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Composition and Utilization of Milled Barley Products. IV. Mineral Components[1]

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ABSTRACT

Eleven elements (P, K, Mg, Ca, Na, Fe, Zn, Mn, Cu, Al, and Mo, in decreasing concentrations) were determined in whole barley, in caryopsis components separated by hand, in products of tangential abrasion of barley, in roller-milled flours, in air-classified flours, and in starch. Germ contained the highest, and central endosperm the lowest, concentrations of mineral components. The amounts and patterns of distribution of elements in various barley tissues resembled those in wheat. Individual elements showed varying gradients of decrease in concentration from the germ or pericarp to the central endosperm, i.e., some elements were more uniformly distributed throughout the kernel than others. Tailings and shorts of roller-milled barley, which were rich in germ and aleurone particles, contained higher concentrations of mineral elements than did the flour. Concentration of mineral components in the flour was up to 500 times higher than in the starch. During air classification, shifts in protein concentration were accompanied by shifts in concentration of mineral components.

Small concentrations of certain elements are essential to the health and growth of plants. It has been shown that there are large qualitative and quantitative differences in mineral requirements of organisms throughout the plant kingdom (1). Those differences might be important, especially with regard to the synthesis and action of various enzymes for which metals are activators or constituents.

A number of claims that mixtures of trace elements increase the overall yield of various crops are of obvious interest to crop physiologists and farmers. However, of more direct importance to processors of barley is the manner in which small amounts of mineral elements added to the soil can influence the composition of the seed. For instance, nitrate reductase, which contains molybdenum in its structure, is involved in the process of converting nitrate-N into amino acid and protein-N. In addition, molybdenum is involved in later stages of protein synthesis and may be related to the types of proteins that are synthesized in the barley. Consequently, it may affect protein stability of beer (2).

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Little information has been published concerning the amounts of metals in barleys and malts. Several such surveys were conducted in recent years for wheat and corn products (3-6). Also, little is known about the amounts of trace elements extracted from the malt into beer, and the distribution of trace elements in the wort, spent grains, brewer's yeast, and rootlets (malt sprouts). Both positive and negative effects of trace elements on beer quality have been reported (7).

The objective of the study reported here was to determine the distribution of mineral elements in barleys, barley tissues, and milled barley fractions, and the relation of that distribution to functional properties of processed barley products. A report on that relationship will be published elsewhere.

MATERIALS AND METHODS

Barley and Barley Fractions

A sample of naked (hull-less) Himalaya barley from the 1963 crop grown at Aberdeen, Ida., was hand-dissected into four parts: germ, part next to the germ, central section, and distal end. The fractions comprised (average of six dissections) 4.3, 20.9, 49.5, and 25.3% of the whole grain, respectively. Starchy endosperm was prepared by hand-dissection from the central endosperm. Removal of outer layers of the barley kernel was done by abrading the Himalaya barley for 30, 90, and 270 sec. on a Strong-Scott barley pearler. The fractions have been described elsewhere (8).The whole grain and the fractions were ground before analysis on a micro-Wiley mill to pass a 20-mesh sieve; the hand-dissected germ was ground in a mortar. Roller-milled and air-separated fractions from Atlas barley (a six-rowed coast-type hulled barley, grown in 1965 in the Sacramento Valley, Calif.) have been described in detail previously (9). Starch was obtained by the procedure given by Hoseney et al. (10).

Analytical Methods

Moisture, ash, and protein were determined as described in the AACC Approved Methods (11). Phosphorus was determined by the colorimetric- (Mo) blue method (12). For mineral analyses by atomic absorption spectroscopy, the samples were

TABLE I. DILUTION FACTORS OF SAMPLES AND THE OPERATING PARAMETERS OF THE PERKIN-ELMER MODEL 403 ATOMIC ABSORPTION SPECTROPHOTOMETER

Element	Dilution Factor[a]	Wave-length Å	Slit Setting	Lamp Current ma.	Acetylene-Air Setting	Optimum Conc. Range For Testing γ per ml.
K	200X	7,665	4	12	37 to 65	0.5 to 2.0
Mg	200X	2,852	4	20	37 to 65	0.1 to 1.5
Ca	5X	4,227	4	20	37 to 65	1.5 to 15
Na	25X	5,890	4	10	37 to 65	0.1 to 3.5
Fe	1X	2,483	3	30	37 to 65	1 to 12
Zn	5X	2,134	4	20	37 to 65	0.2 to 2.0
Mn	1X	2,795	3	20	37 to 65	0.5 to 7.0
Cu	1X	3,248	4	15	37 to 65	1 to 12
Al	1X	3,093	4	25	62 to 40[b]	1 to 3[c]
Mo	1X	3,133	4	30	62 to 40[b]	1 to 3[c]

[a]Further dilutions when original solution volume was 25 ml.
[b]Acetylene-nitrous oxide setting.
[c]With scale expansion 8X and 10X for Al and Mo, respectively.

wet-ashed in a micro-Kjeldahl digestion apparatus. One gram of the ground material was placed in a 30-ml. Kjeldahl flask, and 7 ml. of concentrated HNO_3, 1 ml. of 60% $HClO_4$, and 1 ml. of concentrated H_2SO_4 were added. The mixture was shaken, digested by gradually increasing the temperature, and evaporated to a volume of about 1 ml. The final digest was pale green (white, after cooling). Total digestion time was about 3.5 hr. For analysis of starch, 10 g. was digested with 70 ml. of HNO_3, 10 ml. of H_2SO_4, and 10 ml. of $HClO_4$ in a 300-ml. flask.

The digests were dissolved in 10 ml. of HCl (1:3), filtered through Whatman No. 40 filter paper into a 25-ml. volumetric flask, washed with hot water, and made to volume. The solution was transferred immediately to a polyethylene storage bottle to minimize dissolution of Na and K from the glass. Appropriate controls and standards were prepared. Analyses of all elements were confirmed by determining recovery of added pure compounds.

TABLE II. MEAN (γ per g. TISSUE), STANDARD DEVIATION (γ per g. TISSUE), AND COEFFICIENT OF VARIABILITY (%) IN DETERMINATION OF TEN MINERAL ELEMENTS IN WHOLE ATLAS BARLEY AND NINE ATLAS BARLEY FRACTIONS

Element	Whole Kernel			Bran			Low-Protein Flour			For All Ten Samples
	Mean	S.D.	C.V.	Mean	S.D.	C.V.	Mean	S.D.	C.V.	C.V.
K	4,390	50.0	1.1	7,100	134.8	1.9	2,350	39.7	1.7	1.5
Mg	1,290	16.0	1.2	1,120	27.4	2.5	451	7.6	1.7	1.6
Ca	257	5.1	2.0	335	6.2	1.7	155	3.1	2.0	1.9
Na	138	5.5	4.0	406	8.3	2.1	38.4	0.7	1.8	2.6
Fe	28.0	0.3	1.1	31.8	0.2	0.7	16.1	0.7	4.6	2.4
Zn	22.8	0.5	2.1	6.8	0.3	4.7	10.8	0.4	3.6	2.7
Mn	11.0	0.6	5.0	9.7	0.3	2.9	6.8	0.2	3.1	3.0
Cu	4.0	0.1	3.2	1.6	0.1	4.9	2.0	0.1	5.8	5.2
Al	10.2	0.9	8.3	21.6	0.8	3.5	4.9	0.2	5.0	5.8
Mo	0.37	0.03	7.1	0.43	0.04	8.6	0.21	0.02	9.6	6.7

[a]Further dilutions when original solution volume was 25 ml.

[b]Acetylene-nitrous oxide setting.

[c]With scale expansion 8X and 10X for Al and Mo, respectively.

TABLE III. ASSAYS OF MINERAL ELEMENTS IN DRY-ASHED AND WET-DIGESTED PLANT MATERIALS

Element	Cereal		Fruit Leaves		Corn Leaves		Alfalfa	
	A[a]	B[b]	A	B	A	B	A	B
P, %	0.95	1.00	0.23	0.17	0.36	0.36	0.27	0.25
K, %	0.43	0.45	2.10	2.24	1.96	2.00	2.40	2.60
Ca, %	0.70	0.77	0.58	0.66	0.33	0.37	1.45	1.57
Mg, %	0.14	0.15	0.26	0.29	0.38	0.41	0.20	0.26
Na, %	0.21	0.22	0.023	0.026	0.010	0.015	0.063	0.067
Fe, p.p.m.	1,100	1,150	65.0	66.9	145	122	400	402
Cu, p.p.m.	3.9	4.0	20.8	21.8	9.3	10.8	9.15	9.35
Zn, p.p.m.	23.0	22.7	30.0	30.0	30.0	29.5	24.5	23.7
Mn, p.p.m.	29.3	29.9	195.0	187.0	81.2	80.4	45.8	48.1

[a]WARF Institute, Inc.; dry-ashed; courtesy R. E. Christensen.

[b]Barley and Malt Laboratory; wet-digested; averages of three or four determinations.

TABLE IV. MINERAL-ELEMENT CONTENTS (γ per g. TISSUE) OF WHOLE HIMALAYA BARLEY AND HAND-DISSECTED BARLEY SECTIONS OF HIMALAYA BARLEY

Element	Whole Kernel	Germ	Sections of Degermed Grain			Hand-Dissected Endosperm
			Next to germ	Central	Distal	
P	5,630	12,930	5,280	4,790	5,130	1,120
K	5,070	10,900	5,240	4,170	5,020	1,440
Mg	1,410	2,940	1,500	1,230	1,370	78
Ca	406	740	437	302	404	132
Fe	36.7	56.5	47.6	27.9	30.6	10.0
Zn	23.6	71.3	27.2	14.1	19.9	4.7
Mn	18.9	69.4	19.6	14.1	16.5	10.0
Al	4.9	26.5	8.7	3.6	4.0	traces
Mo	1.35	2.32	2.01	1.06	2.21	0.41

TABLE V. MINERAL-ELEMENT CONTENTS (γ per g. TISSUE) OF WHOLE HIMALAYA BARLEY, PEARLING FRACTIONS, AND HAND-DISSECTED ENDOSPERM OF HIMALAYA BARLEY

Element	Whole Kernel	Fines After Abrasions For, sec.			Pearls After Abrasions For, sec.			Hand-Dissected Endosperm
		30	90	270	30	90	270	
P	5,630	10,350	10,430	8,150	4,140	3,160	2,210	1,120
K	5,070	14,200	12,100	8,780	4,530	3,330	2,830	1,440
Mg	1,410	3,210	3,475	2,280	1,210	779	468	78
Ca	406	902	729	490	320	258	232	132
Na	254	800	472	266	161	102	93	58
Fe	36.7	139.0	104.2	76.4	25.7	17.0	13.0	10.0
Zn	23.6	78.6	54.7	37.4	20.6	16.9	15.7	4.7
Mn	18.9	63.0	39.7	23.2	15.5	13.4	13.3	10.0
Cu	15.1	38.0	20.2	11.3	7.1	5.4	6.1	3.5
Al	4.9	118.0	62.5	36.8	1.2	0.8	traces	traces
Mo	1.35	3.42	2.91	2.56	1.50	1.65	1.11	0.41

A Perkin-Elmer Model 403 atomic absorption spectrophotometer was used for absorption measurements. A three-slot burner head was used for the air-acetylene flame; a nitrous oxide head was used with a nitrous oxide-acetylene flame. Optimum fuel and oxidant flow rates were adjusted according to manufacturer's instructions. The operating conditions are summarized in Table I. Under the given conditions, the absorbance values could be read directly by aspirating standard and sample solutions diluted properly from primary standard solutions or original digest solutions. Distilled water, standards, and blanks were aspirated between every 5 to 7 samples. At least three "100 average" readings were recorded for each standard or sample. A 1,500 γ Na per ml. solution was used in the dilution for determining K in order to minimize the partial ionization of K in the air-acetylene flame and to increase the absorbance values. No scale expansion was applied with the exception of that used for the determination of Mo and Al.

RESULTS AND DISCUSSION

Standard deviations and coefficients of variability were calculated for determinations (by atomic absorption spectroscopy) of 10 elements in whole Atlas

TABLE VI. MINERAL-ELEMENT CONTENTS (γ per g. TISSUE) OF WHOLE ATLAS BARLEY AND FRACTIONS FROM ROLLER-MILLED ATLAS FLOUR AND BARLEY STARCH

Element	Whole Kernel	Bran	Tailings	Shorts	Flour	Starch
P	2,970	970	4,580	4,460	2,280	5
K	4,390	7,100	5,770	7,440	3,150	6
Mg	1,290	1,120	2,190	2,410	855	5
Ca	257	355	348	386	211	6
Na	138	406	139	238	58	...
Fe	28.0	31.8	41.8	35.1	26.3	1.6
Zn	22.8	6.8	39.1	35.0	21.3	0.2
Mn	11.0	9.7	13.6	12.6	10.6	0.1
Cu	4.0	1.6	4.7	4.9	3.4	0.1
Al	10.2	21.6	4.6	13.3	4.6	0.7
Mo	0.37	0.43	0.61	0.68	0.32	...

TABLE VII. PROTEIN (%, d.b.) AND MINERAL-ELEMENT CONTENTS (γ per g. TISSUE) OF FRACTIONS FROM AIR-FRACTIONATED ATLAS BARLEY FLOUR

Protein and Element	Total Flour	High-Protein Fractions		Low-Protein Fractions		Residue
	A	B	C	D	E	EE
Protein	9.8	23.3	11.9	6.5	7.1	10.5
P	2,280	4,830	2,890	1,400	1,480	2,690
K	3,150	4,240	3,360	2,350	2,550	3,910
Mg	855	1,865	1,070	451	513	1,100
Ca	211	258	209	155	188	256
Na	57.7	73.4	40.8	38.4	42.4	69.5
Fe	26.3	58.4	38.6	16.1	22.7	32.2
Zn	21.3	44.9	24.5	10.8	12.8	29.6
Mn	10.6	12.1	9.5	6.8	8.4	15.3
Cu	3.4	5.8	3.5	2.0	2.4	4.4
Al	4.6	15.7	10.9	4.9	4.4	5.0
Mo	0.32	0.46	0.43	0.21	0.27	0.32

barley and in nine barley fractions. Five complete determinations were made on each of the 10 samples. Means, standard deviations, and coefficients of variability for the determinations in whole barley, bran, and a low-protein barley flour, and coefficients of variability for all 10 samples are given in Table II. Samples not listed individually in Table II included tailings, shorts, and five additional flours. As expected, generally, standard deviation increased and coefficient of variability decreased as concentration of mineral element increased. No consistent differences were found in assay variability of individual elements in the 10 samples.

Assays of all elements also were compared with assays made by the Laboratories of the WARF Institute, Inc., Madison, Wis. A fortified cereal product, fruit leaves, corn leaves, and alfalfa were analyzed in those laboratories on dry-ashed material by a colorimetric procedure (for P) and by atomic absorption spectrometry (for all other elements). The results are compared in Table III. This comparison shows excellent agreement between results from Laboratories of the WARF Institute, Inc., and our laboratories. The agreement is especially significant as assays in WARF Institute, Inc., were made on dry-ashed samples and in our laboratories on wet-digested samples. Giron (13) recently reported that determination of Fe in grasses yielded lowered results if Fe assays were made on wet-ashed material.

The mineral-element contents of the whole kernel, germ, various parts of the kernel, and pure endosperm from Himalaya barley are compared in Table IV. The germ contained more, on a percentage basis, of each of the elements than any of the other grain sections or than the whole grain. The hand-dissected starchy endosperm contained, by far, the lowest concentrations of mineral components. The central section of the kernel, presumably, contained relatively more starchy endosperm and less aleurone and bran than the other two (next to the germ and distal) sections of the degermed kernel. That central section also contained lower concentrations of the mineral components than did the next to the germ and distal sections. The results indicated that the outer grain tissues (pericarp and aleurone) were rich in mineral components. A comparison of mineral-element concentrations in the whole grain and in the germ or in the starchy endosperm indicated different patterns of distribution for the individual components. For instance, the concentration of Al in the germ was 5.4 times as high and of Mo 1.7 times as high as in the whole kernel. Concentration in the whole kernel of Mg was 18 times as high and of Mn 1.9 times as high as in the starchy endosperm. Both the concentrations of mineral elements and their general patterns of distribution resembled those in wheat (3,4). Concentrations of Mg and Mn in the barleys were somewhat lower than in wheat (5) and were similar to those reported for barley by Mandl et al. (14). Concentration of Na in the samples used in this study was higher than in wheat. Rasmusson et al. (15) found both in wheat and barley 1.5- to 2.5-fold varietal differences (within species) in P, K, Ca, and Mg.

A pattern of distribution of mineral elements in the pericarp and endosperm tissues of barley can be obtained from the data in Table V. Pearls after abrasion for 270 sec. were closest in composition to the starchy endosperm. Both the pearls and the endosperm contained low concentrations of mineral elements. The pearls contained some attached aleurone cells which were excluded from the hand-dissected starchy endosperm. This resulted in higher concentrations of mineral elements in the pearls than in the starchy endosperm. Fines after abrasion for 30 or 90 sec. contained most of the pericarp and aleurone and were richest in mineral components. Some of the patterns shown in Table IV are confirmed by the data for abraded material in Table V. Both tables showed a much larger decrease (from whole grain to endosperm) in concentrations of Mg than of Ca. This indicated that Ca was more uniformly distributed throughout the kernel than was Mg. The fines (after 30 sec.) were 24 times richer in Al, 3.8 times richer in Fe, and 2.8 times richer in K than was the whole kernel. The high concentration of Al in germ and outer grain layers (presumably aleurone) is of interest in light of high toxicity of Al to some barley cultivars (16).

Distribution of mineral components in roller-milled, Atlas barley flours is summarized in Table VI. Concentrations of most mineral elements were higher in the tailings and shorts, rather than in the bran fraction. Tailings and shorts, presumably, were rich in particles originating in the germ and aleurone layers. The flour which contained mainly particles from the starchy endosperm had lowest concentrations (among the roller-milled fractions) of mineral components. Still, the concentration of mineral components in the flour was in several instances 100 to 500 times higher than in the starch. It would seem that the mineral components are associated with the nonstarchy components of flour (proteins). However, the possibility of washing out soluble mineral components during the preparation of the starch cannot be excluded. The starch contained relatively high concentrations

of Ca and Mg; those mineral elements might have originated, in part at least, with the washing water.

Association between protein concentration and concentration of mineral components is confirmed by the data on air-fractionated flours (Table VII). The high-protein fractions B and C are substantially richer in mineral components than the low-protein fractions D and E. The highest protein fraction B contained more of each mineral component than did the original flour A and of each mineral component except Mn than did the bran-contaminated residual flour EE.

The whole barleys, barley tissues, and barley fractions contained decreasing concentrations of P, K, Mg, Ca, Na, Fe, Zn, Mn, Cu, Al, and Mo; the order is the same as in other cereals, i.e. wheat. Similarly, distribution within barley tissues and changes during processing of barley into flour resembled the distribution pattern and changes in wheat.

The high concentration of K and low concentration of Ca in barley tissues, including the aleurone layer, has been demonstrated recently (17) by a combination of scanning electron microscopy and energy-dispersive X-ray analysis. Those findings are of interest as calcium ions promote the accumulation of amylase by barley endosperm layers in response to gibberellic acid (18) and enhance synthesis and stability of some α-amylase isoenzymes (19).

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