Some Nutritional Properties of Starch and Dietary Fiber in Barley Genotypes Containing Different Levels of Amylose

I. BJÖRCK,¹ A.-C. ELIASSON,² A. DREWS,¹ M. GUDMUNDSSON,² and R. KARLSSON³

ABSTRACT

The nutritional properties of starch and dietary fiber (DF) were studied in barley genotypes containing different amylose contents: Waxy Campana (~8% amylose); Alva, Lina, and Glacier normal (normal varieties, 25-27% amylose); and Glacier high (~35% amylose). On an equivalent starch basis, all barley varieties showed a somewhat higher availability to α amylase than a wheat reference. Among the barley flours, starch in the waxy variety was most available to α -amylase when tested raw. With excess water (90% H₂O), the gelatinization was completed at about 80°C, as measured with differential scanning calorimetry, irrespective of amylose content. At lower moisture (50% H₂O), the temperature interval for gelatinization was considerably broadened. However, the differences in gelatinization behavior between the barley varieties were small. No

The bioavailability of starch is at present an issue of much nutritional concern. Different starchy food items differ considerably in the rate and extent of starch uptake in the human small intestine (Jenkins et al 1981, 1987a). A reduced rate of starch uptake is particularly beneficial to diabetics, because a lowered postprandial glucose response lowers the insulin demand (Jenkins et al 1983). A somewhat incomplete total digestibility may also be nutritionally advantageous; malabsorbed starch reaching the colon could exert physiological effects similar to those of dietary fiber (DF) (Jenkins et al 1987b).

Differences in starch bioavailability among products have been attributed to several factors. One mechanism is the chemical composition of the starch, that is, the amylose/amylopectin ratio (Thorne et al 1983). The starch in normal varieties of cereals contains only moderate levels of amylose, about 25%, whereas that in legumes may amount to 75% (starch basis) (Guilbot and Mercier 1985). It has been suggested that the high amylose content in legume starches is responsible for the extremely low postprandial glucose and insulin responses to lentils or beans, for example, compared with responses to most cereal products (Jenkins et al 1983). The hypothesis concerning amylose/amylopectin ratio as an important determinant of starch bioavailability focused interest on certain genotypes of rice and maize where the amylose content may vary over a broad range.

According to Goddard et al (1984), in healthy subjects, the postprandial levels of glucose and insulin following ingestion of different rice varieties increased with decreasing amylose content (0-25% amylose). The beneficial effect of high-amylose varieties was attributed to a reduced rate of enzymic digestion due mainly to formation of complexes between amylose and lipids. Formation of such complexes is known to considerably reduce the enzymic susceptibility of the amylose component (Holm et al 1983). Furthermore, in a recent study by Behall et al (1989), long-term intake of a high-amylose diet improved fasting triglyceride and cholesterol levels in healthy subjects more than a corresponding high-amylopectin diet. The beneficial effect on blood lipids was discussed in terms of a flattened insulin response following ingestion of the high-amylose diet. However, available data on the impact of amylose on nutritional properties of starch are by no means clear cut. Thus, in an investigation on rice, a slightly higher

¹Dept. of Food Chemistry, University of Lund, Chemical Center, Box 124, S-221 00 Lund, Sweden. Address all correspondence to the first author. ²Dept. of Food Technology, University of Lund, Chemical Center. ³Svalöf AB, S-268 00 Svalöv, Sweden. differences in rate of starch hydrolysis were seen between boiled barley flours. In contrast, autoclaving produced a slower course of amylolysis in Glacier high, despite complete gelatinization. This material also contained a somewhat higher level of retrograded enzyme-resistant starch, 3% (straigh basis). The contrast of calculate DE

Cereal Chem. 67(4):327-333

contained a somewhat higher level of retrograded enzyme-resistant starch, 3% (starch basis). The content of soluble DF was lower in Alva and Lina (4.8%) compared with 6.5% in the other genotypes (dwb). The viscosity of suspensions of isolated DF (1.6%, w/v) correlated to the proportion of soluble DF and was in decreasing order: Waxy > Glacier high > Alva. When added to a starch suspension, isolated barley DF preparations were equally effective in reducing the rate of gastric emptying in rats.

amylose content (22 vs. 15%) was accompanied by an increased rate of in vitro α -amylolysis and an increase in postprandial glucose in healthy subjects (Srinivasa Rao 1971).

Reports on the effect of amylose/amylopectin ratio on total starch digestibility are also somewhat contradictory. In a study by Wolf et al (1977), an appreciable amount of starch (11%) was malabsorbed in healthy subjects following ingestion of amylomaize muffins, whereas no starch appeared in the stool when reference muffins were baked from a normal corn meal variety. The malabsorption of the high-amylose starch ($\sim 70\%$ amylose) was explained in terms of incomplete gelatinization during baking of amylomaize muffins. In contrast, although high-amylose varieties of maize were less digestible in the rat than normal maize, no obvious correlation was found with the amylose content in a study on raw flours by Borchers (1962).

It is known that the gelatinization behavior of the starch granule is affected by its amylose content. According to several reports, the gelatinization temperature of maize and pea starches is generally increased at a higher amylose content (Colonna and Mercier 1985, Eliasson et al 1988). Recently, it was demonstrated that a close correlation exists between the degree of starch gelatinization and the rate of enzymic hydrolysis both in vitro and in vivo (Holm et al 1988). Thus, provided a higher amylose content restricts granule swelling at conditions used during food processing, a reduced enzymic availability would be expected. A higher amylose content also increases the probability for complex formation with lipids. In addition, during heat treatment at high moisture levels, starch may retrograde so firmly that it becomes totally resistant to amylases both in vitro and in vivo (Englyst et al 1985, Björck et al 1987, Ring et al 1988). This resistant starch is believed to consist of retrograded amylose, as the amount formed increases with increasing amylose content (Berry 1986). Maldigestion of high-amylose starch in heat-treated food items could thus be related not only to the presence of undigestible raw granules but also to formation of resistant starch.

Barley is a common crop grown in Sweden and can be obtained in varieties that cover a comparatively broad range of amylose content. Despite a high DF content, in particular a high proportion of soluble viscous DF components, its use for human consumption is limited. The purpose of the present investigation was to evaluate some nutritional properties of starch and DF in different genotypes of barley. Special emphasis was put on starch bioavailability and in particular, the impact of the amylose/amylopectin ratio. The content of starch and DF was determined and compared with that of normal barley varieties. The rate of α -amylolysis of starch in raw and heat-treated samples was evaluated as was

^{© 1990} American Association of Cereal Chemists, Inc.

the gelatinization behavior at different moisture levels. The formation of resistant starch during heat treatment was determined. Furthermore, the viscosity of suspensions of DF isolated from three different samples was recorded. The effect of these fiber preparations on the rate of gastric emptying was also evaluated by using a rat experimental model.

MATERIALS AND METHODS

Materials

Five barley genotypes harvested in 1986 were obtained from Svalöv AB, Svalöv, Sweden. The following varieties were studied: Waxy Campana (~8% amylose); Lina, Alva, and Glacier normal (normal varieties, 25–27% amylose); and Glacier high (~35% amylose). The intrinsic amylase activity, measured as described by Olered and Jönsson (1968) was low in Alva, Lina, Glacier normal, and Glacier high (K α 0.6–1.7) and somewhat higher (K α 12) in Waxy Campana. The grains were milled to pass a 0.5mm screen.

Chemical Analysis

Starch content was analyzed as glucose released following incubation with a thermostable α -amylase (Termamyl 120L, Novo A/S, Copenhagen, Denmark) and amyloglucosidase (Aspergillus niger, suspension 10 mg/ml, 14 units (U)/mg, Boehringer Mannheim, W. Germany). Liberated glucose was quantified with glucose-oxidase-peroxidase reagent, and starch content was expressed on a polysaccharide basis. The procedure has been described in full previously (Holm et al 1986). For comparison, starch was also analyzed following an initial solubilization of the raw granules in NaOH according to Östergård et al (1988). The β -glucanase activity in the amyloglucosidase preparation was evaluated by analyzing "starch content" in a pure β -glucan fraction isolated from barley (Grindstedt A/S, Brabrand, Denmark). Only 1.4% of the β -glucan was recovered as starch. The contribution of β -glucans during analysis of starch in barley flour must therefore be considered negligible.

Quantification of amylose was done as described by BeMiller (1964).

The contents of total, soluble, and insoluble DF were determined according to the enzymic gravimetric method developed by Asp and co-workers (Asp et al 1983).

Resistant starch content (RS), that is starch resistant to amylases in vitro unless solubilized in alkali, was analyzed as previously reported (Björck et al 1986). The total amount of starch remaining in the DF residue obtained with the enzymic gravimetric method was determined by dissolving the residue in 2*M* KOH followed by neutralization and incubation with amyloglucosidase as above. Residual starch was determined by omitting the KOH step. RS was calculated as the difference between total and residual starch.

The lipid content was analyzed gravimetrically following hydrolysis in 7.7N HCl and extraction in di-ethyl ether and petroleum ether according to a recommended procedure by Nordisk Metodikkommité (1974).

In Vitro Starch Hydrolysis with Pancreatic α -Amylase

The susceptibility of starch to α -amylolysis was evaluated as described by Holm et al (1985). An equivalent amount of sample (starch basis) was incubated with pancreatic α -amylase at 37°C.

TABLE I				
Gross Nutrient Composition in Barley Genotypes (%, dwb)				
Crude	Amylose	Dietary		

Barley	Protein [*]	Starch ^b	(% of starch)	Fiber	Ash	Fat
Waxy Campana	14.5	53.9 ± 0.2	7.9	21.0	2.3	4.4
Alva	12.2	59.3 ± 0.5	25.2	20.1	2.4	4.4
Glacier normal	13.8	57.9 ± 0.3	27.1	20.4	2.1	4.6
Lina	10.4	59.2 ± 0.3	27.7	20.3	2.3	4.4
Glacier high	13.6	52.5 ± 0.2	34.9	23.3	2.2	5.6

^aCalculated as $6.25 \times N$.

^bEnzymic method according to Holm et al (1986).

^c Amylose content determined as described by BeMiller (1964).

Samples were withdrawn at time intervals for determination of reducing sugars with a dinitrosalisylic acid reagent. Maltose was used as standard, and the extent of hydrolysis was expressed in maltose equivalents and calculated on the basis of starch content (100 × maltose equivalents [mg] × 0.95/mg of starch). In some experimental series, the samples were preincubated with pepsin prior to incubation with α -amylase (Holm et al 1985). In addition, in the case of raw materials the α -amylase level was increased 5- or 10-fold over that normally used. Barley samples were tested raw, after boiling in water (4% w/v), or after autoclaving at an added pressure of 1.45 bar (~127°C) for 60 min (30% starch basis, w/v). For studying pure barley starch, the starch was isolated as described by Karlsson et al (1983). Whole meal wheat flour or isolated wheat starch were included in some experiments.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) thermograms of raw barley flour (90 or 50% H₂O, w/w), autoclaved and freeze-dried flour (90% H₂O w/w), or boiled flour suspensions (4% w/v, starch basis) were recorded with a Perkin-Elmer DSC-2 instrument. The samples were heated from 21 to 137°C at a scanning rate of 10°C/min. The onset of gelatinization (T_{O}), the temperature at peak maximum (T_{G}) and the conclusion of gelatinization (T_{C}) were determined for the gelatinization endotherm. In the transition due to the amylose-lipid complex, the temperature at peak maximum (T_{Cx}) was recorded. The transition enthalphy was calculated from the peak area and denoted as ΔH_{G} for the gelatinization endotherm and ΔH_{CX} for the complex endotherms. The values given are the means of three to four independent measurements. All ΔH values are expressed as joules per gram of dry matter.

Isolation of DF

DF in barley was isolated for viscosity measurements and animal experiments using the enzymic gravimetric method essentially as described above for determination of total fiber. However, the incubation with the thermostable α -amylase Termamyl was omitted. Total DF was obtained after ethanol precipitation and centrifugation. Furthermore, in order to improve rehydration properties, the DF residue was not washed with acetone.

Viscosity Measurements

The viscosity of suspensions prepared from isolated DF (1.6% DF basis, w/v) was recorded on a rotary viscometer (Bohlin Rheometer System, Lund, Sweden) at 37°C. After 30 min of gentle agitation at 37°C, the samples were transferred to the cup of the rotary viscometer, and measurements were taken at a variable shear rate ranging from 1.5 to 146.5/sec.

Rate of Gastric Emptying of Starch

After an overnight fast, male Sprague Dawley rats (140 g) were given suspensions (2.5 ml) by orogastric intubation under light anesthesia. The reference suspension contained 100 mg of starch only (soluble starch "nach Zulkowsky," Merck, Darmstadt, W. Germany), whereas isolated barley DF was added to the test suspensions (3% DF basis, w/v). NaCl was added to a final concentration of 0.9%, w/v. The animals were killed with CO₂ after 15 min. Their abdomens were cut open and clamps were placed at the cardia and pylorus. The stomachs were removed and immediately frozen on solid CO₂ and stored frozen until analyzed (Tovar et al 1989). All the tissue was homogenized, diluted, and analyzed for remaining starch content as described above. DF preparations from Waxy Campana, Glacier high, and Alva were studied. Guar gum (0.8%, w/v) was used as a reference substance.

RESULTS AND DISCUSSION

Content and Composition of DF and Starch

The gross composition of nutrients in five barley varieties is shown in Table I. Protein content ranged from 10 to 14%, starch content from 53 to 59%, and DF from 20 to 23% (dwb). The amylose content varied from 7.9% in the waxy barley to 34.9%

in the high-amylose variety. Thus, the amylose content covered the range in most ordinary starchy foods, the highest level being similar to that reported in normal varieties of legumes or highamylose varieties of rice (Goddard et al 1984, Guilbot and Mercier 1985, Hoover and Sosulski 1985, Eliasson 1988). However, the amylose/amylopectin ratio was considerably lower in the barley genotypes than in, for instance, high-amylose maize or wrinkled pea starch. Both methods for starch analysis produced similar results (data not shown). That is, pretreatment with alkali prior to amylolytic digestion (Östergard et al 1988) did not improve the analytical yield compared with the method employing solubilization with Termamyl (Holm et al 1986). Consequently, pretreatment with alkali is not a prerequisite despite a comparatively high amylose content in Glacier high.

The total DF content was similar in the normal varieties (Lina, Alva and Glacier normal), about 20%, and also similar to that reported in a previous study on barley flour (Östergard et al 1989). The highest DF content was seen in Glacier high. This variety also contained a higher lipid content. A concomitant increase in amylose and lipid content is also known from studies of barley starch covering a similar range of amylose content (Morrison et al 1984).

Waxy Campana, Glacier normal, and Glacier high contained a considerably higher level of soluble DF components, 6.5% (dwb) compared with about 4.8% (dwb) in Alva and Lina (Table II). Due to a concomitant increase in insoluble DF, the differences in distribution of soluble to insoluble DF were less pronounced. However, the proportion of soluble DF averaged 24% in Alva and Lina and ranged from 28 to 32% in the other varieties. Obviously, it is possible by plant breeding to affect not only the content of DF and starch but also the chemical composition of these polysaccharides.

Viscosity and Nutritional Properties of Isolated DF Preparations

The viscous properties of suspensions of isolated barley DF are shown in Figure 1. The viscosity at different shear rates was in decreasing order: Waxy Campana > Glacier high > Alva. That is, the DF components in two of the genotypes were more viscous than in a normal barley variety. The proportion of soluble DF was 31, 28, and 23% in Waxy Campana, Glacier high, and Alva, respectively. Hence, there appeared to be a correlation between the viscous properties and the proportion of soluble components.

The effect of adding isolated barley DF on the rate of gastric emptying of starch suspensions in rats is shown in Table III. All DF preparations significantly increased the amount of starch remaining in the stomach 15 min after intubation. Suspensions containing barley DF (3% total and 0.7-0.9% soluble DF) reduced the rate of gastric emptying similar to the reduction produced by guar gum (0.8% DF). No significant difference was obtained between the different DF preparations or between barley DF and guar gum. Hence, the physiological properties of DF were similar within the narrow range of soluble DF studied.

Availability of Starch for Enzymic Digestion

Enzyme susceptibility of raw flours and isolated starches following 60 min of incubation with α -amylase only or in combination with a pepsin pretreatment is shown in Table IV. The degree of hydrolysis in wheat was used as reference. Incubations of flours with α -amylase only indicated higher availability of starch in barley than in wheat. Starch in waxy barley was most susceptible

TABLE II	
Dietary Fiber Content ^a (%, dwl)

Barley	Insoluble	Soluble	Total	
Waxy Campana	$14.5 \pm 0.3 \text{ b}$	$6.5 \pm 0.1 \text{ b}$	$21.0\pm0.4~\mathrm{c}$	
Alva	15.5 ± 0.2 a	$4.7\pm0.4~\mathrm{a}$	$20.1 \pm 0.3 a$	
Glacier normal	13.9 ± 0.2 b	6.5 ± 0.6 b	$20.4\pm0.5~\mathrm{ac}$	
Lina	15.5 ± 0.4 a	$4.8 \pm 0.7 \; a$	$20.3 \pm 0.4 \text{ ab}$	
Glacier high	16.7 ± 0.5 b	$6.5\pm0.7~\mathrm{b}$	$23.3\pm0.9~\mathrm{d}$	

^aFigures followed by different letters are significantly different at P < 0.05 (Student's *t* test).

to hydrolysis. Experiments with isolated starches revealed a similar pattern. The waxy barley starch still displayed the highest enzyme susceptibility, and all barley samples were hydrolyzed somewhat more rapidly than wheat. However, the differences between barley and wheat were much less attenuated in isolated starches. The higher availability of starch in the waxy flour persisted even when it was pretreated with pepsin before incubation with an excess of α -amylase (Table IV). Waxy barley might thus be advantageous in feed for animals where a high energy utilization and feed conversion ratio usually is requested.

The gelatinization temperature of starch in the different barley varieties was evaluated by DSC measurements of raw flours (90% H_2O , w/w) (Fig. 2 and Table V). Despite the differences in amylose content, T_G varied within a comparatively narrow range 62–69°C. Although the broadest gelatinization interval was obtained with Glacier high, no obvious correlation was seen with amylose content. The endothermic transitions corresponding to the amylose-lipid complex were most prominent in Glacier high, whereas no transition could be detected in the waxy variety. DSC scans were also recorded at a higher dry matter content (50% H_2O , w/w) in order to simulate conditions during low moist-heat treatment of cereal products (Fig. 2 and Table V). The gelatinization endotherm was considerably broadened, particularly in the case of Glacier high. However, all barley flours were completely gelatinized at about 95°C.

 TABLE III

 Starch Remaining in the Rat Stomach 15 min After Intubation^a

% of Intubated Amount				
$30.8 \pm 10.8 a$				
59.1 ± 7.9 b				
$50.8\pm13.2~\mathrm{b}$				
55.6 ± 10.3 b				
51.1 ± 11.7 b				

^aFigures followed by different letters are significantly different at P < 0.05 (Student's *t* test).



Fig. 1. Viscous properties (viscosity versus shear rate) of suspensions of isolated dietary fiber components (1.6%, w/v) from three barley varieties: Waxy Campana (•), Alva (\blacktriangle), and Glacier high (\bigcirc).

TABLE IV Starch Hydrolysis (%) in Raw Flour or Starch Isolated from Barley After 60 min of Incubation with α-Amylase Only or in Combination with Pepsin^a

Source	Raw Flour	Raw Starch	Raw Flours Pretreated with Pepsin		
	α-Amylase (100 U)	α-Amylase (100 U)	α-Amylase (500 U)	α-Amylase (1,000 U)	
Wheat reference	6.2	18.1	42.7	51.1	
Glacier high	22.9	23.5	47.0	56.2	
Glacier normal	24.8	23.5	47.0	56.2	
Lina	25.4	21.7	47.0	51.1	
Alva	28.5	23.5	51.2	61.3	
Waxy Campana	37.2	36.2	68.3	76.7	

^aAll α -amylase concentrations expressed as units (U) per 500 mg of starch.

The shift towards gelatinization temperatures exceeding 100° C, seen for instance in high-amylose genotypes of maize and pea starch (Colonna and Mercier 1985), was not present in the amylovariety of barley containing approximately 35% amylose (Table V). Thus, inclusion of Glacier high in food items such as bread will probably not affect the degree of gelatinization to any appreciable extent. In contrast, in a study of maize products, baking and even boiling of flours was not sufficient for complete gelatinization of the high-amylose genotype containing about 70% amylose (Wolf et al 1977). It is possible, however, that swollen granules with a considerable amount of RS may show birefringence, thus leading to false conclusions regarding the degree of gelatinization.

Gelatinization by boiling in water (4%, w/v, starch basis) rendered the starch in all barley flours equally available to α amylolysis (Fig. 3). Pretreatment with pepsin slightly increased



Temperature (C°)

Fig. 2. Differential scanning calorimetry of three barley varieties containing different amylose levels at 90 and 50% H₂O.

	TABLE V		
Differential Scanning	Calorimetry of Raw	Barley	Flours

		Gelatinization Transition ^a				Amylose-Lipid Complex Transition ^b	
Barley	Т ₀ (°С)	Т _G (°С)	Т _с (°С)	ΔH_{G} (J/g dry matter)	$T_{\rm CX}$	ΔH_{CX}	
90% (w/v) water			· · · · · · · · · · · · · · · · · · ·		()	(o/g di y matter)	
Waxy Campana ^c Alva Glacier normal Lina Glacier high 50% (w/v) water	48 50 50 48 48	$\begin{array}{c} 64.9 \pm 0.2 \\ 63.2 \pm 0.4 \\ 62.4 \pm 0.8 \\ 63.3 \pm 0.4 \\ 69.4 \pm 0.4 \end{array}$	77 76 78 76 83	$5.5 \pm 0.2 \\ 6.6 \pm 0.7 \\ 5.6 \pm 0.4 \\ 6.2 \pm 0.3 \\ 3.8 \pm 0.2$	$\begin{array}{c}\\ 94.3 \pm 0.5\\ 94.4 \pm 0.5\\ & \text{not de}\\ 93.7 \pm 1.0 \end{array}$	 1.36 ± 0.03 1.05 ± 0.1 termined 2.22 ± 0.46	
Waxy Campana ^c Lina Glacier high	43 46 44	$\begin{array}{c} 67.8 \pm 0.6 \\ 65.1 \pm 0.4 \\ 69.3 \pm 0.1 \end{array}$	93 89 93	$\begin{array}{c} 6.8 \pm 0.4 \\ 7.5 \pm 1.0 \\ 4.0 \pm 0.1 \end{array}$	 105.5 ± 0.5 105.5 ± 0.3	 1.1 ± 0.3 1.4 ± 0.3	

^a Endothermic transition corresponding to gelatinization transition temperature (T_0 at onset; T_G at peak maximum; T_C at conclusion) and transition enthalphy (ΔH_G).

^bEndothermic transition corresponding to transformation of the amylose-lipid complex transition temperature (T_{CX} at peak maximum) and transition enthalphy (ΔH_{CX}).

[°]No endothermic transition was detected in Waxy Campana.

the course of amylolysis but no differences between the barley varieties could be detected (data not shown). Thus, the amylose content had no impact on the rate of enzyme digestion in boiled flours within the interval tested. The absence of differences in enzyme susceptibility is in accordance with a complete gelatinization of boiled barley flour suspensions (4%, w/v) irrespective of amylose content. Hence, in DSC measurements, no endothermic transition corresponding to the melting of raw starch could be detected in any of these samples. In contrast, the availability to α -amylase of boiled maize starches has been reported to be affected by amylose content (Azemi and Wotton 1984). The rate of hydrolysis decreased in the following order: waxy maize > normal maize > high-amylose maize. In studies by Fuwa et al (1977), it was demonstrated that differences in digestibility of maize starches containing different levels of amylose disappeared following alkali treatment. It is known that complete solubilization of starch can be obtained at alkaline conditions suggesting that the barrier towards enzyme digestion is not related to the chemical structure of the starch molecules as such, but rather to the degree of crystallinity.

It should be noted that although a higher amylose content has been associated with a higher gelatinization temperature, the temperature interval for gelatinization of amylomaize starch, for example, varies considerably in different studies employing DSC. According to Colonna and Mercier (1985) the intervals range from about 58 to 125°C (>60% amylose), whereas in other reports gelatinization appears to be completed below 100°C (~70%) amylose) (Russel 1987, Eliasson et al 1988). This might result from real differences in granular structure not related to the amylose content as such. However, it has been pointed out that the gelatinization range as measured with DSC may be overestimated in certain high-amylose varieties due to overlapping with the endothermic transition for the amylose-lipid complexes (Russel 1987). In the present work no such overlapping existed, and the comparatively low gelatinization temperatures obtained for all barley samples (70°C) are in accordance with the high enzyme susceptibility observed following boiling.

The RS yield during autoclaving of barley suspensions (30%, w/w, starch basis) was strongly related to the amylose content (Fig. 4). No RS was formed in waxy barley, which is in agreement with studies on waxy maize starch by Berry (1986). With increasing amylose content there was an increase in RS formation. Approximately 3% of the total starch in Glacier high was rendered resistant due to autoclaving. This RS fraction can be expected to withstand enzymic digestion even in vivo (Björck et al 1987). The lack of RS formation during autoclaving of waxy barley strongly suggested that RS consists of firmly retrograded amylose. The RS yield with Glacier high was, however, considerably lower than that obtained in a previous work with pure wheat starch (6% dwb) autoclaved at equivalent conditions, suggesting that amylose retrogradation is facilitated in a pure system (Bjorck et al 1987).



Fig. 3. Rate of α -amylolysis of starch in boiled barley flour suspensions: Waxy Campana (•), Lina (\blacktriangle), Alva (\bigstar), Glacier normal (\bigcirc), and Glacier high (\triangle).

In a study by Fleming and Vose (1979) using rats, autoclaving of cereal, tuber, and legume starches resulted in an apparent digestibility close to 100%. However, the digestibility of wrinkled field pea starch was significantly lower, 97%. Consequently, an incomplete digestibility of starch in autoclaved high-amylose varieties has been observed also in vivo.

The rate of α -amylolysis of starch in autoclaved barley flours is shown in Figure 5. Similar results were obtained following a pretreatment with pepsin (data not shown). The course of amylolysis was most rapid in the case of Waxy Campana. As judged from the high initial level of hydrolysis, this was probably due to its high level of intrinsic amylases capable of hydrolyzing starch before reaching elevated temperatures in the autoclave. Starch



Fig. 4. Formation of resistant starch (RS) as a function of amylose content in autoclaved suspensions of barley flours.



Fig. 5. Rate of α -amylolysis of starch in autoclaved barley flour suspensions: Waxy Campana (Δ), Lina (\bullet), Alva (\star), Glacier normal (\bigcirc), and Glacier high (\blacktriangle). An autoclaved suspension of whole grain wheat flour was used as a reference (\diamondsuit).

in autoclaved flours from wheat, Alva, Lina, and Glacier normal were hydrolyzed at a similar rate. In contrast, the degree of hydrolysis with Glacier high was significantly lower at all time intervals. DSC measurements of autoclaved and freeze-dried materials indicated complete gelatinization. The somewhat lower susceptibility might be related to a more prominent retrogradation reducing the rate of hydrolysis of the amylose component despite the fact that only a minor fraction was rendered resistant. Thus, in a previous work on autoclaved suspensions of wheat starch $(\sim 25\%$ amylose), formation of RS was accompanied by a decrease in the over-all rate of α -amylolysis compared with a boiled wheat starch reference containing no RS. Another plausible explanation is the formation of amylose-lipid complexes (Holm et al 1983). Whether this phenomenon occurring in autoclaved samples is similar to that described by Goddard et al (1984) following boiling of intact rice kernels remains to be elucidated. However, in that study, postprandial levels of glucose and insulin were affected within a similar range of amylose content as that used in the present work with barley.

It is concluded that the amylose/amylopectin ratio in different barley genotypes had only a marginal influence on gelatinization behavior. Waxy barley showed the highest susceptibility to α amylolysis when tested raw, whereas no differences were seen following boiling. However, with increasing amylose content there was a concomitant decrease in in vitro digestibility of autoclaved flours due to retrogradation. Autoclaving also produced a somewhat slower rate of hydrolysis in Glacier high than in the other varieties. Finally, addition of isolated barley DF to a starch solution significantly delayed the rate of gastric emptying in rats, the effect being similar to that with an equivalent amount of guar gum (soluble DF basis).

LITERATURE CITED

- ASP, N.-G., JOHANSSON, C.-G., HALLMER, H., and SILJESTRÖM, M. 1983. A rapid enzymatic method for assay of insoluble and soluble dietary fiber. J. Agric. Food Chem. 31:476.
- AZEMI, M., and WOTTON, M. 1984. In vitro digestibility of hydroxypropyl maize, waxy maize and high amylose maize starches. Starch/Staerke 36: 273.
- BEHALL, K. M., SCHOLFIELD, D. J., YUHANIAK, I., and CANARY, J. 1989. Diets containing high amylose vs. amylopectin starch: Effects on metabolic variables in human subjects. Am. J. Clin. Nutr. 49:337.
- BEMILLER, J. N. 1964. Iodometric determination of amylose. Page 39 in: Methods in Carbohydrate Chemistry. Vol. 4. Starch. Academic Press: New York.
- BERRY, C. 1986. Resistant starch: Formation and measurement of starch that survives exhaustive digestion with amylolytic enzymes during the determination of dietary fiber. J. Cereal Sci. 4:301.
- BJÖRCK, I., NYMAN, M., PEDERSEN, B., ASP, N-G., and EGGUM, B.-O. 1986. On the digestibility of starch in wheat bread—Studies invitro and in-vivo. J. Cereal Sci. 4:1.
- BJÖRCK, I., NYMAN, M., PEDERSEN, B., ASP, N.-G., and EGGUM, B.-O. 1987. Formation of resistant starch during autoclaving of wheat starch: Studies in-vitro and in-vivo. J. Cereal Sci. 6:159.
- BORCHERS, R. 1962. A note on the digestibility of the starch of highamylose corn by rats. Cereal Chem. 39:145.
- COLONNA, P., and MERCIER, C. 1985. Gelatinization and melting of the maize and pea starches with normal and high-amylose genotypes. Phytochemistry 24:1667.
- ELIASSON, A.-C. 1988. Physical and chemical characteristics of legume starches. Pages 89-94 in: ISI Atlas of Science: Animal and Plant Sciences. 89-94.
- ELIASSON, A.-C., FINSTAD, H., and LJUNGER, G. 1988. A study of starch-lipid interactions for some native and modified maize starches. Starch/Staerke 40:95.
- ENGLYST, H., and CUMMINGS, J. 1985. Digestion of the polysaccharides of some cereal foods in the human small intestine. Am. J. Clin. Nutr. 42:778.
- FLEMING, S.E., and VOSE, J.R. 1979. Digestibility of raw and cooked starches from legume seeds using the laboratory rat. J. Nutr. 109:2067.
- FUWA, H., NAKAJIMA, M., and HAMADA, A. 1977. Comparative susceptibility to amylases of starches from different plant species and several single endosperm mutants and their double-mutant combinations with *opaque-2* in bread 0h43 maize. Cereal Chem. 54:230.

- GODDARD, M., YOUNG, G., and MARCUS, R. 1984. The effect of amylose content on insulin and glucose responses to ingested rice. Am. J. Clin. Nutr. 39:388.
- GUILBOT, A., and MERCIER, C. 1985. Starch. Pages 209-282 in: The Polysaccharides. Vol. 3. Academic Press: Orlando, FL.
- HOLM, J. BJÖRCK, I., OSTROWSKA, S., ELIASSON, A.-C., ASP, N.-G., LARSSON, K., and LUNDQUIST, I. 1983. Digestibility of amylose-lipid complexes in-vitro and in-vivo. Starch/Staerke 35:294.
- HOLM, J. BJÖRCK, I., ASP, N.-G., SJÖBERG, L.-B., and LUNDQUIST, I. 1985. Starch availability in vitro and in vivo after flaking, steam cooking and popping of wheat. J. Cereal Sci. 3:193.
- HOLM, J., BJÖRCK, I., DREWS, A., and ASP, N.-G. 1986. A rapid method for the analysis of starch. Starch/Staerke 38:224.
- HOLM, J., LUNDQUIST, I., BJÖRCK, I., ELIASSON, A.-C., and ASP, N.-G. 1988. Relationship between degree of gelatinization, digestion rate in-vitro and metabolic response in rats. Am. J. Clin. Nutr. 47:1010.
- HOOVER, R., and SOSULSKI, F. 1985. Studies on the functional characteristics and digestibility of starches from *Phaseolus vulgaris* biotypes. Starch/Staerke 6:181.
- JENKINS, D., WOLEVER, T., TAYLOR, R., BARKER, H., FIELDEN, H., BALDWIN, J., BOWLING, A., NEWMAN, H., JENKINS, A., and GOFF, D. 1981. Glycaemic index of foods: A physiological basis for carbohydrate exchange. Am. J. Clin. Nutr. 34:362.
- JENKINS, D., WOLEVER, T., JENKINS, A., THORNE, M., LEE, R., KALMUSKY, J., REICHERT, R., and WONG, G. 1983. The glycaemic index of foods tested in diabetic patients: A new basis for carbohydrate exchange favouring the use of legumes. Diabetologia 24:257.
- JENKINS, D., JENKINS, A., WOLEVER, A., COLLIER, G., VENKET RAO, A., and THOMPSON, L. 1987a. Starchy foods and fiber: Reduced rate of digestion and improved carbohydrate metabolism. Scand. J. Gastroenterol. 22:132.
- JENKINS, D., CUFF, D., WOLEVER, T., KNOWLAND, D., THOMPSON, L., COHEN, Z., and PROKIPCHUK, E. 1987b. Digestibility of carbohydrate foods in an ileostomate: Relationship to dietary fiber, in-vitro digestibility and glycemic response. Am. J. Gastroenterol.

82:709.

- KARLSSON, R., OLERED, R., and ELIASSON, A.-C. 1983. Changes in starch granule size distribution and starch gelatinization properties during development and maturation of wheat, barley and rye. Starch/ Staerke 35:335
- MORRISON, W. R., MILLIGAN, T. P., and AZUDIN, M. N. 1984. Relationship between the amylose and lipid contents of starches from diploid cereals. J. Cereal Sci. 2:257.
- NORDISK METODIKKOMMITÉ FÖR LIVSMEDEL. 1974. Fedt. Bestemmelse i kødvarer efter SBR (Schmid-Bondzynski-Ratzlaff). Nordisk Metodikkommité för Livsmedel. No. 88.
- OLERED, R., and JÖNSSON, G. 1968. Elektrophoretishe Studien von amylase in Weisen. Getreide Mehl 18:95.
- ÖSTÉRGAÅRD, K., BJÖRCK, I., and GUNNARSSON, A. 1988. A study of native and chemically modified potato starch. Part I. Analysis and enzymic availability. Starch/Staerke 40:58.
- ÖSTERGÅRD, K., BJÖRCK, I., and VAINIONPÄÄ, J. 1989. Effects of extrusion-cooking on content of starch and dietary fiber in barley. Food Chem. 34:215.
- RING, S., GEE, J., WHITTAM, M., ORFORD, P., and JOHNSON, J. 1988. Resistant starch: Its chemical form in foodstuffs and effect on digestibility in-vitro. Food Chem. 28:97.
- RUSSEL, P. 1987. Gelatinization of starches of different amylose/amylopectin content. A study by differential scanning calorimetry. J. Cereal Sci. 6:133.
- SRINIVASA RAO, P. 1971. Studies on the nature of carbohydrate moiety in high yielding varieties of rice. J. Nutr. 101:879.
- THORNE, M., THOMPSON, L., and JENKINS, D. 1983. Factors affecting starch digestibility and the glycemic response with special reference to legumes. Am. J. Clin. Nutr. 38:481.
- TOVAR, J., BJÖRCK, I., and ASP, N.-G. 1989. On the nutritional properties of starch and dietary fiber in cassava bread. Nutr. Rep. Int. 39:1237.
- WOLF, M. J., KHOO, U., and INGLETT, G. E. 1977. Partial digestibility of cooked amylomaize starch in humans and mice. Starch/Staerke 29:401.

[Received July 10, 1989. Revision received December 26, 1989. Accepted December 28, 1989.]