Effect of Milling on Trace Element and Protein Content of Oats and Barley[1,2]

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ABSTRACT

Barley and oats were analyzed for trace element (iron, zinc, manganese, copper, chromium, and nickel) and protein content at various stages of milling from the whole grain to flakes and flours. Trace element and protein analysis was also performed on laboratory-dissected hull and groat fractions. All nutrients studied except for chromium were significantly reduced in the milling of barley into flour, primarily as a result of decortication operations. The by-product feeds from the decortication operations, which contained the barley hulls and much of the bran, aleurone, and germ, contained higher concentrations of nutrients than did other fractions. For oats, dehulling in the preparation of groats resulted in higher levels of the nutrients studied, reflecting the lower concentration of nutrients in the hull as compared to that in the groat, except for chromium, which was greater in the hull and not reduced by dehulling. Further refining of oats into flakes and flour did not have a uniform effect on the various trace elements and protein.

Trace element content of diets is of great current interest to the nutrition community because of increasing evidence of marginal or inadequate intakes among segments of the population. Although cereals can be significant contributors of trace elements, some concern is evident that those persons who subsist on refined and processed foods may receive inadequate amounts of micronutrients.

The effect of milling on wheat and corn has been reported (Czerniejewski et al 1964, Garcia et al 1974, Schroeder 1971, Zook et al 1970). Trace elements are concentrated in the germ of corn; thus, the influence of refining on the concentration of these nutrients depends upon the degree to which the germ is removed (Garcia et al 1974). Refining of wheat was shown to result in the removal of between 40 and 88.5% of seven essential trace elements (Schroeder 1971). Zook et al (1970) also reported high levels of reduction of trace elements in refined flours as compared to levels in wheat and wheat blends. Less information has been published on

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the removal of trace elements by milling in other cereals. Liu et al (1974) analyzed roller-milled and air-classified barley flours for content of protein and 11 elements, including the trace elements iron, zinc, manganese, copper, aluminum, and molybdenum but not including chromium and nickel. Barley is the most widely adapted cereal crop. Human consumption is an important use of barley in Asian countries, but it is less popular in Europe and North America, where it is used primarily in baby cereals and snack foods. Barley ranks behind oats in importance in the United States. The primary use of oats for human consumption is in the form of rolled oat groats or oat flour. Oat flours are used mainly in baby cereals and ready-to-eat breakfast cereals. The effects of milling on trace element content of oats has not been reported.

The purpose of the study reported here was to determine the amount of protein and of six trace elements (iron, zinc, manganese, copper, nickel, and chromium) contained in barley and oat grains and their milled fractions. Grains separated into the hull and groat were also analyzed in order to interpret the effect of various milling processes on removal of nutrients.

MATERIALS AND METHODS

Cereal Fractions

Barley fractions were obtained from Minnesota Grain Pearling Co. (H. C. Knoke Division, 5728 N. Roosevelt Road, Chicago, IL 60650). Barley was milled according to the flow chart diagrammed in Fig. 1. Eleven fractions were obtained from the sampling points indicated. The barley was first passed through a Carter disk separator to remove grains other than barley. A flat stone mill or rice huller knocked off the tips of the grains, and the decorticators pearled the barley. Decorticator No. 1 removed approximately 90% of the hull. After the barley had passed through decorticator No. 2, most of the bran had been removed and after decorticator No. 3, much of the aleurone, germ, and some of the endosperm had been removed. The byproducts of the decorticators were used for animal feeds. The dehulled barley was flattened through rollers, cut, and ground. Overs were fed back into the grinder, and the fines were blended to achieve the finished product barley flour.

Oat samples were obtained from the Quaker Oats Co. (Cedar Rapids, IA 52406). Samples included whole kernel oats, grade A groats, grade B groats, regular "old fashioned" rolled oat flakes, quick flakes, and oat flour milled and sampled according to the scheme given in Fig. 2. The whole grain oats were untreated, whereas the groats had been cleaned and hulled by an impact huller. The hulls were removed by aspiration. Grade A groats had more hull removed than did grade B groats. Regular rolled oats were prepared from grade A groats by drying, steaming, and rolling. The final moisture content approximated 10–12%. Quick flakes were prepared from grade B groats by drying and steel cutting into 2–3 pieces by a Kipp Kelley cutter that loosened the hull. The hulls were removed by aspiration, making the hull content similar to that of grade A flakes. Oat flour was rolled and ground (to pass a tuft tex wire sieve No. 36) from cut, steamed grade B groats.

Samples of the whole kernel oats were separated in our laboratory into the hull and groat, using a specially designed Plexiglas impact huller. Whole kernel barley was hand-dissected into the hull and caryopsis. Dissected fractions were analyzed for minerals and protein in duplicate or triplicate.

Analytical Methods

Moisture and protein were determined as described by the AOAC (1980). A conversion factor of 5.83 was used for protein calculations from nitrogen content for both barley and oats. Minerals were analyzed by atomic absorption spectroscopy following a nitric acid-perchloric acid digestion. Wet ashing of National Bureau of Standards wheat flour was found to yield better precision and accuracy than did dry ashing in this laboratory. Approximately 2 g of sample was placed in a Folin-Wu digestion tube containing 3–5 glass beads; 10 ml of concentrated redistilled HNO_3 was added; and the mixture was allowed to predigest overnight at room temperature. The predigested mixture was ashed by placing the tube in a cold heating block and bringing the temperature slowly to 130°C, where it was maintained until the acid was nearly evaporated. Then 3 ml of redistilled 70% perchloric acid was added, and the tube was heated to 210°C and held until most of the acid was evaporated. The final digest was clear. The digest was then transferred to a 10-ml volumetric flask and brought to volume with water. The solution was transferred immediately to a Nalgene storage bottle. Blanks were prepared in the same way as

TABLE I
Percent Recovery[a] of Standards Added to Cereal Samples

Element	Wheat Flour[b]	Oat Flakes
Fe	95.4 ± 4.6	107.2 ± 25.3
Zn	102.8 ± 4.0	111.3 ± 14.4
Mn	100.2 ± 3.9	103.7 ± 19.4
Cu	103.7 ± 5.7	95.2 ± 5.7
Cr	119.6 ± 2.6	71.0 ± 6.6
Ni	105.7 ± 5.6	94.3 ± 4.9

[a]Mean and standard deviation of three trials.
[b]National Bureau of Standards 1567.

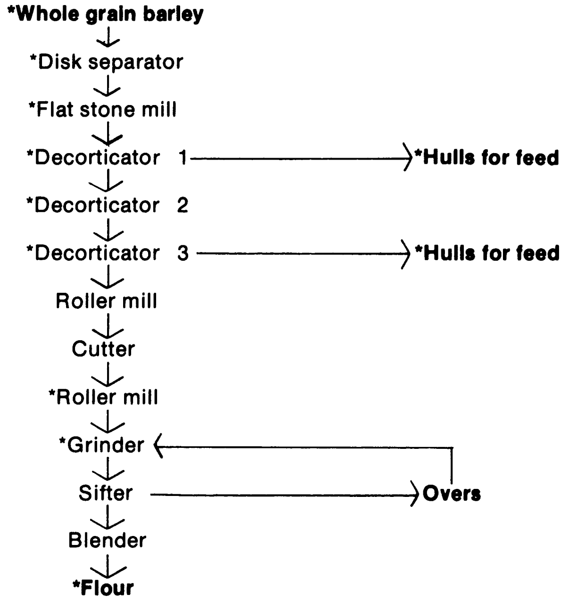

Fig. 1. Flow chart of milling process used to prepare barley flour. Asterisks indicate sampling points.

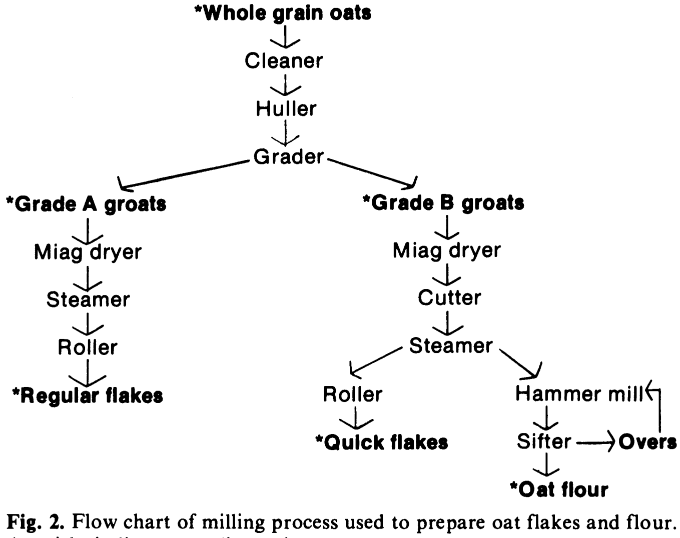

Fig. 2. Flow chart of milling process used to prepare oat flakes and flour. Asterisks indicate sampling points.

the samples and standards. A Perkin-Elmer Model 360 atomic absorption spectrophotometer was used for mineral analysis. Ultrahigh purity water was used. Glassware and storage containers were soaked in 50% HNO_3 for one week, rinsed, allowed to soak in ultrapure water overnight, and air dried before use.

Percent recovery of standards added to cereal samples before digestion is given in Table I. To resolve the discrepancy between percent recovery of chromium added to wheat flour and oat flakes, percent recovery of ^{51}Cr added to oat flour was determined. Aliquots of approximately 170,000 cpm ^{51}Cr were added to digestion tubes before digestion. Percent recovery following digestion for triplicate determinations averaged 90.0 ± 1.7%. Wolf et al (1974) suggested that a volatile fraction of chromium is formed during digestion of biological samples. Kumpulainen et al (1979) found a 10–15% loss of added ^{51}Cr in digestions using HNO_3 but no loss of endogenous chromium with different acid treatments.

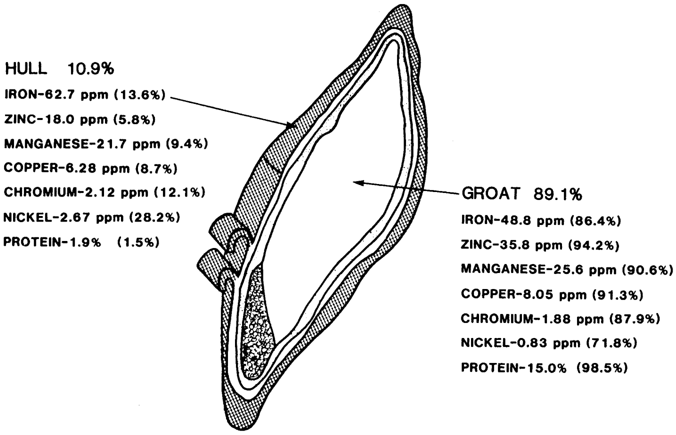

Fig. 3. Trace element and protein concentration and percent of nutrient content in barley hull and groat. The hull is depicted in crosshatch and the groat includes all other fractions.

Statistical Analysis

One way analysis of variance was used to determine whether statistical differences existed between cereal fraction means.

RESULTS AND DISCUSSION

The trace element and protein content of barley flour samples representing the products of various stages of milling is given in Table II. For all of the nutrients except chromium, the finished product flour contained significantly lower amounts ($P < 0.01$) than the barley from which the flour was milled. Protein content was decreased 8% by milling. Trace element reduction averaged 14% for copper, 30% for manganese, 32% for zinc, 35% for iron, and 36% for nickel. Whole kernel barley separated into hull and groat fractions was analyzed for protein and mineral content (Fig. 3). Barley consisted of 10.9% hull and 89.1% caryopsis. In comparison to the groat, the hull contained significantly higher ($P < 0.05$) concentrations of iron and nickel but not of the other minerals analyzed. Minerals that were more concentrated in the hull were reduced to a greater extent by milling. For elements other then chromium, which was not significantly reduced by milling, the by-products of the decortication operations generally contained significantly greater ($P < 0.05$) concentrations than did any other fraction. Exceptions to this included the by-product from decorticator No. 1, which did not differ significantly in copper content from barley sampled at the disk separator nor in zinc content from whole kernel barley, and the by-product from

TABLE II
Trace Element (ppm, db) and Protein (%, db) Contents of Barley and Milled Fractions

Sampling Points	Trace Elements: Fe n[a]	Fe X[b]	Zn n	Zn X	Mn n	Mn X	Cu n	Cu X	Cr n	Cr X	Ni n	Ni X	Protein[c] n	Protein[c] X
Whole grain	9	45.2 ± 1.8	11	34.4 ± 2.9	11	27.2 ± 3.5	11	6.25 ± 0.66	10	2.05 ± 0.13	9	0.89 ± 0.12	6	13.2 ± 0.7
Disk separator	8	46.6 ± 2.1	9	34.3 ± 1.7	11	27.4 ± 1.3	10	7.07 ± 0.40	9	2.15 ± 0.27	8	0.81 ± 0.20	9	13.4 ± 0.8
Flat stone mill	9	45.3 ± 1.9	9	32.6 ± 0.6	10	27.3 ± 1.8	11	6.46 ± 0.54	8	2.05 ± 0.30	8	1.06 ± 0.23	8	13.3 ± 0.7
Decorticators														
1	9	43.1 ± 2.0	10	33.2 ± 1.1	12	25.1 ± 1.7	11	6.67 ± 0.68	8	2.11 ± 0.34	8	0.91 ± 0.20	9	13.9 ± 0.6
2	11	39.5 ± 3.2	10	31.3 ± 2.9	9	23.1 ± 2.0	12	6.47 ± 0.52	7	2.26 ± 0.29	10	0.69 ± 0.20	9	13.0 ± 0.7
3	10	27.4 ± 0.9	11	25.9 ± 1.4	11	18.1 ± 1.2	11	5.75 ± 0.25	7	2.10 ± 0.29	7	0.81 ± 0.19	6	13.2 ± 1.0
Roller mill	10	30.4 ± 2.5	11	26.7 ± 0.9	11	18.0 ± 1.2	10	5.95 ± 0.33	9	2.07 ± 0.34	9	0.77 ± 0.19	6	12.9 ± 0.7
Grinder	8	26.7 ± 1.4	9	23.7 ± 1.1	9	17.7 ± 0.4	12	5.67 ± 0.85	10	2.16 ± 0.24	9	0.55 ± 0.11	6	12.1 ± 0.9
Flour	10	29.2 ± 3.4	9	23.4 ± 1.3	10	19.0 ± 1.5	12	5.41 ± 0.55	10	1.99 ± 0.02	7	0.57 ± 0.11	6	12.2 ± 0.5
Hulls from														
Decorticator 1	9	143 ± 18	8	36.1 ± 1.1	10	55.4 ± 5.1	12	7.29 ± 0.29	8	1.86 ± 0.06	7	1.48 ± 0.11	6	11.4 ± 0.7
Decorticator 3	11	80.0 ± 18.6	9	52.5 ± 4.4	10	30.8 ± 1.2	12	9.72 ± 1.06	9	2.00 ± 0.17	9	0.86 ± 0.10	6	19.2 ± 1.1

[a] n = Number of replicates.
[b] Mean ± SD.
[c] Protein = N × 5.83.

TABLE III
Trace Element (ppm, db) and Protein (%, db) Contents of Oats and Milled Fractions

Sampling Points	Trace Elements: Fe n[a]	Fe X[b]	Zn n	Zn X	Mn n	Mn X	Cu n	Cu X	Cr n	Cr X	Ni n	Ni X	Protein[c] n	Protein[c] X
Whole grain	11	40.1 ± 2.7	10	35.0 ± 3.0	10	83.6 ± 4.1	11	5.92 ± 0.55	10	0.39 ± 0.10	9	3.35 ± 0.41	11	13.0 ± 1.7
Grade A groats	8	46.2 ± 4.1	11	44.3 ± 12.3	13	97.5 ± 29.0	12	7.54 ± 1.34	12	0.37 ± 0.08	13	4.36 ± 1.14	12	17.7 ± 0.6
Regular flakes	8	49.3 ± 4.3	7	43.6 ± 4.4	6	85.4 ± 7.2	9	6.60 ± 0.27	9	0.41 ± 0.07	5	3.04 ± 0.31	12	18.3 ± 1.9
Grade B groats	11	56.8 ± 13.1	12	48.7 ± 15.1	12	108.1 ± 38.2	12	7.21 ± 0.99	13	0.46 ± 0.08	13	4.77 ± 1.84	12	18.7 ± 1.0
Quick flakes	10	40.3 ± 5.2	10	38.3 ± 11.2	10	73.6 ± 13.3	10	6.83 ± 0.98	11	0.37 ± 0.12	9	3.49 ± 0.43	10	18.7 ± 0.7
Flour	12	43.9 ± 1.8	12	38.9 ± 2.3	12	75.7 ± 11.9	13	6.96 ± 0.47	11	0.27 ± 0.10	10	3.83 ± 0.54	11	19.1 ± 1.1

[a] n = Number of replicates.
[b] Mean ± SD.
[c] Protein = N × 5.83.

decorticator No. 3, which did not differ significantly in nickel content from other milled fractions until it had passed through the grinder nor in iron content from the fraction at the flatstone mill. The by-product hulls from decorticator No. 1 were significantly lower ($P < 0.05$) in protein than were the other milling fractions, reflecting the low concentration of hull protein (Fig. 3).

Most of the reduction in nutrient content occurred in the decortication operations. Significant reductions ($P < 0.05$) occurred at each decorticator for iron, at decorticator No. 2 for nickel, at decorticators No. 2 and 3 for zinc and manganese, and at decorticator No. 3 for copper. Iron was the only nutrient that was reduced significantly by the removal of the hulls at decorticator No. 1, which reflects the higher concentration of iron in the hull as compared to that in the groat (Fig. 3). The other nutrients were not significantly reduced until much of the bran, aleurone, and germ had been removed at decorticators No. 2 and 3. Zinc was also significantly reduced ($P < 0.01$) by the flat stone mill or rice huller that knocks off the tips of the grain, and iron, zinc, nickel, and protein were significantly reduced ($P < 0.05$) by the grinding operation. Iron was significantly increased ($P < 0.05$) after passing through the roller mill and the sifting and blending operations, which may indicate contamination through contact with steel equipment. Manganese was also increased ($P < 0.05$) by the sifting and blending process. Copper content was increased by removing grains other than barley at the disk separator.

Liu et al (1974) analyzed barley flour milled on a Miag "multomat" and found lower concentrations of trace minerals in flour than in the whole kernel. A 15% reduction of copper as a result of roller milling was comparable to the finding reported here, but reductions of 4% for manganese, 6% for iron, and 7% for zinc were less than those found in our laboratory. The concentrations of most minerals were lower in the bran than in the tailings and shorts, which contain the germ and aleurone layers. They also reported that minerals were associated with protein-rich fractions of barley. In the present study, analysis of the distribution of protein revealed that much less protein is contained in the hull than in the groat, whereas the six trace elements are more evenly distributed between the two fractions (Fig. 3).

Trace element and protein contents of milled oat fractions and the whole kernel oats from which they were milled are presented in Table III. Both grade A and grade B groats contained significantly higher ($P < 0.05$) levels of the nutrients studied than did the whole kernel oats, except for chromium and for manganese in grade A groats. Manganese content was greater for the grade A groats than for the green oats, but the difference was not significant ($P = 0.15$). Whole kernel oats dehulled on a Plexiglas impact huller consisted of 33.7% hull and 66.3% groat. Analysis of protein and trace element content of these two fractions (Fig. 4) revealed that concentrations of all nutrients except chromium were lower in the hull than in the groat. Therefore, the increase in concentration for all nutrients except chromium can be explained by the fact that the hulls have been removed in the preparation of groats. The concentration of chromium in the hull was not found to be significantly different than that in the groat ($P = 0.211$). Toepfer et al (1972) reported that chromium remained with the endosperm to a greater extent than did other milling fractions excluded from wheat flour.

Grade B groats were not significantly different ($P > 0.05$) from grade A groats for any nutrient except that chromium was found in higher concentration in grade B groats, which also contain more hull than do grade A groats. Regular "old fashioned" rolled oat flakes were not significantly different from the grade A groats from which they were milled except in nickel content, which was significantly reduced ($P = 0.02$) by flaking. Quick cooking flakes were significantly reduced ($P < 0.05$) in iron, manganese, and chromium as compared to the grade B groats from which they were milled. Oat flour was significantly less ($P < 0.05$) in concentration of iron, zinc, manganese, and chromium than were the grade B groats. The cutting process, which loosens previously unremoved hull, could lower the chromium content, which is concentrated in the hull. Perhaps the cutting operation removes part of the seed coat or aleurone layer in addition to the hull, which may be rich in

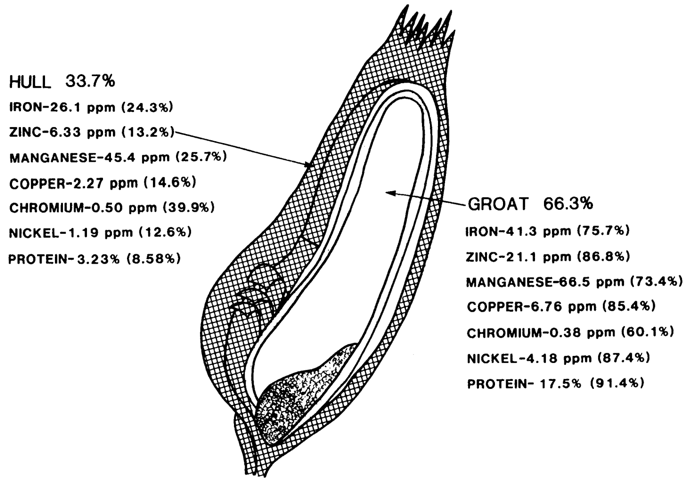

Fig. 4. Trace element and protein concentration and percent of nutrient content in oat hull and groat. The hull is depicted in crosshatch and the groat includes all other fractions.

iron and manganese. Oat flour and quick cooking flakes contained similar protein and mineral concentrations except for iron, which was found in greater ($P = 0.04$) amounts in the flour than in the flakes.

No general conclusions can be drawn for all the nutrients studied when comparing the finished products to the whole grain oats from which they were milled. Regular flakes were significantly greater ($P < 0.01$) than green oats in zinc, iron, copper, and protein content, which were increased by removing the hulls in making grade A groats. Quick cooking flakes exceeded green oats in protein and copper content ($P < 0.05$) and contained a lesser concentration of manganese ($P = 0.04$), although other nutrients were not significantly different. Oat flour exceeded green oats in protein, iron, zinc, and copper content ($P < 0.01$) but contained less chromium and nickel ($P < 0.05$). Ferretti and Levander (1974) reported little change in selenium content as a result of milling of oats.

Reductions in mineral content by milling were not as great for barley as has been reported for wheat (Schroeder 1971, Toepfer 1974, Zook et al 1970). For oats, some minerals were even increased by milling because of the removal of the hull. A greater portion of the bran, aleurone layer, and especially the germ is removed in the milling of wheat than in the milling of barley and oats. Levels of minerals in oats and barley will vary with variety and environmental conditions (Kleese et al 1968, Peterson et al 1975).

Chromium was distributed or affected by milling differently than were other elements. Although standards prepared at the levels investigated in this study could be determined with accuracy, reassessment of the distribution and effect of milling on chromium content in cereals by a method other than atomic absorption would be of interest. Studies are being planned to grow cereal crops hydroponically and to intrinsically label them with ^{51}Cr in order to follow the distribution of and effect of milling on the radionuclide.

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