

DISTRIBUTION OF SOLUBLE CARBOHYDRATES IN BARLEY GRAIN AT LATE STAGE OF MATURITY AND RELATION TO VISCOSITY

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ABSTRACT

Cereal Chem. 55(3): 341-347

Layers of barley grain harvested at late maturity (19% moisture) were successively removed by abrasive milling. The fractions removed were extracted with 80% ethanol followed by extraction with phosphate-citrate buffer at pH 7.0. The distributions of crude protein, crude fat, and ash were determined in each fraction. The distributions of these proximate principles were essentially the same as in barley harvested early. The ethanol extracts contained mainly sucrose, together with stachyose, raffinose, glucose, fructose,

glucitol, and myoinositol. The distribution of the ethanol-soluble carbohydrates within the barley kernel showed great similarity to those of barley harvested early. Acid hydrolysates of the buffer extracts contained mainly glucose, together with galactose, mannose, rhamnose, arabinose, and xylose. The decrease of viscosity of buffer extracts between early and late stages of maturity formed peaks at 45 and 75% abrasion. This coincided with maximal decrease of glucose in hydrolysates of buffer extracts.

Barley harvested at early maturity exhibits high viscosity when ground and suspended in water or buffer. After reaching maximum viscosity at yellow ripeness, the viscosity decreases as the barley matures (1). The distribution of the viscous factor or factors in the barley kernel harvested at early and at late stages of maturity was investigated in a previous report (2). Since plant hydrocolloids are generally composed of sugar units, the distribution of carbohydrates in barley harvested early was also determined. In the present work, we have investigated the distribution of low molecular weight (ethanol-extractable) and viscous-yielding (buffer-extractable) carbohydrates of barley kernels harvested at late maturity. The change in distribution in the barley kernel of buffer-extractable carbohydrates between the two stages of harvest has been related to the change in distribution of the decrease in viscosity.

MATERIALS AND METHODS

Material

As in an earlier report (2), the barley used was of the cultivar Ingrid, but was harvested somewhat later in the year at combine-ripe harvest maturity (19% moisture). After harvest, the barley was immediately dried.

Methods

The barley grain was abraded in a Scott-Strong Seedburo mill in the same way as used for barley harvested early (2). The percentage of each fraction is given in Table I. Crude protein, crude fat, and ash were determined according to methods of the Association of Official Analytical Chemists (3). The defatted fractions were carefully extracted with boiling 80% ethanol as described earlier (2). The residues after ethanol extraction were then further extracted with 0.1M phosphate-citrate buffer, pH 7.0 (2). The low molecular weight carbohydrates

were transformed to trimethylsilyl derivatives according to Sweeley *et al.* (4) and analyzed by gas-liquid chromatography (glc) (2,5). The dried buffer extracts, 100 mg, were hydrolyzed in 15 ml of 0.5*N* H₂SO₄; the monosaccharides formed were reduced to their corresponding alditols, acetylated, and analyzed by glc (2,6).

The decrease in viscosity between the two stages of maturity was calculated from measurements of viscosity of buffer extracts of the abraded barley fractions. The viscosity of each extract was measured in a Contraves Rheomat 15, using system "0". The finely ground sample, 1.2 g, was extracted for 5 min with 8 ml of 0.1*M* phosphate-citrate buffer, pH 4.0, and thereafter centrifuged for 5 min. The clear supernatant, 4 ml, was then poured into the measuring beaker and the viscosity measured at 30°C.

RESULTS AND DISCUSSION

The content of crude protein (Table I) was low in the hull, while the layer between 15 and 45% abrasion contained about 20% crude protein on a dry matter basis. Crude fat reached its maximum concentration of about 7% when 15% of the kernel had been abraded. The concentration of crude fat in the center of the kernel was low—less than 1%. The concentration of ash decreased from a maximum of between 7 and 8% in the hull to about 0.5% in the center of the kernel. Compared with barley harvested early, distribution of crude protein, crude fat, or ash within the kernel is no different. As was expected and as has been shown (7), the proximate constituents of the barley kernel are essentially constant after about 40% moisture content of the barley grain had been reached. The same applies to amylose and amylopectin, which is the reason why starch was not determined in the present experiment.

TABLE I
Chemical Composition of Barley Fractions^a

Kernel Abraded (%)	Crude Protein ^b (%)	Crude Fat (%)	Ash (%)	Ethanol-Extractable Carbohydrates ^c (%)	Buffer-Extractable Carbohydrates (%)
0— 7.8	12.7	4.6	7.3	3.1	0.5
7.9— 10.5	17.6	6.3	7.0	3.2	0.7
10.6— 16.3	19.7	7.2	6.8	3.2	0.9
16.4— 21.1	19.7	7.1	4.9	3.3	1.0
21.2— 26.7	19.4	5.5	4.4	3.7	0.9
26.8— 31.9	20.7	5.1	4.0	3.2	0.8
32.0— 36.8	20.8	3.8	3.1	2.6	0.8
36.9— 41.3	21.8	3.1	2.4	1.9	1.1
41.4— 50.1	19.3	2.0	1.5	1.7	1.1
50.2— 57.7	17.3	1.5	1.0	1.3	0.9
57.8— 64.7	15.3	1.2	0.8	1.5	0.9
64.8— 69.8	14.0	0.9	0.7	1.6	0.7
69.9— 74.1	13.3	0.8	0.7	1.3	0.6
74.2—100.0	10.0	0.6	0.5	2.0	0.2

^aAll figures are given on dry matter basis.

^bN × 6.25.

^c80% ethanol:20% water, v/v.

The total amount of ethanol-extractable carbohydrates increased from 1.93% at early maturity (2) to 2.27% at late maturity (Table I). The concentration of ethanol-extractable carbohydrates was more than 3% in the outer 30% of the

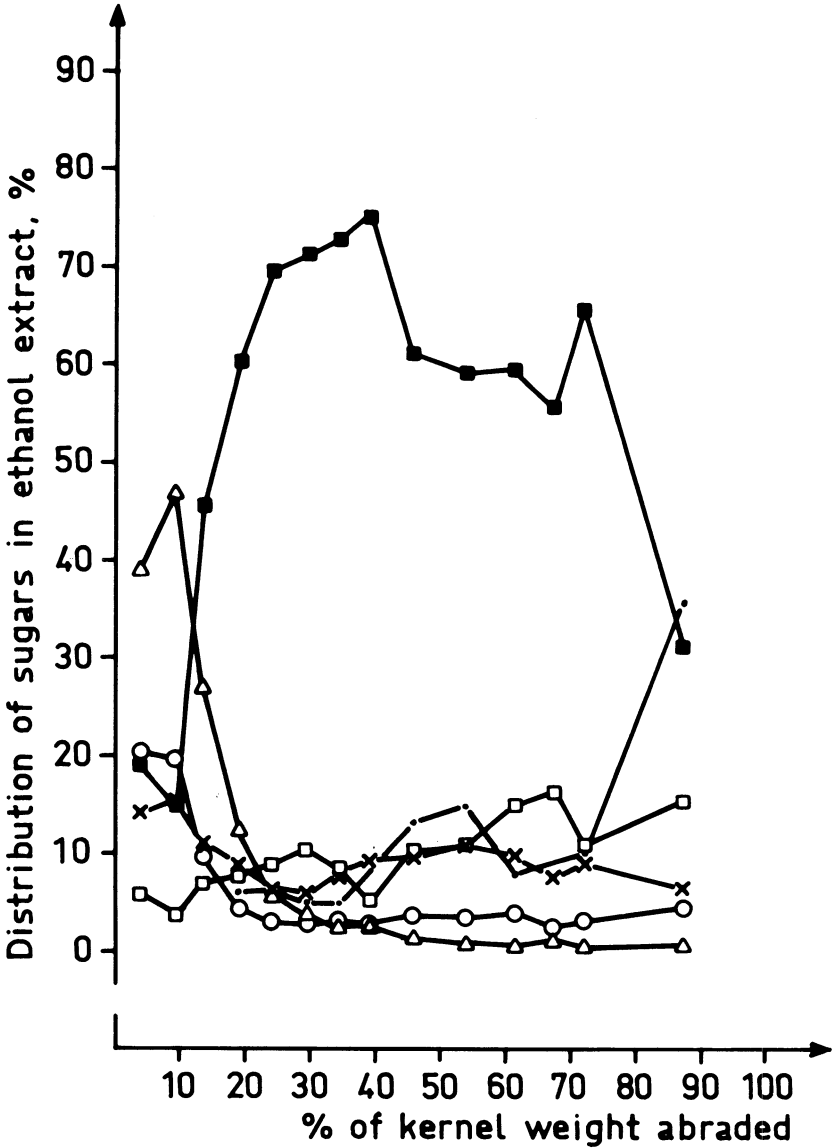


Fig. 1. Distribution of sugars as percentages of ethanol-extractable carbohydrates in fractions abraded from barley grain harvested late. x—x, Glucose; ■—■, sucrose; ●—●, stachyose; □—□, raffinose; △—△, glucitol; o—o, fructose.

kernel and between 1 and 2% in the remaining part of the kernel. The relative distribution of carbohydrates of the ethanol extracts is given in Fig. 1. In addition, traces of myoinositol could be detected in all fractions. The only differences of importance compared with barley harvested early relate to

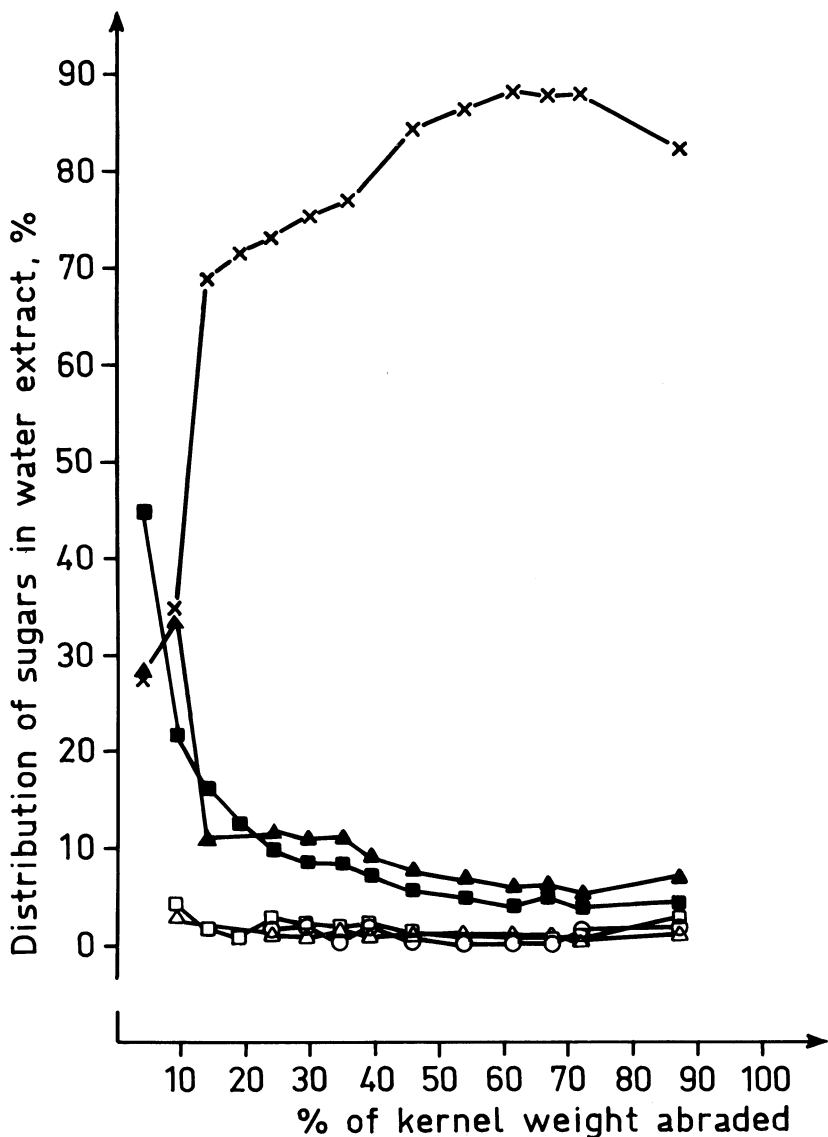


Fig. 2. Distribution of sugars after strong hydrolysis as percentages of buffer-extractable carbohydrates in fractions abraded from barley grain harvested late. x—x, Glucose; ■—■, arabinose; ▲—▲, xylose; □—□, galactose; △—△, mannose; o—o, rhamnose.

raffinose and stachyose. The concentration of stachyose has increased considerably, especially in the center of the kernel. This increase is partly at the expense of raffinose.

The buffer extracts were analyzed by gas chromatography in the same way as the ethanol extracts to confirm that they did not contain low molecular weight carbohydrates. As can be seen in Fig. 2, glucose dominates in hydrolysates (in 0.5*N* H₂SO₄) of all fractions after 10% abrasion. Arabinose, xylose, and smaller amounts of mannose, rhamnose, and galactose were also found in all fractions. The total amount of buffer-extractable carbohydrates had decreased between the two stages of ripeness by 0.79 percentage units to 0.68% by weight of the dry, mature barley kernel. Most of this difference was due to a lower content of carbohydrates yielding glucose after hydrolysis. The ratio between xylose and

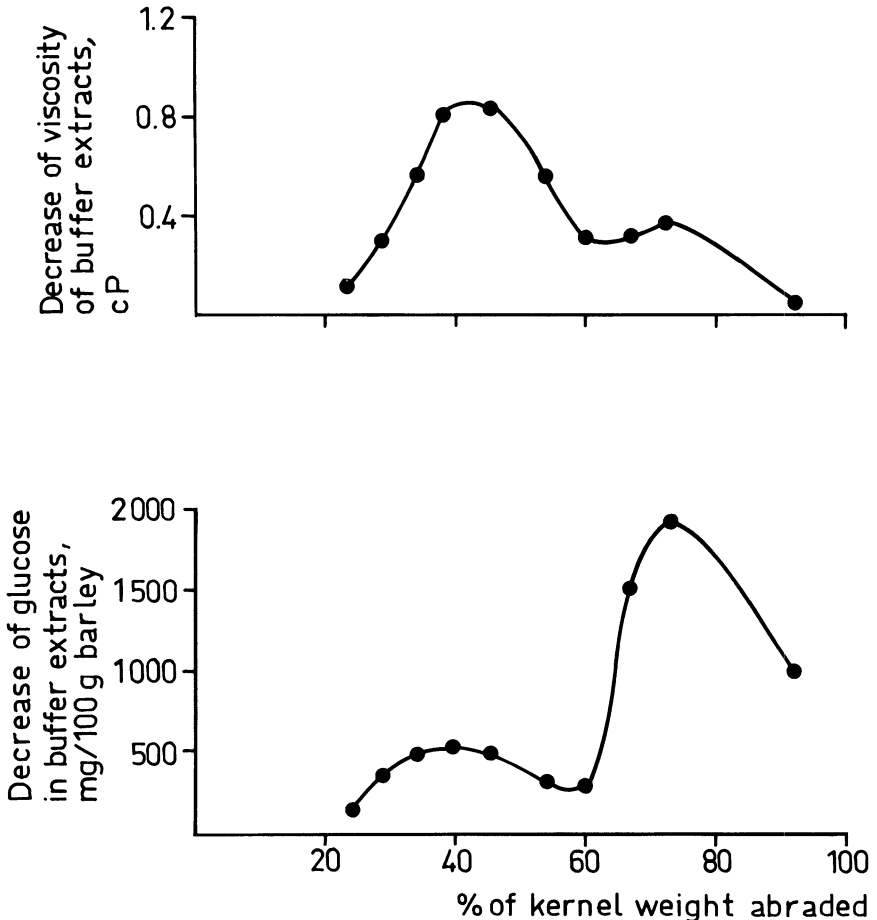


Fig. 3. Decrease of viscosity and glucose in buffer extracts of fractions of abraded barley between two stages of ripeness (yellow ripeness and combine-harvest ripeness).

arabinose in the hydrolysates was still the same when barley had reached late maturity. Only at one point—35% abrasion—did arabinose decrease more than xylose.

The differences of glucose contents in buffer extracts of barley between early (2) and late stages of maturity have been calculated for the different fractions of barley (Fig. 3) and compared with the reduction of viscosity for the same fractions. As the fractions from the abrasions of barley harvested early and late do not correspond, the values of barley harvested late were subtracted from smoothed curves of values of barley harvested early. The decrease of viscosity forms peaks at 45 and 75% abrasion. This coincides with peaks in the decrease of glucose liberated after strong hydrolysis of buffer extracts. The viscosity of barley is generally attributed to a β -glucan (8,9), and the decrease in glucose is therefore expected to follow the decrease in viscosity, as found here.

Other experiments (1) indicate that an arabinoxylan may be responsible for part of the viscosity of barley. Viscosity of barley can be reduced through the action of endogenous enzymes if the barley is ground and mixed with water for a few hours (1). Treating barley harvested early with water not only increased the amount of free glucose but also liberated xylose and arabinose (1). According to Neukom and Markwalder (10), a soluble arabinoxylan is responsible for the high viscosity of aqueous wheat-flour extracts. In the present experiment, xylose and arabinose liberated after hydrolysis of buffer extracts also decreased between the two stages of ripeness. The differences were much smaller than for glucose and formed maximally between 35 and 50% abrasion.

The results obtained in the present investigation seem to support the view that viscosity of barley is mainly caused by a water-soluble glucan, but that a water-soluble arabinoxylan may also be involved.

Acknowledgments

We are indebted to Professor O. Theander and Fil.kand. K. Larsson for valuable discussions and criticism of the manuscript. The financial support of the Swedish National Board of Agriculture is gratefully acknowledged.

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[Received April 11, 1977. Accepted November 4, 1977]