MINERAL CONTENT OF DEVELOPING AND MALTED BARLEY[1]

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ABSTRACT

Three hulled and two naked barley cultivars were harvested at five stages of development. Between 2 and 3 weeks after anthesis, the barley kernels contained 73.0–89.9% of the ash, 48.3–75.3% of the protein, and 61.1–84.9% of the dry weight of the mature kernels. Ratios of specific elements in the immature and mature barleys varied widely. For mature kernels, naked barleys contained more K, P, Mg, Ca, Zn, Fe, Mn, and Cu than covered barleys, but the differences for Fe and Ca were smaller than those for the other elements. Total ash and mineral components of grain were more concentrated in the germ end than in the central section; the distal end section contained intermediate amounts. During steeping, the germ end lost relatively large amounts of mineral components (mainly K, the major mineral component). During malting there was a redistribution of mineral components within the barley kernel. Rootlets and shoots contained substantially more total ash, K, P, Fe, Zn, Mn, and Cu than kilned malt. Ca was translocated to rootlets but not to shoots.

Previously, we reported on distribution of ash and mineral components in tissues of naked and hulled barleys, in fractions of roller-milled barleys, and in air-classified flours (1). The present investigation was concerned with changes in levels and distribution of ash and mineral components in barley during grain development and malting.

MATERIALS AND METHODS

Barleys Harvested at Various Stages of Development

Three hulled, six-rowed malting barleys (*Hordeum vulgare* L.) were grown in Madison, Wis., in 1971. They were the white-aleurone cultivars 'Larker' and 'Dickson', and the blue-aleurone cultivar 'Conquest'. Five samples were obtained from each cultivar at about weekly intervals throughout the grain development cycle. Primary spikes were hand-cut from the field, freeze-dried to about 12% moisture, and deawned.

Two naked barleys, 'Hiproly' and its sister line CI-4362, were grown in Aberdeen, Idaho, in 1972. Five samples from each cultivar represented stages of development similar to those of hulled cultivars. Spikes were oven-dried at 40° C to constant weight.

Barley and Barley Fractions from Malted Grain

'Klages', a two-rowed, white aleurone malting barley was grown in Aberdeen, Idaho, in 1973. Samples of 170 g were cleaned, sized, and malted under uniform

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conditions (2). Barley was steeped in tap water to 45% moisture (about 42 hr) at 16° C and germinated in malting chambers at 16° ± 0.5° C for 3 or 7 days. Final kiln temperature was 65° C for 4 hr. Steeping losses were about 2.2% and respiration losses about 0.8%.

Rootlets separated by hand from the 3- and 7-day malts comprised 2.1 and 4.2%, respectively, of the total weight. Shoots (acrospires) separated from the 7-day malt comprised 3.8% of the malt weight. The original and steeped barleys and the 3- and 7-day malts were then sectioned into three parts: germ end (including the germ and adjacent tissues), central section, and distal end. Those parts comprised 21.5, 52.5, and 26.0%, respectively, of the whole grain or malt.

Methods

Before analysis the barleys and malts were ground on a micro-Wiley mill to pass a 20-mesh sieve; the hand-dissected fractions, including rootlets and shoots,

TABLE I
Some Characteristics of Barleys Harvested at Various Stages of Development

Variety	Days after Anthesis	Kernel Wt mg[a]	Moisture %	Ash %	Protein[a,b] %
Dickson[c]	6	11.0	78.0	3.93	10.5
	14	25.4	60.0	3.08	9.6
	20	26.2	50.4	2.97	11.0
	28	31.4	22.5	2.70	11.5
	34	30.3	24.3	2.75	11.8
Larker[c]	6	12.5	77.3	3.68	10.4
	14	25.1	60.4	2.92	10.4
	20	31.9	48.9	2.69	12.3
	28	29.7	22.8	2.66	12.5
	34	30.0	24.3	2.59	12.5
Conquest[c]	5	11.2	78.4	3.68	10.3
	13	22.1	64.0	3.05	10.4
	19	25.8	49.9	2.89	11.9
	27	31.5	17.7	2.70	12.2
	33	28.3	24.2	2.70	12.2
Hiproly[d]	7	5.0	76.9	3.41	19.5
	14	16.1	71.4	2.76	19.0
	21	31.8	62.3	2.32	19.6
	28	39.4	55.2	2.26	19.5
	35	40.6	17.5	2.24	21.6
CI-4362[d]	7	5.8	77.3	3.12	18.9
	14	24.4	69.7	2.62	18.2
	21	41.2	59.1	2.13	17.1
	28	54.4	50.1	2.07	18.1
	35	55.8	26.5	2.08	20.1

[a]On a moisture-free basis.
[b]N × 6.25.
[c]Grown at Madison, Wis., in 1971.
[d]Grown at Aberdeen, Idaho, in 1972.

were ground in a mortar. Moisture, crude protein (expressed as Kjeldahl N % × 6.25, on a moisture-free basis), and ash were determined according to AACC Approved Methods (3). Phosphorus was determined by the colorimetric molybdenum blue method (4). For mineral analyses by atomic absorption spectroscopy, the samples were wet-ashed and analyzed as described previously (1).

RESULTS AND DISCUSSION

Barleys Harvested at Various Stages of Development

As the barleys matured, ash, expressed as per cent in the grain, consistently decreased (Table I). Ash was lower in the naked Hiproly and CI-4362 than in the three hulled cultivars. The low ash in the naked barleys could be attributed to relatively large kernel size and starchy endosperm that is low in ash and to the absence of hulls that are high in ash. To determine the pattern of kernel weight increase, ash deposition, and protein biosynthesis in the kernel, the data in Table I were calculated in three ways. The increase from stage l to stage n, compared to stage l, was $\frac{X_n - X_l}{X_l} \times 100$

where

X_l = weight (or protein content or ash content) per kernel at stage l, and
X_n = weight (or protein content or ash content) per kernel at stage n.

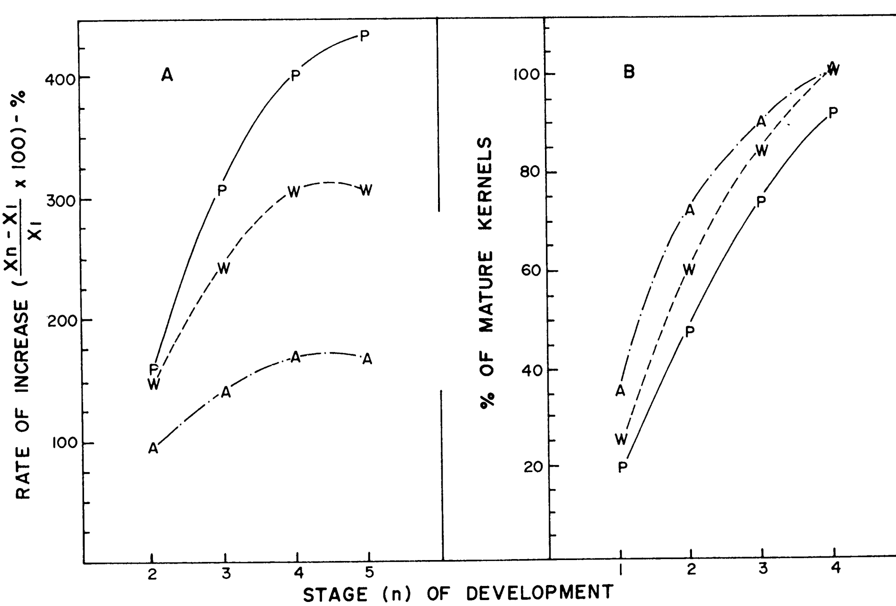

Fig. 1. Average changes in dry weight (W), ash (A), and protein (P) in barleys harvested at five stages of development. A) Component increase from stage l to stage n, as per cent of that in stage l (see text for definitions), and B) component at a given stage as per cent of that in the mature kernel.

That comparison (Fig. 1A) indicates that rate of increase was fastest for protein, slowest for ash, and intermediate for kernel weight. The increase from one to the next stage $\frac{(X_n - X_{n-1})}{X_{n-1}} \times 100$ was consistently higher at earlier than at later stages of development. The average percentage increase for the five cultivars was:

Between stages	*Average increase (%) in* Kernel weight	*Ash*	*Protein*
1–2	148.6	97.0	160.5
2–3	38.9	23.1	55.9
3–4	18.8	12.5	24.0
4–5	−0.8	−1.1	7.1

However, if the parameters are calculated at a given stage as percentage of the mature kernel, the order given in Fig. 1A is reversed (Fig. 1B). The immature kernel contained a higher percentage of the ash and a lower percentage of the protein of the mature kernel. Thus, for instance, between 2 and 3 weeks after anthesis, the barley kernels contained 73.0–89.9% of the ash, 48.3–75.3% of the protein, and 61.1–84.9% of the dry weight of mature kernels. The results indicate that mineral components were deposited earlier than proteins. MacGregor *et al.* (5) reported that ash and total Kjeldahl N increased at the same rate as dry matter; but whereas dry matter and protein reached a maximum 36 days after emergence and remained constant thereafter, ash reached that maximum after 32 days.

When the mineral components are expressed as milligrams per 1000 kernels, all components increased during kernel development (Fig. 2). Comparison of amounts and changes in individual mineral components in hulled and naked barleys is complicated because the two groups were grown under different conditions and the naked barleys were smaller than the hulled in the earliest stages of development. In mature kernels, naked barleys contained more of each of the elements studied (30.6% Fe, 45.0% Ca, 58.8% Zn, 60.0% Cu, 73.3% Mg, 77.1% K, 88.3% P, and 133.3% Mn) than hulled barleys. The higher amounts of those elements in the kernels of naked barleys are explained in part by their higher kernel weights. There were no consistent varietal differences among the three hulled and between the two naked barleys in amounts or rates of increases in the individual mineral components.

The average ratios of specific elements in the mature and immature (earliest stage) kernels varied widely. Those ratios were:

Hulled barleys Element	Ratio	*Naked barleys* Element	Ratio
K	1.43	Ca	1.48
Ca	1.50	K	4.63
Cu	1.97	Mn	7.72
Mg	2.47	Mg	7.81
Mn	2.52	P	8.00
P	2.96	Cu	8.73
Zn	2.99	Zn	8.77
Fe	3.22	Fe	11.75

The order of increasing ratios was similar in both groups. The relatively small increase in Ca in developing hulled and naked barleys indicates that most of this element is deposited at early stages of barley development. Ca is present in the middle lamella of cell walls (6) and enhances synthesis and stability of some α-amylase isoenzymes (7). MacGregor *et al.* (5) have shown that α-amylase decreased to one-tenth of its maximum level between 11 and 28 days after emergence and thereafter remained almost constant until maturity.

There were consistent and large decreases in K and Ca, when expressed as μg/g, as hulled barleys developed (data not shown). As naked barleys developed, there were small decreases in P, Mg, Mn, and Cu; large decreases in K and Ca; and no consistent changes in Zn; Fe increased slightly (data not shown). Composition of the ash changed considerably during barley development (Table II). Changes in concentrations of mineral components in the ash of hulled and naked cultivars showed similar trends during development: increases in P, Mg, Zn, Fe, Mn, and Cu, and decreases in K and Ca. Those changes could not be related to the mobility of the mineral components in plant tissues (6). K, P, and Mg are known to be highly mobile; Mn, Ca, and Fe are generally considered to be immobile. Yet, concentrations in the ash of both the highly immobile Ca and mobile K decreased during barley development.

Our results for barley differ from those for wheat; Lallukka (8) reported that during ripening of spring wheat, K content decreased, Ca increased, and amounts of other mineral elements were unchanged. Kuchko *et al.* (9) found that

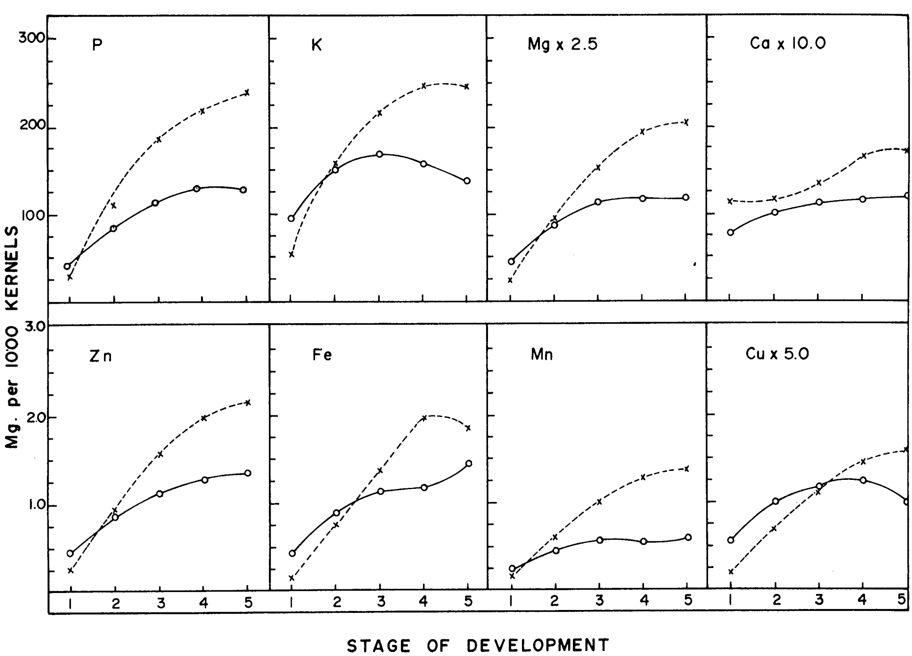

Fig. 2. Average mineral composition of three hulled (O——O) and two naked barleys (X- - - -X) harvested at five stages of development. Milligrams of Mg, Ca, and Cu per 1000 kernels have been multiplied by 2.5, 10.0, and 5.0, respectively, before plotting.

most Cu and a substantial part of Zn accumulated in wheat during the period between the waxy and fully ripened stages. There was no consistent or significant change in concentrations (expressed as $\mu g/g$) of Zn or Cu in developing naked barley in this study. On a kernel basis, however, the amounts of Zn and Cu in developing barley increased significantly and consistently.

Barleys and Barley Fractions from Malted Grain

Steeping somewhat decreased concentration of ash, presumably by leaching (Table III). The monovalent cation K decreased significantly, presumably because it is water-soluble in plant tissues. Concentrations of ash and individual mineral elements in steeped barley and malt were similar. In all cereal grains there is a general mobilization of mineral elements from the storage tissues to the developing seedling. We have not observed large decreases in total ash and mineral elements because rootlets and shoots formed during malting (unlike in the developing seedling) were relatively small and changes in concentrations of

TABLE II
Average Concentrations of Mineral Components in Ash of Hulled and Naked Barleys

	Concentration (%) in Ash of			
	Hulled barleys		Naked barleys	
Element	Immature	Mature	Immature	Mature
P	9.7	15.7	16.4	22.5
K	22.0	17.4	29.7	23.5
Mg	4.40	5.98	5.86	7.85
Ca	1.83	1.51	6.47	1.65
Zn	0.103	0.168	0.138	0.204
Fe	0.102	0.179	0.087	0.178
Mn	0.055	0.076	0.100	0.130
Cu	0.026	0.026	0.021	0.031

TABLE III
Ash and Mineral Contents of Barley Grains, Malts, Rootlets, and Shoots from Grains Malted for 3 and 7 Days

Material and Treatment	Ash %	P	K	Mg	Ca	Fe	Zn	Mn	Cu
		$\mu g/g$ tissue							
Barley	2.44	3,160	4,570	1,360	259	26.1	20.1	14.9	4.15
Steeped barley	2.20	3,210	3,840	1,340	293	28.2	21.9	15.2	3.59
Kilned malt after									
3 days	2.33	3,500	3,310	1,290	289	29.1	23.8	13.0	4.65
7 days	2.40	3,500	3,360	1,340	303	31.3	20.5	14.1	4.83
Rootlets from kilned malt after									
3 days	6.01	7,390	23,040	1,790	673	67.8	102.0	74.0	14.00
7 days	5.26	5,960	22,080	1,500	692	55.9	84.9	45.1	15.50
Shoot from kilned malt after 7 days	3.81	7,770	15,230	1,400	271	43.1	93.0	39.6	12.50

minerals were masked, in part, by metabolism of organic components and increases in relative concentrations of inorganic components. Both rootlets and shoots contained substantially more total ash, P, K, Fe, Zn, Mn, and Cu than the kilned malt. Translocation of Mg was relatively small. The rootlets contained 2.3 times as much Ca as the kilned malt, but there was little translocation into the shoot.

The high content of K in the rootlets and the shoots confirms highly active translocation of this element from the caryopsis to the developing organs. It is generally recognized (10) that K is highly mobile within the plant tissue and is

TABLE IV
Effect of Steeping on Ash Content and Mineral Concentration of Klages Barley Kernel and its Fractions

Material and Treatment	Ash	P	K	Mg	Ca	Fe	Zn	Mn	Cu
	%	μg/g tissue							
Barley	2.44	3,160	4,570	1,360	259	26.1	20.1	14.9	4.15
Steeped barley	2.20	3,210	3,840	1,340	293	28.2	21.9	15.2	3.59
Germ end from									
Barley	3.65	5,290	6,570	1,930	456	47.3	40.4	32.9	6.00
Steeped barley	3.07	4,830	5,000	1,740	436	50.6	39.4	29.8	5.81
Central section from									
Barley	2.03	2,890	4,000	1,150	202	18.8	14.5	10.5	2.99
Steeped barley	1.86	2,900	3,130	1,090	231	20.1	15.9	10.2	3.22
Distal section from									
Barley	2.74	3,610	4,820	1,450	264	24.1	17.7	13.4	3.61
Steeped barley	2.46	3,450	3,670	1,370	289	25.5	21.0	12.3	3.88

TABLE V
Ash Content and Mineral Concentration of Fractions from Steeped Klages Barley and Malts Malted for 3 and 7 Days

Material and Treatment	Ash	P	K	Mg	Ca	Fe	Zn	Mn	Cu
	%	μg/g tissue							
Germ end from									
Steeped barley	3.07	4,830	5,000	1,740	436	50.6	39.4	29.80	5.81
3-day malt	3.55	4,730	6,670	1,630	481	55.4	42.9	28.20	6.47
7-day malt	3.85	4,940	7,730	1,590	448	54.3	43.5	31.10	8.40
Central section from									
Steeped barley	1.86	2,900	3,130	1,090	231	20.1	15.9	10.20	3.22
3-day malt	1.78	2,650	2,480	1,150	236	22.7	15.9	8.80	3.49
7-day malt	1.90	2,610	2,040	1,240	250	21.4	14.9	9.16	2.71
Distal section from									
Steeped barley	2.46	3,450	3,670	1,370	289	25.5	21.0	12.30	3.88
3-day malt	2.44	3,600	3,120	1,420	284	28.6	18.7	10.60	4.46
7-day malt	2.65	3,810	2,640	1,460	308	28.6	17.7	12.00	4.26

present in high concentrations in meristematic tissues rather than in the starchy endosperm. The high concentration of Ca in rootlets and low concentration in shoots suggest that Ca may be involved in the uptake function of the rootlets. Lauchli and Epstein (10) reported that in the presence of Ca, plant tissue absorbs ions essentially in a unidirectional fashion without any measurable efflux and that the cell plasmalemma is highly impermeable to diffusive permeation by inorganic ions.

Eastwood and Laidman (11) found that during wheat germination, the macronutrient elements (Mg, Ca, and K) were redistributed from the aleurone tissue to the developing seedling. The movement of Ca was much slower than the movement of Mg and K. They germinated individual wheat kernels in flat dishes for 10 days in the presence of liberal amounts of water. We malted for 7 days a fairly compact mass of barley kernels that were steeped to attain relatively low moisture levels. Seedling development and translocation of nutrients in the study of Eastman and Laidman were probably much more extensive than during experimental malting.

Analyses of barley and steeped barley sectioned into three parts (Table IV) showed that total ash and mineral components were more concentrated in the germ end than in the central section (which comprised most of the starchy endosperm); amounts in the distal section were intermediate. Losses in total ash during steeping were 16, 8, and 10% in the germ end, central section, and distal section, respectively. The greatest losses were in K, the major mineral element, which decreased 22 to 24% in the three sections. Losses in mineral components during steeping were accompanied generally by increases in Ca, presumably from the tap water.

Metabolism of organic components and redistribution of mineral components during malting affected concentrations of minerals within the three sections of the barley kernel (Table V). During malting for 7 days, total ash increased little in the central and distal sections. The ash in the germ end of barley malted for 7 days increased 25% above the ash in steeped barley. Similarly, marked increases were found in concentrations of K, Fe, Zn, and Cu in the germ end. The results point to considerable, selective translocation from the central and distal sections to the germ end of malted barley.

There were differences in distribution patterns of individual mineral components in barleys malted for up to 7 days. K concentrations increased steadily in the germ end but decreased in the central and distal sections. On the other hand, Mg concentrations decreased in the germ end but increased in the other two sections. The results suggest that the translocation of minerals within the barley kernel during malting is not in a simple unidirectional fashion.

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