucan concentration. This resulted in β-glucan enrichment of bran by an average of 36% in 15 Canadian cultivars of hulled and HB (Bhatty 1992), almost similar to that reported in oat bran of 50% extraction by Wood et al (1991). In a subsequent study (Bhatty 1995a), 10–30% fractions of HB bran obtained by successive pearling in a Satake mill showed increasing concentration of β-glucan; the 30% bran fraction had ≈75% more β-glucan than the 10% fraction. These data further suggested that β-glucan concentration was higher in the subaleurone layers of these barleys and was responsible for bran enrichment. However, Miller and Fulcher (1994) did not observe thickness of subaleurone cell walls in any of the five cultivars of barley, examined by microspectrofluorometry. The highest concentration of β-glucan was found in the central endosperm and not in the subaleurone layers.

Solubility and viscosity of HB β-glucan are largely responsible for glucose regulation and serum cholesterol reduction in hypercholesterolemic subjects. Extract viscosity of HB has been reported

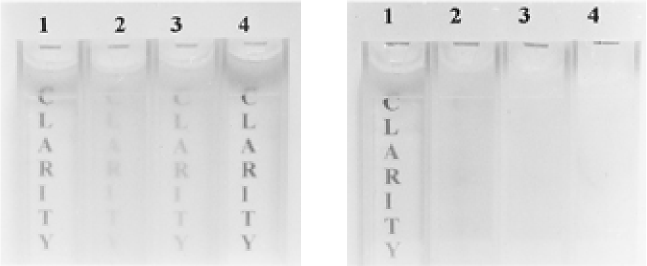

Fig. 3. Freeze-thaw stability of zero amylose hull-less barley starch compared to other starches. Left: fresh pastes (4%, w/v). Right: pastes (4%, w/v) after one freeze-thaw cycle. Lanes 1–4: zero amylose hull-less barley starch; 5% amylose hull-less barley starch; 1% amylose corn starch; and 2% amylose potato starch, respectively.

TABLE IV
Composition (%) of Total Dietary Fiber and Soluble Fiber Obtained from Scout Hull-less Barley Bran and Flour[a,b]

	Total Dietary Fiber		Soluble Fiber	
Component	**Bran**	**Flour**	**Bran**	**Flour**
β-Glucan	22.4	20.3	38.4	26.8
Resistant starch	6.3	8.3	5.4	6.9
Klason lignin	7.8	6.4	nd[c]	nd
Pentosans	19.7	13.9	6.5	5.7
Uronic acid	1.2	2	1.1	1.2

[a] Bhatty (1993a).
[b] Freeze-dried preparations obtained by the method of Prosky et al (1988).
[c] Not detected.

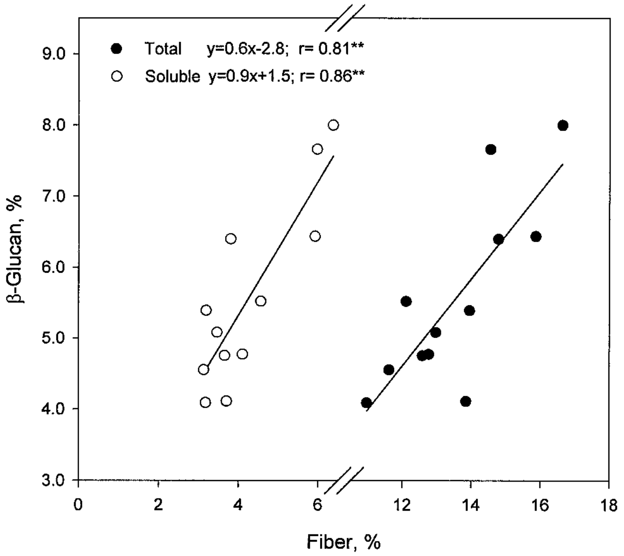

Fig. 4. Correlation between β-glucan and dietary fiber in 12 Canadian hull-less barley cultivars. Reprinted from Bhatty and Rossnagel 1998.

TABLE V
β-Glucan and Dietary Fiber Content (%) of Waxy and Normal Starch Hull-less Barleys

	Bhatty and Rossnagel (1998)	Xue et al (1997)	Fastnaught et al (1996)
Waxy starch	(*n* = 3)	(*n* = 18)	(*n* = 5)
β-Glucan	7.4	6.1	7.1
Total dietary fiber	15.7	16.2	15.6
Soluble fiber	6.1	5.8	6.5
Normal starch	(*n* = 9)	(*n* = 18)	(*n* = 2)
β-Glucan	5.0	4.9	4.5
Total dietary fiber	12.9	14.6	15.3
Soluble fiber	3.7	4.8	4.2

by a number of workers (Bhatty et al 1991, Xue et al 1991, Yoon et al 1995, Fastnaught et al 1996, Lee at al 1997). Solvents used to extract β-glucan from barley have included extraction with water (Lee et al 1997), acid buffer at pH 1.5 (Bhatty et al 1991), and an alkaline extraction at pH 10 (Yoon et al 1995, Fastnaught et al 1996). Bhatty et al (1991) reported the concentrations of components in the extracts and their influence on extract viscosity. In 13 hulled and HB, the mean solubility for β-glucan in the acid buffer was 45%, 2% for starch, 82% for protein, and 15% for pentosans. Soluble β-glucan, starch, and pentosan contents were correlated with acid-extract viscosity (r = 0.71, 0.90, and 0.61, respectively, at $P < 0.05$ and 0.01). The acid buffer solvent extracted very little starch but almost all of the protein, which had no apparent effect on viscosity. Hydrolysis of the neutralized acid extracts of barleys by α-amylase, pronase, and xylanase had small effect on viscosity, but hydrolysis by β-glucanase almost completely abolished it. Viscosity of acid buffer extracts was, therefore, largely due to soluble β-glucan and, to a minor extent, to soluble pentosans and starch. The soluble β-glucan expressed as % of the total β-glucan was 27–45% in two HB cultivars grown at several locations (Bhatty 1987) and 26–50% in 13 cultivars of hulled and HB (Bhatty et al 1991). Lee et al (1997) reported higher soluble β-glucan (60–71%) in nine waxy hulled and HB based on indirect calculation. Knuckles et al (1992) reported total, soluble, and insoluble β-glucan contents of four U.S. barleys and their fractions. The water-soluble fraction was ≈55%, except in Wanubet barley where it was 60–70% of the total β-glucan.

Extraction and Enrichment

β-Glucan may be extracted and enriched from barley by dry milling and sieving (Knuckles et al 1992), air classification, and sieving (Sundberg et al 1995b, Knuckles and Chiu 1995, Wu et al 1994) or solvent-extracted and purified (Bhatty 1993b, 1995b; Saulnier et al 1994; Temelli 1997; Burkus and Temelli 1998). Knuckles et al (1992) reported that dry milling and repeated sieving gave a coarse fraction (yield 18–30%) from four barleys (two dehulled and two HB) containing 16–27% β-glucan. In a later report (Knuckles and Chiu 1995), the same barleys were hammer-milled and air-classified. The coarse fraction (D) contained 16–19% β-glucan. The enriched fraction yield was 20–25%. Wu et al (1994) reported β-glucan and protein-enriched fractions from dehulled, high-protein barley. The C3 fraction obtained by Vasanthan and Bhatty (1995) from pin milling and air classification of three HB cultivars contained 24% β-glucan in waxy, 13% in normal starch, and 22% in high-amylose HB starch. The yields of the C3 fraction in the three cultivars were 8, 10, and 21%, respectively. Thus, dry processing yields fractions containing various levels of β-glucan as by-products. These fractions may have applications in food products. However, they may need further processing to meet specific market requirements.

Wet extraction and purification yields high concentrations of β-glucan. Bhatty (1993b) reported β-glucan extraction and purification from HB with three solvents. Solvent 3 (4% NaOH) was most effective and extracted 80% of the total β-glucan from HB bran. The final product after purification contained 60% β-glucan, 11% pentosans, 13% ash, and <1% total nitrogen and starch. Mass balance showed 96% of the extractable β-glucan was recovered from HB bran. In a subsequent study (Bhatty 1995b), β-glucan was extracted with NaOH from HB brans in the laboratory and at a pilot plant to yield, in the latter case, preparations containing 50–76% β-glucan. The pseudoplastic behavior (shear sensitivity) showed high flow index behavior (η value), suggesting partial degradation during extraction and purification. It is possible that the alkaline solvent was partly responsible for the shear-thinning behavior of the preparations. Based on these studies, a U.S. patent on β-glucan extraction was obtained (Bhatty 1996b). Other studies (Saulnier et al 1994, Temelli 1997, Burkus and Temelli 1998, Knuckles and Chiu 1999) reported on extraction and properties of purified β-glucan from barley. The isolated β-glucan may be further purified by selective precipitation or column chromatography. Morgan and Ofman (1998) reported extraction of a new form of β-glucan from barley, Glucagel, with novel functional properties. Glucagel formed soft, thermoreversible, translucent gels that melted at 60°C.

Fine Structure

Literature on fine structure of barley β-glucan was reviewed by MacGregor and Fincher (1993). The earlier studies were based on the 40 and 65°C water-soluble fractions from barley flour or endosperm cell walls. The fractions were depolymerized with endo (1→3),(1→4)-β-glucan-4-glucanohydrolases, releasing 28–31% cellotriose and 69–72% cellobiose as the major oligosaccharides. Edney et al (1991) reported the structure of total β-glucan. The proportions of trisaccharides (G3) and tetrasaccharides (G4) were similar to that reported by other workers in the 65°C water-soluble β-glucan fraction. In 18 cultivars of hulled and HB, the average concentration was 59% for trisaccharide (G3), 30% for tetrasaccharide (G4); 2% for G2, 5% for G5, 2% for G6, and 3% for G9. Statistical analysis showed significant differences in the structure of total β-glucan among the barley cultivars. Commercial barley β-glucan (MW 250,000, Megazyme, Australia) was readily hydrolyzed by cellobiohydrolase II preparation from *Trichoderma reesei* (Henriksson et al 1995). ^{1}H nuclear magnetic resonance (NMR) analysis showed the polymer contained 29% (1→3) linkages and 71% (1→4) linkages. Gomez et al (1997) reported detailed physicochemical properties of 65°C extract of barley β-glucan partially hydrolyzed by lichenase.

A number of studies reported on the average MW of barley β-glucan (Knuckles and Chiu 1999, Beer et al 1997, Knuckles et al 1997a, Manzanares et al 1993, Saulnier et al 1994). The MW determined by HPLC showed wide variations and was affected by the solvents used for β-glucan extraction and was different in waxy and nonwaxy barley cultivars. Wood (1994) reported that despite their similar methylation analysis and almost identical ^{13}C-NMR spectra, oat and barley β-glucan were structurally distinct. HPLC analysis of lichenase-released oligosaccharides showed approximately one-third molar proportion of the structure β-(1→3)-linked cellotetrasyl units in oats, while in barley and wheat this proportion was closer to one-quarter.

TOCOPHEROLS AND TOCOTRIENOLS (TOCOLS)

Barley contains α, β, γ, and δ tocotrienols, isomers of α, β, γ, and δ tocopherols, which are ubiquitous, naturally occurring antioxidants. The essential difference between tocotrienols and tocopherols is the presence of double bonds at carbons 3, 7, and 11 in the isoprene chain of tocotrienols. Their role as inhibitors of cholesterogenesis in barley was first reported by Qureshi et al (1986). In a later study (Qureshi et al 1991a), hypercholesterolemic pigs fed a standard diet supplemented with a tocotrienol-rich fraction decreased total cholesterol (44%), low density lipoprotein (LDL) cholesterol (60%), apolipoprotein B (26%), thromboxane-B_2 (41%), and platelet factor 4 (29%). These effects were also observed in humans fed ingredients made from brewer's grain that were enriched in tocols (Weber et al 1991) and by a palm oil product (Qureshi et al 1991b).

Wang et al (1993a) reported tocols and oil concentrations in whole grain, milling, and pearling fractions of two waxy HB cultivars. The pearling flour fraction, containing 20% of kernel weight, contained 3–4 times more α-tocotrienol and α-tocopherol, total vitamin E, and oil concentration than did the barley grain. Peterson (1994) reported that barley by-product containing hull, aleurone, and subaleurone tissues (bran) contained high contents of all tocols, suggesting their concentrations in the outer layers of the kernel. Tocol concentrations in barley were 42–80mg/kg; the mean of 30 genotypes was 59 mg/kg. Location of growth had no significant effect on tocols (Peterson and Qureshi 1993). α-Tocotrienol and α-tocopherol were the predominant isomers in barley; β- and γ- tocotrienols were also present in significant quantities. Peterson (1994) analyzed tocols in products resulting from milling, malting, and mashing of barley and, in addition, in hand-dissected kernel fractions. Removal of the hull, aleurone, and germ by pearling significantly lowered tocol concentration of the pearled barley as compared to the whole kernel; the by-product was rich in tocols. Malting had essentially no effect on tocol concentration, but brewer's spent grain was enriched in tocols. In hand-dissected fractions of Morex barley, hull, endosperm, and germ contained 5, 0.6, and 94% of the total tocopherol and 26, 46, and 29% of the total tocotrienols in these fractions (Table VI). Thus, in this study, barley germ was rich in tocopherols (94% of the total) but contained only one-third of the tocotrienol. Wang et al (1993b) reported that α-tocotrienol and γ-tocotrienol concentrations of barley oil were 24 and 17 times greater than those in corn oil.

HYPOCHOLESTEROLEMIA

Serum cholesterol reduction by plant fibers from various sources was reviewed by Shinnick et al (1991) and Glore et al (1994). In the case of oats, such effects were largely attributed to β-glucan. HB barley contains more β-glucan than oats and should have similar physiological function in monogastric animals.

In the 1990s, hypocholesterolemic effects of HB-based diets were reported in varying degrees in chicken by Newman et al (1991, 1992), Martinez et al (1992), Wang et al (1992), and Sundberg et al (1995a); in mice, rats, and Syrian hamsters by Oda et al (1991, 1992, 1993), Jackson et al (1994), Wang et al (1997), and Ranhotra et al (1998); and in human subjects by Lupton et al (1994) and Ikegami et al (1996). In the chick-feeding studies, several factors contributed to the hypocholesterolemic effect of barley-based diets. Newman et al (1991) reported lower total serum cholesterol and LDL-cholesterol than those fed corn diets, regardless of β-glucanase supplementation, suggesting factors other than β-glucan alone contributed to hypocholesterolemic affects of waxy HB. Newman et al (1992) suggested that soluble β-glucan appeared to be the strongest predictor of the serum cholesterol response in chicken and rats. Wang et al (1992) reported significant ($P < 0.01$) negative correlations between viscosity of the small intestine contents and average daily weight gain, plasma total LDL-cholesterol concentration, and digestibility of lipids and proteins. In the Japanese study (Oda et al 1991), both oat- and barley-soluble gums suppressed liver lipid accumulation and elevation of plasma cholesterol concentrations in obese (Zucker) rats; these effects were less marked in lean rats. Oda et al (1992) reported a significant inverse relationship between SF intake and liver cholesterol accumulation in male Sprague-Dawley cholesterol-fed rats. Water-soluble fractions of oat, barley, and wheat were the active components that suppressed liver cholesterol accumulation in male Sprague-Dawley rats according to Oda et al (1993). Ranhotra et al (1998) reported that a 25% HB-supplemented diet fed to hamsters lowered serum cholesterol by 16%. This effect was not linear when HB levels were increased to 50 or 75% in the diet. The lowering pattern for serum triglycerides, however, suggested a dose-dependent response.

TABLE VI
Total Tocol Concentration of Hand-Dissected Morex Barley Fractions[a]

	Tocopherols		Tocotrienols	
Fraction	**mg/kg**	**%**	**mg/kg**	**%**
Whole grain	6.8	. . .	33.9	. . .
Hull	10.7	5.4	18.2	25.9
Endosperm	1.2	0.6	32.1	45.7
Germ	186.5	93.7	20	28.5

[a] Peterson (1994).

In the human study (Lupton et al 1994), 79 hypercholesterolemic men and women were given barley bran flour (dried and milled brewer's spent grain) or barley oil extract. Both of these significantly decreased total serum cholesterol and LDL-cholesterol. Barley bran flour, but not barley oil, significantly decreased high density lipoprotein (HDL) cholesterol. The effect of barley bran flour on serum cholesterol fractions must be due to tocols as barley bran was unlikely to contain β-glucan which is degraded during malting. Brewer's spent grain was enriched in tocols (Peterson 1994). In a related study on colon physiology (Lupton et al 1993), barley bran flour increased fecal bulk and decreased transit time in 22 human volunteers. Thus, taken together, these studies (Lupton 1993, 1994) concluded that barley bran flour had the dual effect of lowering serum cholesterol while increasing fecal bulk and accelerating transit time. Ikegami et al (1996) reported a significant decrease in serum lipids (total cholesterol, LDL-cholesterol, phospholipids, and very low density lipoprotein [VLDL] cholesterol) in hypercholesterolemic Japanese men and in mildly hypercholesterolemic Japanese women fed boiled barley-rice mix (50:50, w/w). Two studies were reported in which human subjects with ileostomies were used. Increased fecal cholesterol excretion was suggested to be the primary mechanism for the serum LDL-cholesterol lowering effect of brewer's spent grain (Zhang et al 1991). The excretion of cholesterol was higher in the barley diet (13 g of β-glucan/day) than in the oat bran diet supplemented with β-glucanase (3.8 g of β-glucan/day) or wheat flour diets (1.2 g of β-glucan/day). The mechanism behind this effect of barley fiber was not known (Lia et al 1995).

Two distinct mechanisms were reported for cholesterol reduction by barley products in experimental animals, although this does not exclude factors other than β-glucan and tocols. One was the inhibition in activity of the rate-limiting enzyme 3-hydroxy-3-methylglutaryl coenzyme A (HMG-CoA) reductase by tocols present in barley products. In humans, regulation of this reaction in the liver was thought to be a major factor controlling cholesterol synthesis. The structure of the inhibitor isolated from barley was first reported by Qureshi (1986). Subsequently, Qureshi and coworkers (see Bhatty 1993c) reported a number of studies showing reduced activity of HMG-CoA reductase in animal subjects fed barley-based diets. A more definitive study (Qureshi et al 1991a) showed hypercholesterolemic pigs fed tocotrienol-rich fraction isolated from palm oil had 44% lower total serum cholesterol, 60% lower LDL-cholesterol, and significant decreases in other lipid components. This effect was later confirmed in human subjects (Qureshi et al 1991b). Serum cholesterol reduction was associated with tocols in animal studies fed brewer's spent grain diets enriched in tocols that were largely free of β-glucan (Peterson and Qureshi 1997).

The mechanism of SF in hypocholesterolemia is controversial. Part of this controversy is related to complexity of SF and lack of agreement among researchers on its composition. In some countries, resistant starch is not considered part of SF. Englyst and Hudson (1996) reported new classification of dietary carbohydrates into rapidly digestible starch, slowly digestible starch, and resistant starch. In addition, a new category of rapidly available glucose was described. A large part of the evidence on the role of SF in hypocholesterolemia has come from oats and other gums and only a little from HB. Glore et al (1994), in an excellent review on the subject, listed the following mechanisms for the hypolipidemic effect of SF: a) binding of bile acids that results in reduced bile acid pool and serum cholesterol; b) fermentation of SF by colonic bacteria to produce short chain fatty acids (acetate, propionate, and butyrate) that may inhibit hepatic cholesterol synthesis; c) increased breakdown of LDL-cholesterol; and d) indirect effect of replacement of dietary saturated fat and cholesterol by SF.

Peterson and Qureshi (1997) reported on the effects of tocols and β-glucan from barley and oats on serum lipids in chicken. A decrease in HMG-CoA-reductase activity and an increase in cholesterol 7 α-hydroxylase activity, an enzyme that breaks cholesterol in the synthesis of bile acids, was correlated with the presence of β-glucan in the chicken diet. The reduction in HMG-CoA-reductase activity by cereal grains has been attributed to tocol content (see above). But this study showed the decrease in the enzyme activity in the absence of significant tocol concentration. The authors suggested β-glucan lowered HMG-CoA-reductase activity, which resulted in serum cholesterol reduction. This is unusual as inhibitors of enzymes are, unlike β-glucan, low MW compounds able to interfere with the enzyme-substrate complex. Bourdon et al (1999) reported that cholecystokinin remained elevated for a longer time after eating meals containing barley. These meals appeared to stimulate reverse cholesterol transport, which may contribute to the cholesterol-lowering ability of barley. Thus, although SF is recognized as an important dietary ingredient, its exact mechanism in serum cholesterol metabolism remains elusive.

HYPOGLYCEMIC EFFECTS

The hypoglycemic effect of HB in human subjects has been reported recently. This effect is measured as a glycemic index (GI), which is the rise in blood glucose after eating a food against a standard blood glucose curve (Truswell 1992). Studies in which barley and its products reduced GI (and GII or insulinemic response) in human subjects were reported by Liljeberg et al (1992, 1996), Granfeldt et al (1992, 1994), Narain et al (1992), Yokoyama et al (1997), and Pick et al (1998). The lower GI and GII response were attributed to barley β-glucan or soluble β-glucan fraction of barley dietary fiber. Yokoyama et al (1997) reported that five adult subjects fed waxy (Waxbar) barley and durum wheat pasta containing 12 g of β-glucan lowered glycemic and insulin responses. Part of their data (Fig. 5) shows reduced insulin response in barley pasta meal when compared to plain or durum-only pasta meal. It may, therefore, be useful to include β-glucan-enriched barley flour in wheat flour as a means of controlling postprandial glycemic and insulin response. Pick et al (1998) reported that barley bread products containing 5 g of β-glucan/day prepared from CDC Candle waxy HB increased insulinemic response, thereby reducing oral hypoglycemics in some subjects. The HB products were well tolerated and could easily be incorporated into the diet. In another study, Bourdon et al (1999) reported that carbohydrate was more slowly absorbed from high-fiber meals containing naturally high β-glucan or flour enriched β-glucan due to lower plasma concentration of insulin. In two other studies, streptozotocin-induced diabetic rats were used as experimental animals (Ikegami et al 1991, Naismith et al 1991). Glucose tolerance was more significantly suppressed in diabetic than in normal rats (Ikegami et al 1991). Naismith et al (1991) reported significantly lower water intake and weight loss in diabetic rats given barley than in those given wheat.

ANTICARCINOGENIC EFFECTS

McIntosh et al (1993, 1996) reported that insoluble dietary fiber from barley spent grain was more effective in preventing dimethyl hydrazine (DMH) induced tumors than soluble fiber-rich commercial bran. In the second study (McIntosh et al 1996), three barley bran fractions were compared with wheat bran and cellulose in a seven-month feeding study. Commercial barley bran (13% DF) and wheat bran (44% DF) were most effective in reducing tumor incidence and burden. The incidence of tumors fell significantly from 70% in outerlayer barley bran including the germ (26% DF) and from 50% in spent barley grain to 10 and 20% in commercial barley and wheat brans, respectively. In a second experiment, commercial barley bran and spent barley grain introduced after DMH-dosing were less effective. Commercially available barley and wheat brans appeared to reduce tumor incidence and burden, influencing both the initiatory as well as promotional stages of chemically induced carcinogenesis.

HB PRODUCTS

Bran and Flour

Roller milling of HB was reported recently (Bhatty 1997). Light microscopy of pearled HB fractions showed that a 70% pearl yield was devoid of grain's outercovering, including the aleurone and subaleurone layers. The remaining 30%, therefore, constituted true bran in HB. HB was then milled to ≈70% flour and 30% bran yields. The milling study showed that: a) HB was at best dry-milled on an as-is moisture basis (7–9% grain moisture under Canadian conditions); b) tempering HB from 9–16% moisture or drying it to 5 or 7% moisture did not improve flour yields; c) flour yield at the as-is grain moisture was 59% for the regular HB starch and only 42% for the waxy starch cultivars, the balance in both types of HB was a mixture of bran and shorts. Low flour yields of waxy HB milled in a Buhler mill were also reported by Sundberg and Åman (1994), but no explanation was given for the yield differences in waxy and regular barley starch.

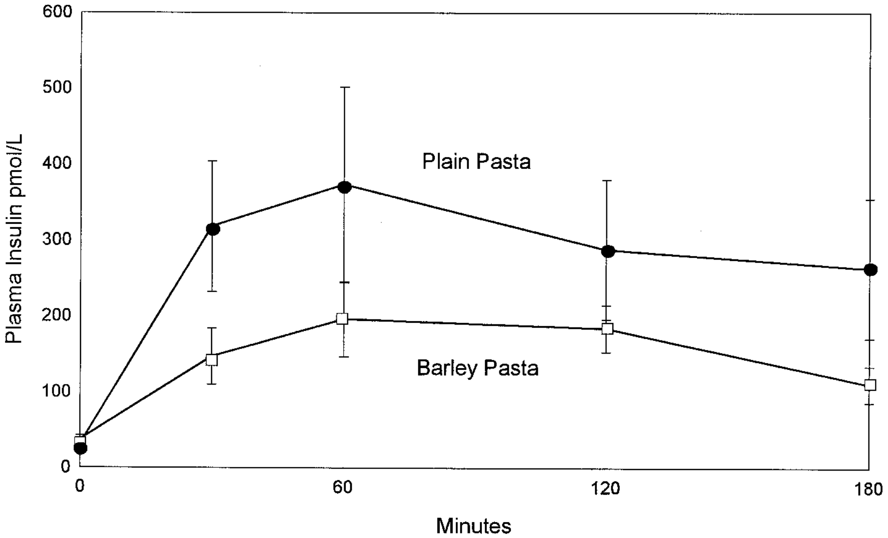

Fig. 5. Plasma insulin measurements (mean ± standard error) in human subjects after consumption of plain durum pasta (●) and barley pasta (□). Reprinted from Yokoyama et al 1997.

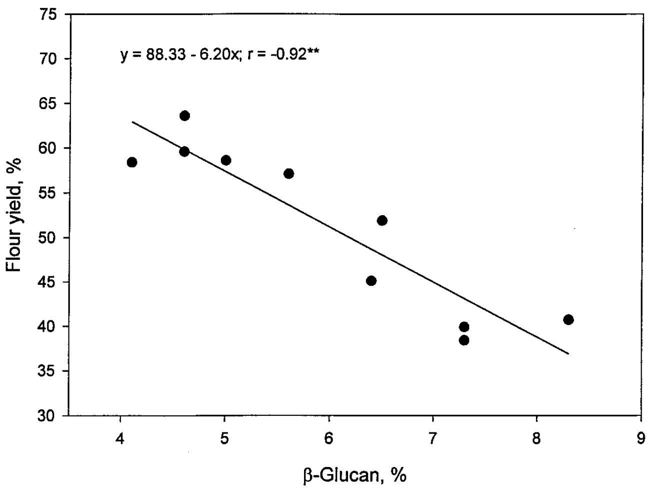

Fig. 6. Correlation between β-glucan and flour yield in hull-less barley dry-milled (as-is moisture) in a Buhler mill. Reprinted from Bhatty 1999.

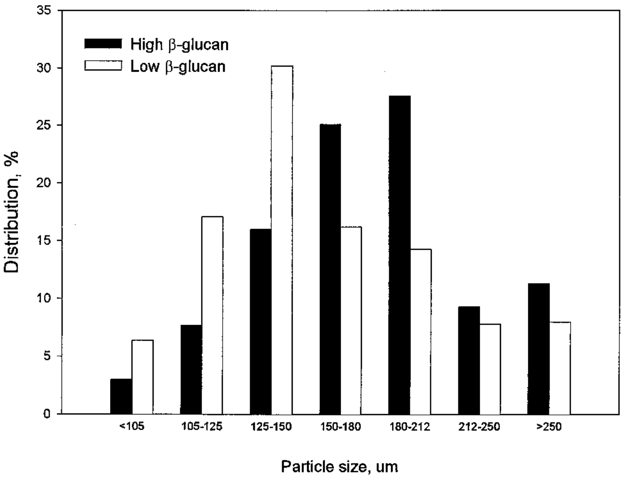

Fig. 7. Particle size distribution in high or low β-glucan hull-less barley milled in a Buhler mill. Reprinted from Bhatty 1999.

TABLE VII
Flour Yield (%), β-Glucan (%), and Grind Time (sec) of Hull-less Barleys[a]

Cultivar	Starch Type	Flour Yield[b]	β-Glucan	Grind Time
CDC Dawn	Normal	59.6	4.6	68
Merlin	Waxy	45.1	6.4	68
Significance[c]	–	**	**	ns

[a] Bhatty (1997).
[b] Milled on as-is grain moisture: Merlin 8%, CDC Dawn 9%.
[c] ** = $P < 0.01$, ns = not significant.

The difference in flour yields of waxy and normal HB starch may be associated with β-glucan content which was significantly different in normal and waxy HB starch (Table VII). To test this hypothesis further, 10 HB genotypes and cultivars containing low or high β-glucan were milled under identical conditions in the Buhler mill and their yields were compared (Bhatty 1999). A highly significant negative correlation was obtained between β-glucan level and flour yield ($r = -0.92$, $P < 0.01$) (Fig. 6). High β-glucan flour had a higher proportion of particles of 150–250 μm, which constituted 62% of the total flour. Particles <105–150 μm formed 27% of high β-glucan HB flour. In low β-glucan HB flour, the proportions of flour in the same particle ranges were reversed. The 105–150 μm particles made up 38% and the <105–150 μm particles made up 54% of the flour (Fig. 7). Thus, the low flour yield in high β-glucan (usually waxy) cultivars appeared due to high proportion of the large particles. β-Glucan present largely in endosperm cell walls resists particle-size reduction during the milling process which leads to lower flour yields. The mechanism of this resistance is not known. Practical waxy HB milling will require milling process optimization and possibly a longer milling time.

The physicochemical and nutritional properties of HB bran of 30% extraction were reported (Bhatty 1995a). HB bran is a high β-glucan, high SF, cholesterol-lowering alternative to oat bran that is suitable for use in ready-to-eat cereals, bakery products, and for extraction of β-glucan. HB flour was slightly darker due to its higher ash content but it contained more protein, β-glucan, and iron than AC Reed soft white Canadian wheat milled under identical conditions (Bhatty 1997). The availability of HB cultivars containing 0, 5, and 25% (normal) amylose allows production of HB flour with unique physicochemical and nutritional properties. Mixographs of HB and wheat flours (Fig. 8) showed high water absorption in waxy cultivar (CDC Candle) flour which made it an excellent food thickener, suitable for use in wheat-barley flour blends and as an ingredient in comminuted (finely ground) meat products. Waxy HB barley meal or flour added to lean meat batters had desirable low purge or high water retention characteristics. This effect was due to both β-glucan and waxy starch. The use of HB in various bakery products was reported in several publications (Newman and Newman 1991, Hudson et al 1992, Berglund et al 1992, Gupta et al 1992, Marklinder and Johansson 1995, Knuckles et al 1997b, Newman et al 1998). Extruded snack products from waxy HB were prepared by Dudgeon-Bollinger et al (1997). The extruded snacks provided higher β-glucan SF per 28 g of serving than that required by the U.S. Food and Drug Administration (FDA) for labeling oat products. Ranhotra et al (*unpublished data*) prepared seven bakery products from waxy HB containing 0.6–1.3 g of SF per serving size, meeting the FDA requirement of 0.75 g of SF per serving size for oat-based foods. Köksel et al (1999) prepared barley bulgur that retained the high SF originally present in the grain. HB flour showed poor dough development, even poorer than soft wheat flour, and was therefore less suitable for making yeast-leavened baked products.

Food and Brewer's Malts

Commercial malt products such as extracts, syrups, and solid and liquid diastatic and nondiastatic malts are routinely added to processed foods for enhancement of flavor, color, enzyme activity, and nutritional quality. Malt extracts added to wheat flour enhance α-amylase, soluble sugars, and protein in the dough, and promote yeast activity, bread texture, and loaf volume. The processing, type, and uses of malt extracts and syrups was described by Hickenbottom (1993, 1996). Malt extracts and syrups are prepared essentially to eliminate the hull which prevents the addition of brewer's and distiller's malts directly to foods. In contrast, malt produced from HB has no such limitation and can be directly added to a variety of products after milling without the cost and inconvenience of preparing malt extracts and syrups. However, liquid or solid extracts can also be prepared from HB malt without the problem of hull disposal. Bhatty (1996a) reported the production of malt from HB and compared its composition and enzyme activities with that of regular barley and wheat malts prepared under identical conditions. HB had a 16-hr shorter steep time than malting barley or wheat and produced malts that were comparable in composition and enzyme activities (α-amylase, diastatic power, β-glucanase, and proteolytic) to the malting barley malts and superior to wheat malt.

The fine grinding of brewer's and distiller's malts and the development of new mash filter technology (still experimental) may reduce the use of hulled barley in malting as barley hull may not be needed to form a filter bed during wort filtration. HB offers

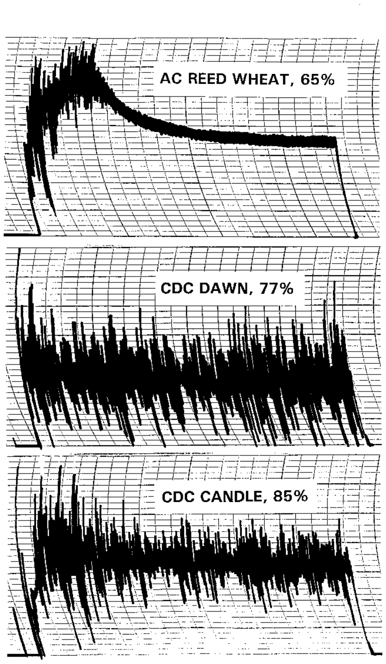

Fig. 8. Mixograph absorption in AC Reed soft wheat, CDC Dawn (regular starch) and CDC Candle (waxy starch) hull-less barley (at 65, 77, and 85% water absorption). Reprinted from Bhatty 1997.

several advantages in preparing brewer's and distiller's malts: a short steep time; high extract yield due to fine grind of malt and more fermentable materials per unit weight of malt; low polyphenols due to absence of hull and consequently less chill haze problem in the beer; and low shipping costs of hull-less malt. Preliminary results obtained in pilot-scale malting of HB were encouraging. Pilot-scale brewing, however, showed prolonged wort filtration time. The reasons for slow wort filtration are not known and need further investigation (R. S. Bhatty, *unpublished data*).

Fuel Alcohol Production

Two studies have been reported in which HB cultivars have been used as feedstock for fuel alcohol production (Ingledew et al 1995, Thomas et al 1995). HB were easily milled, mashed, and fermented to yield >10% (v/v) alcohol. Problems experienced with viscosity were eliminated by addition of β-glucanase (Ingledew et al 1995). In the second study (Thomas et al 1995), very high gravity mashes (30 g of dissolved solids/100 mL) were prepared from HB and fermented with active dry yeast. The ethanol yield in this case was 17.1% (v/v). These studies concluded that no major problems were encountered in converting starch to ethanol in HB. Fermentation efficiency was ≈94%. Fermentation times appeared to be somewhat better when compared with those of wheat.

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