# Composition and Utilization of Milled Barley Products. I. Gross Composition of Roller-Milled and Air-Separated Fractions[1]

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**ABSTRACT**

Barleys of five varieties were milled by conventional roller-milling and composites of flour streams, comprising 65% of the products, were air-classified. Ash of roller-milled samples was highly correlated with protein, color, free lipids (extractable with petroleum ether), and crude fiber. Free lipids contained mainly nonpolar components (primarily triglycerides). Bound lipids (extractable with butanol following petroleum ether) contained mainly phospholipids and glycolipids. The relation between protein determined by the Kjeldahl and dye-binding methods indicated two groups (with Kjeldahl protein below and above 9.0%) varying in slopes of regression lines. Air fractionation gave a fraction (5% of total products) containing about 15% more protein than the original flour (around 10%). A protein shift was accompanied by a shift in ash, free lipids, and bound lipids.

The most important uses of barley are as grain feed; as malt for manufacturing beverages or malt-enriched food products; as seed; and as human food in the form of parched grain, pearled grain for soups, flour for flat bread, and ground or partly ground grain to be cooked and eaten as porridge (1,2,3). Two main types of barley, depending on the arrangement of grains in the ear, are two-row and six-row. The former predominates in Europe and in parts of Australia; the latter is more resistant to extremes of temperature and is grown in North America, India, and the Middle East. Both types can be malted. In addition, small amounts of hull-less ("naked") barley, that is more easily processed for food, are grown in countries with a primitive form of agriculture.

The barley grain consists of the endosperm and the embryo enclosed within the remains of the original glumes, called the husk. On a dry-matter basis, barley contains 63 to 65% starch, 1 to 2% sucrose, about 1% of other sugars, 1 to 1.5% soluble gums, 8 to 10% hemicellulose, 4 to 5% cellulose, 2 to 3% lipids, 8 to 11% protein (N X 6.25), 2 to 2.5% ash, and 5 to 6% other components (4). In regular barley, the linear starch component comprises 24% of the total starch. A high-amylose (47% of the total starch) barley with small starch granules was recently developed (5). The proteins of whole barley have been studied by most of

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the available methods: solubility and selective precipitation, ultracentrifugation, chromatography including gel filtration, and various forms of electrophoresis (6-14). Barley and malt lipids were studied by Walsh et al. (15) and Banasik and Gilles (16).

Limited information has been published on milled barley products (17-24). Flour produced by conventional roller-milling contains particles of different sizes and compositions. Fine grinding of conventionally milled flour particles followed by air classification can separate, in part, protein from starch in roller-milled flours (25). Air classification of corn, sorghum, wheat, and rice flours was described by Stringfellow et al. (26).

This report is part of an extensive investigation on the composition and utilization of milled barley products. We determined the gross composition of representative barley varieties milled by conventional roller-milling, air-separated the flours into high-protein and low-protein fractions, and evaluated the potential use of the various fractions.

## MATERIALS AND METHODS

### Barleys

Five barleys were used in this study. Some of their characteristics are given in Table I. Primus, grown in South Dakota, is a six-row, white malting variety. Larker, from Casselton, N. Dak., is one of the leading six-row malting varieties for the Red River Valley in the United States. Paragon, also from Casselton, N. Dak., is a six-row, aleurone-blue barley, released as a malting variety in Canada. Betzes, grown in Aberdeen, Idaho, is a two-row, white malting variety, grown extensively in Montana, Colorado, and Idaho. Atlas, a six-row coast-type barley formerly used for malting in England and considered poor in malting quality, is now used to a limited extent for malting in California. The sample was grown in the Sacramento Valley, Calif.

### Milling

The samples were milled on a Miag "Multomat." The flow sheet is shown in Fig. 1. The barley samples were tempered 30 min. before milling with 0.5% water. The feed rate was set at approximately 400 g. per min. Fourteen fractions were collected. The break shorts, reduction shorts, and red dog fractions were combined and ground on an Alpine pin mill at 15,000 r.p.m. The ground material was sifted through a 10XX sieve, and the throughs (tailings flour) were mixed with the

TABLE I. SOME CHARACTERISTICS OF BARLEYS USED IN THE MILLING STUDY

| Variety | Crop Year | Kernel Weight mg. | Kernel Size Assortment: Over 7/64 % | Over 6/64 % | Over 5/64 % | Through 5/64 % | Plump Barley % | Moisture % | Agtron Color |
|---|---|---|---|---|---|---|---|---|---|
| Primus | 1968 | 27.2 | 7.7 | 43.3 | 41.0 | 8.0 | 51.0 | 10.0 | 48 |
| Larker | 1967 | 33.0 | 18.5 | 65.6 | 14.4 | 1.5 | 84.1 | 11.0 | 84 |
| Paragon | 1968 | 31.8 | 6.0 | 57.4 | 36.6 | 0 | 63.4 | 11.1 | 80 |
| Betzes | 1967 | 35.2 | 33.0 | 57.5 | 8.4 | 1.1 | 90.5 | 10.5 | 90 |
| Atlas | 1965 | 38.4 | 30.6 | 54.3 | 15.0 | 0.1 | 84.9 | 9.0 | 66 |

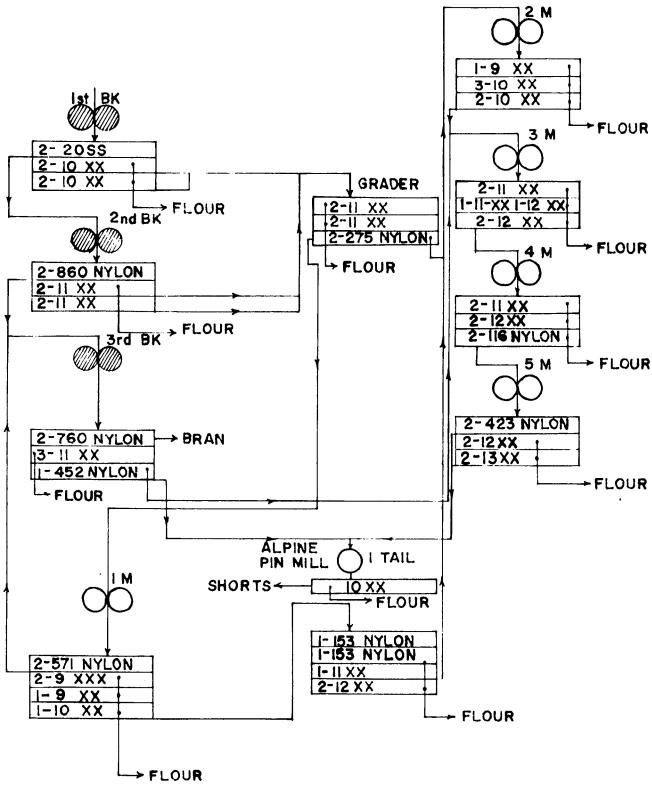


**Fig. 1. Flow sheet of Miag "Multomat" used to mill barley samples.**

original flour fractions to a straight-grade flour of 65% extraction. The scheme is summarized in Fig. 2.

#### Air Classification

Straight-grade flours (65% extraction) were fractionated into high- and low-protein streams in a Pillsbury Laboratory Model No. 1 classifier according to a scheme given elsewhere (27). The fractionation procedure involved removing

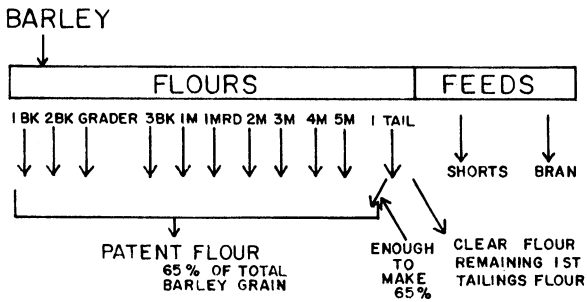


**Fig. 2. Streams used in preparing a patent barley flour.**

high-protein fractions B and C and low-protein fractions D and E from the original flour A. Residual coarse flour was designated EE.

#### Analytical Determinations

Analytical determinations were made on milled products or on material ground to pass a 40-mesh screen of a Micro-Wiley mill. Moisture, ash, Kjeldahl nitrogen, and crude fiber were determined as described in AACC Approved Methods (28). Kjeldahl-N was converted to protein by the factor 6.25. Protein by a dye-absorption method (29) and colors of barley and milled barley on an Agtron were determined according to manufacturer's instructions. Particle size (average diameter in $\mu$) was determined in a Fisher Sub-Sieve Sizer (No. 14-411) as described by Croteau (30). The free lipids were extracted in a Goldfish extractor with petroleum ether (b.p. 35° to 60°C.). Petroleum ether was allowed to evaporate from the extracted products at room temperature, and the products were re-extracted with water-saturated butanol (31). The butanol extract (bound lipids) was filtered, evaporated under reduced pressure, and redissolved in petroleum ether.

Thin-layer chromatography (TLC) was performed on 100 $\gamma$ of free or bound lipids. The lipids were fractionated on glass plates coated with Silica Gel G and identified according to a previously published procedure (32).

## RESULTS AND DISCUSSION

Some chemical characteristics of the barleys used in the milling study are summarized in Table II. For calculation of carbohydrates (by difference), bound lipids were not included. The barley samples varied widely in protein and crude fiber contents. The ash of Atlas was significantly lower than that of the other varieties. Differences in free and bound lipids were small.

Data on yield and gross composition of the milled barley products are summarized in Figs. 3 and 4. To evaluate the results, regression equations and correlation coefficients were calculated (Table III). Data on tailings flour, shorts, and bran were not included in the calculations. The protein content was positively correlated with ash content ($r = 0.733$). The low-protein Atlas variety had lower protein content (at corresponding ash content) than the other four varieties tested. In all varieties, samples of 1st break flour had higher protein content than expected from their ash content. When ash vs. protein correlation was calculated excluding 1st break samples, the correlation increased ($r = 0.891$). The correlation between Agtron color values vs. ash contents was negative; the slope was curvilinear, and a

TABLE II. SOME CHEMICAL CHARACTERISTICS[a] OF BARLEYS USED IN THE MILLING STUDY

| Variety | Ash % | Protein (N × 6.25) % | Lipids Free % | Lipids Bound % | Crude Fiber % | Carbohydrates (by difference) % |
|---|---|---|---|---|---|---|
| Primus | 2.29 | 10.5 | 1.56 | 1.33 | 5.4 | 66.2 |
| Larker | 2.30 | 10.7 | 1.59 | 1.37 | 4.2 | 67.2 |
| Paragon | 2.51 | 9.4 | 1.51 | 1.26 | 4.2 | 68.4 |
| Betzes | 2.23 | 10.9 | 1.47 | 1.49 | 3.6 | 67.8 |
| Atlas | 1.87 | 7.7 | 1.47 | 1.27 | 5.0 | 69.9 |

[a]Expressed on a 14% moisture basis.

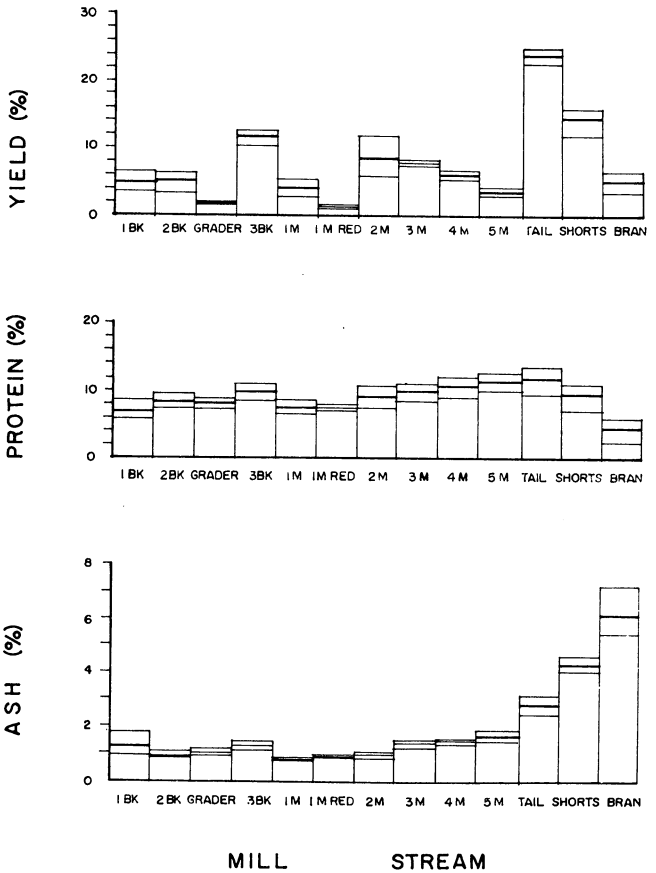


**Fig. 3. Yield, protein, and ash contents of milled barley products. BK, break; M, middlings; RED, reduction; and TAIL, tailings. For each stream, the top and bottom thin lines denote the range and the heavy middle line the average of determined parameters.**

transformation to a log (Agtron color) vs. linear (ash) relation gave a negative correlation ($r = -0.633$). Free lipid contents increased as ash increased; the correlation coefficient was $r = 0.826$.

Ash and crude fiber contents were positively correlated ($r = 0.689$). As expected, carbohydrate content (calculated by difference) increased as ash (or correlated with it protein, free lipid, or crude fiber) contents decreased.

Among the correlation coefficients given in Table III, those of ash with protein, Agtron color, and crude fiber were the lowest. The data indicate that distribution of those components or attributes in the grain tissues varied. Consequently, calculation of extraction rates on the basis of composition can vary according to the parameter used to determine extraction.

No consistent relation was found between free and bound lipids. With increase in extraction (as assessed by ash, color, or crude fiber determination), total lipid contents increased; but the ratio of bound to free lipids decreased, as the germ and aleurone lipids were richer than the endosperm lipids in nonpolar components.

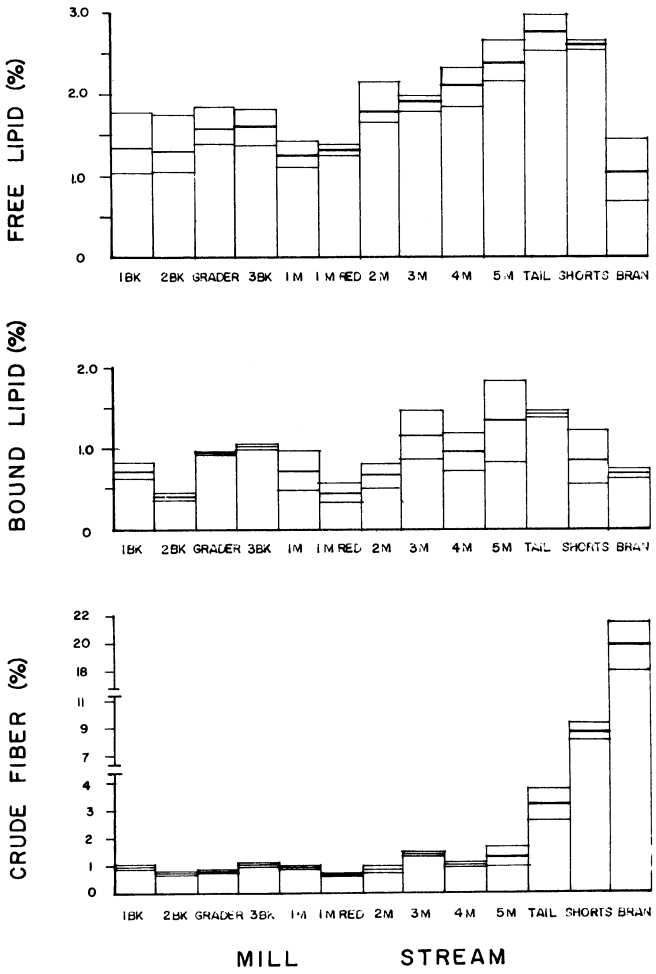


**Fig. 4. Free lipid, bound lipid, and crude fiber of milled barley products. Legend as in Fig. 3.**

Results of TLC of barley lipids are illustrated in Figs. 5 and 6. Free lipids of whole barley (Fig. 5) contained mainly nonpolar components (primarily triglycerides) that were fractionated by chloroform. The amount of polar components in free lipids was negligible and much smaller than in wheat (32). Bound lipids, extracted with water-saturated butanol following petroleum ether (Fig. 6), contained (as in wheat) mainly polar components and small amounts of nonpolar components. Unlike that in wheat, the glycolipids comprised a smaller proportion than the phospholipids in bound barley lipids.

Separation by TLC (not shown in this report) indicated that free nonpolar lipids in milling streams were mainly triglycerides and smaller amounts of sterol esters, diglycerides, monoglycerides, and fatty acids. No consistent differences in lipids in milling streams were observed, except that tailings, shorts, and bran had less sterol

TABLE III. REGRESSION EQUATIONS AND CORRELATION COEFFICIENTS FOR COMPONENTS IN MILLED BARLEY PRODUCTS

| Relation | Regression Equations | Correlation Coefficient (r) |
|---|---|---|
| Roller-milled products | | |
| Protein (y) vs. ash (x) | | |
| All samples | y = 4.18 + 4.23 x | 0.733*** |
| Without 1 Bk flour | y = 3.94 + 4.86 x | 0.891*** |
| Log Agtron color vs. ash | y = 1.91 − 0.17 x | −0.633*** |
| Free lipids vs. ash | y = 0.32 + 1.23 x | 0.826*** |
| Crude fiber vs. ash | y = 0.27 + 0.60 x | 0.689*** |
| Dye-binding protein vs. Kjeldahl protein | | |
| Below 9.0% | y = 6.65 + 3.74 x | 0.923*** |
| Above 9.0% | y = 11.60 x − 62.16 | 0.843*** |
| Air-Fractionated Products | | |
| Ash (y) vs. protein (x) | | |
| All samples | y = 0.63 + 0.08 x | 0.713*** |
| Without EE | y = 0.40 + 0.09 x | 0.868*** |
| Free lipids vs. protein | | |
| All samples | y = 0.71 + 0.11 x | 0.831*** |
| Without EE | y = 0.49 + 0.12 x | 0.970*** |
| Bound lipids vs. free lipids | y = 0.10 + 1.56 x | 0.907*** |

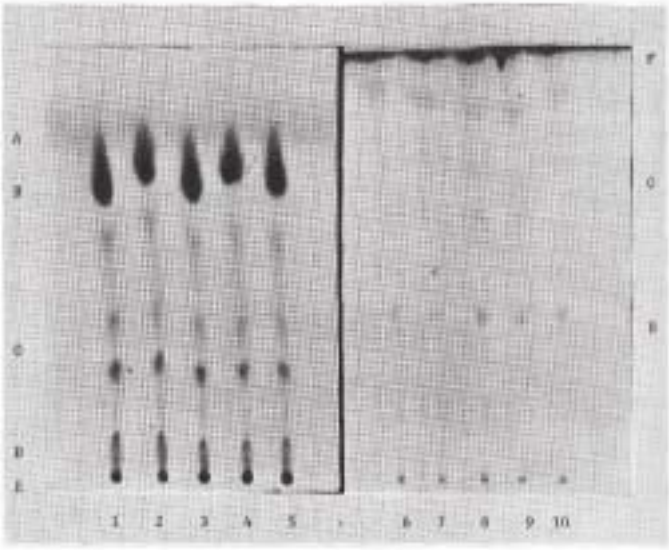


**Fig. 5. Thin-layer chromatography of 100 γ-free (petroleum ether extractable) lipids from five barley varieties. Spots 1 and 6 from Primus, 2 and 7 Larker, 3 and 8 Paragon, 4 and 9 Betzes, and 5 and 10 Atlas. Spots 1 to 5 separated with chloroform, 6 to 10 with chloroform:methanol:water (65:25:4, v./v./v.). Tentatively identified as: A, sterol esters, B, triglycerides, C, diglycerides, D, free fatty acids, E, monoglycerides and unfractionated polar lipids, F, unfractionated nonpolar lipids, G, glycolipids, and H, phosphatidyl choline.**

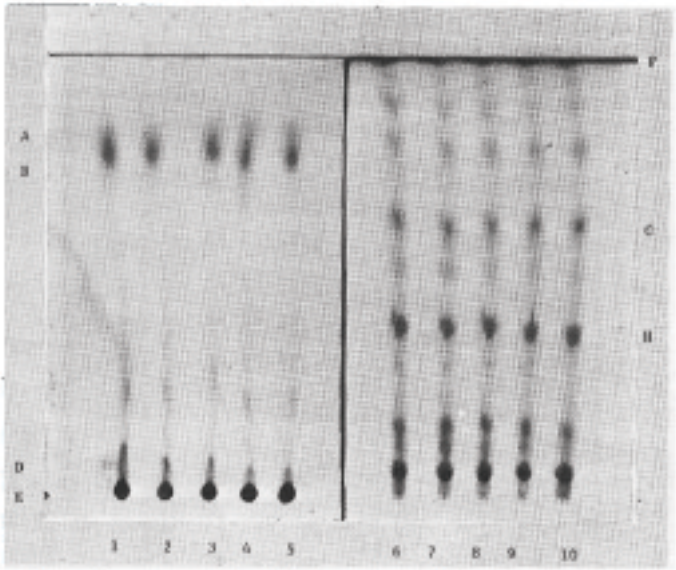


**Fig. 6. Thin-layer chromatography of 100 γ-bound (water-saturated butanol following petroleum ether) lipids from five barley varieties. Legend as in Fig. 5.**

esters and more free fatty acids and diglycerides than the low-ash milling streams. Free lipids in milling streams were low in polar components; the smallest amounts of polar lipids were in tailings, shorts, and bran. Bound lipids in shorts and bran were higher in triglycerides, and lower in polar components, than bound lipids in low-ash milling streams.

A comparison is shown in Fig. 7 between protein determinations of all mill streams by the Kjeldahl and dye-binding procedures. The data seem to indicate two groups of samples, those with Kjeldahl protein contents below and those above 9.0%. The regression equations and correlation coefficients for the low-protein group were $y = 6.65 + 3.74\ x$ and $r = 0.923$, and for the high-protein group $y = 11.60\ x - 62.16$ and $r = 0.843$. This is in general agreement with the results on wheat and milled wheat products reported by Banasik and Gilles (33).

Some physical and chemical characteristics of air-fractionated barley flours are summarized in Figs. 8 and 9. The relatively high crude fiber content of fraction EE indicates that it was rich in bran particles. In all five varieties, the protein-rich fraction B comprised over 5% of the total pin-milled flour. Fraction B contained, on the average, about 15% more protein than the original flour A. Two major fractions (D and E) were relatively low in protein (about 4% less than A). The residual flour (EE) was consistently higher in protein than the original flour A. A shift in protein content was accompanied by shifts in ash and free lipids. The correlation coefficient between ash and protein for all samples was 0.713, and increased to 0.869 if EE fractions were not included in calculations (Table III). Correlation between free lipids and protein was 0.831 and increased to 0.970 if EE samples were excluded. Free and bound lipids were positively correlated ($r = 0.907$). The correlation between ash and crude fiber for all samples was $r = 0.390$; if the high crude fiber EE samples were not included in calculations, the correlation

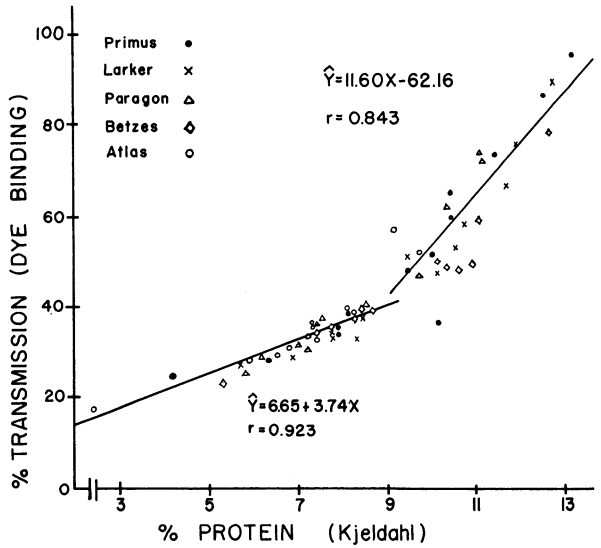


**Fig. 7. Scatter diagram and regression lines for correlation between Kjeldahl protein and transmission by the dye-binding method of milled barleys.**

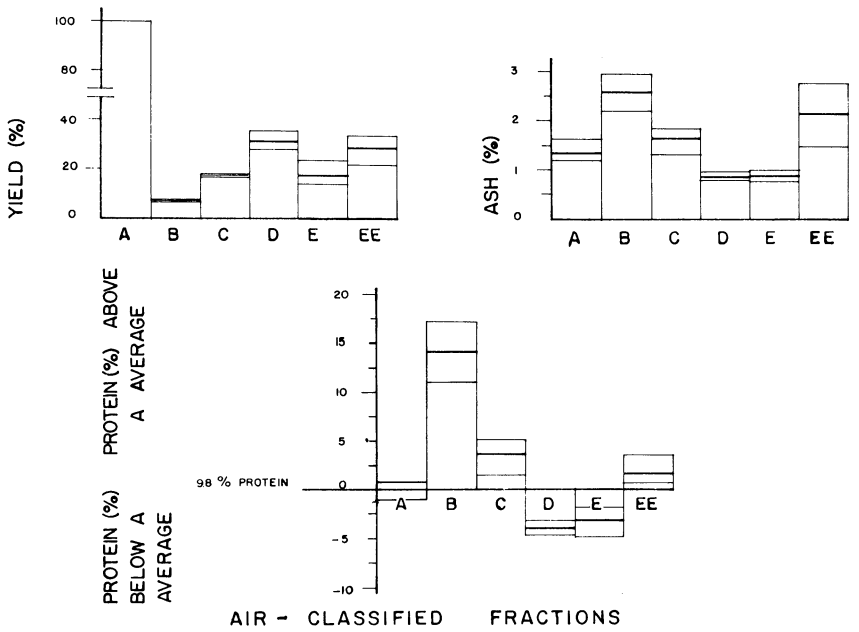


**Fig. 8. Yield, ash, and protein contents of air-fractionated flours. A, original; B and C, high-protein fractions; D and E, low-protein fractions; and EE, residual flour. For each fraction, the top and bottom thin lines denote the range and the heavy middle line the average of determined parameters. (Protein ranges and averages are compared with the average protein of A samples.)**

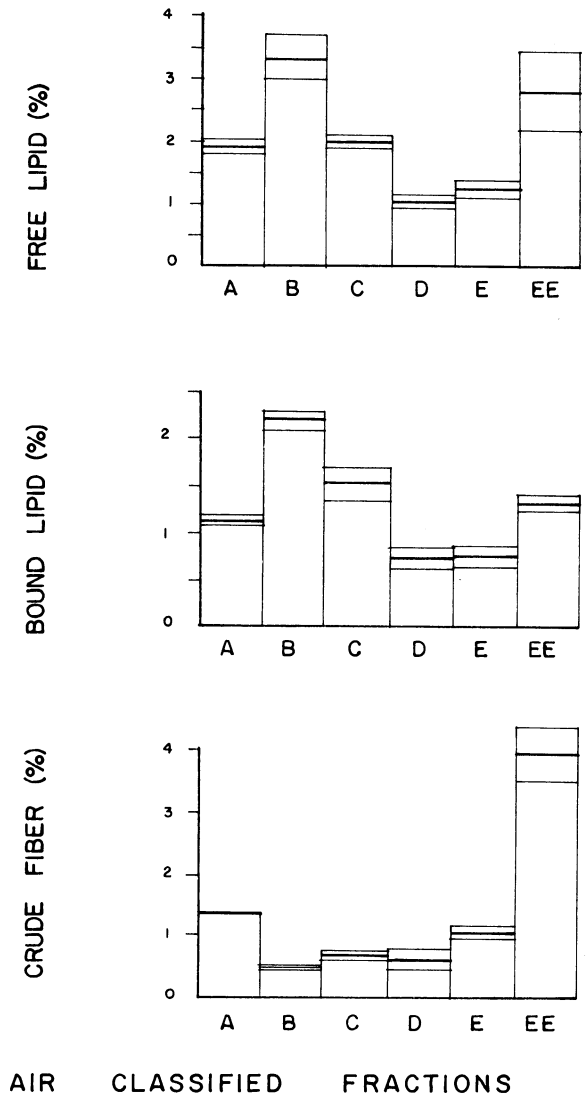


**Fig. 9. Free lipid, bound lipid, and crude fiber of air-classified flours. Legend as in Fig. 8.**

was not statistically significant at the 0.05% level. Free and bound nonpolar lipids in air-fractionated flours were similar in composition (as assessed by TLC, not shown in this report) to nonpolar components in conventionally roller-milled flours. Fractions E and EE contained fewer (than other fractions) bound polar components with high $R_f$ values (mainly digalactosyl diglycerides and phosphatidyl ethanolamine) and slightly more slow-moving components (presumably lysophosphatidyl choline and phosphatidyl serine).

The large shift in protein during air fractionation indicates new possibilities of utilizing milled barley products. The high-protein fraction would be a useful raw material in production of nutritional preparations low in carbohydrates but rich in proteins, minerals, and lipids. The low-protein fraction may be particularly useful as an adjunct in the brewing industry. Studies on utilization of air-classified barley products for such purposes were reported elsewhere (34).

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