

Lipid Changes During Storage of Milled Hulless Barley Products

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Waxy hulless barley is being utilized as a food ingredient because of its naturally elevated levels of soluble fiber (β -glucan). This soluble fiber reduces lipids in mildly hypercholesterolemic men and women (Behall et al 2004). In developing foods that contain barley, the stability of the raw material during storage is important and little is known about the storage stability of barley that has been processed into flours or steam-rolled flakes.

Flavor deterioration in cereal grain flours and flakes during storage is mostly caused by lipid oxidation, although other processes such as reactions of phenolics should also be included. There are two types of reactions of lipids that contribute to lipid degradation and, ultimately, to off-flavors and odors. These reactions are hydrolytic degradation of the triacylglycerides (TG) and phospholipids (PhL) due to activity of lipase with the release of free fatty acids and the following oxidation of released polyunsaturated fatty acids (PUFA). Free fatty acids impart a bitter flavor to foods, while products of oxidation are the substances that are responsible for rancidity.

Barley contains 2–4% lipid (Morrison 1993). A majority of the lipid is unsaturated fatty acids (Palmer 1989) of which \approx 57% is linoleic acid and 5% is linolenic acid (Morrison 1978). PUFA readily undergo oxidation, both enzymatic and nonenzymatic, producing lipid peroxides that decompose, producing aldehydes, ketones, and alcohols. Many of these secondary products of oxidation are volatile and responsible for undesirable odors while others undergo reactions producing compounds with undesirable flavor. The hydroperoxides formed from linoleic acid, the major PUFA found in barley, decompose rapidly, producing many products that have rancid flavors.

Two enzymes play a role in the deterioration of lipids: lipase and peroxidase. Lipases release free fatty acids from TG and PhL, while peroxidases are responsible for the conversion of PUFA to lipid peroxides. Lipases can be inactivated by heat treatment but in oats this inactivation induces nonenzymatic oxidation (Lehtinen et al 2003). The degradation of the peroxides leading to the undesirable odors and flavors is proceeded by a free radical mechanism. Barley contains high concentrations of vitamin E (Peterson and Qureshi 1993), a free radical scavenger that will reduce the formation of undesirable odors and flavors resulting from the degradation of peroxides.

As a relatively new product, little information is available on the storage characteristics of processed barley. This study was initiated to monitor lipid degradation in milled barley flours and a steam-rolled barley flake under both accelerated and standard conditions.

MATERIALS AND METHODS

Milling

Merlin waxy hulless barley provided by WestBred LLC of Bozeman, MT, was milled at Roman Meal Milling Co. (Fargo, ND). Commercial quantities of six experimental treatments were produced (Fig. 1). Whole grain was ground with a hammer mill fitted with a 4/64-in. screen producing whole grain barley meal (WB). Whole grain was pearled to remove 20% of the outer grain layer referred to as pearlings (PL) and the pearl barley was hammer-milled (4/64-in. screen) producing a pearled and ground barley flour (PG). A portion of the PG was sieved using a U.S. No. 100 mesh to produce two fractions: 1) particle size >150 μ m (HF), 2) particle size <150 μ m (LF). A barley flake (FL) was prepared by cutting, steaming, and flaking the whole grain.

Sampling and Storage

The six treatments were vacuum-sealed in plastic bags (4 mil) (200 g/bag for each treatment \times storage temperature \times storage period) (model 18011/SAM, Dazey Vacuum Seal-a-Meal Industrial Airport, KS) and placed in dark chambers at 4, 25, and 37°C. Samples stored at 37°C were removed for analysis every two weeks for three months. Samples stored at 4 and 25°C were removed after 8, 28, 36, 44, and 52 weeks.

Chemical Analyses

Chemical analyses were performed on all treatments before storage using Approved Methods (AACC International 2000): moisture (44-15A), starch (76-12), total lipid (30-25), β -glucan (32-22), total, soluble, and insoluble fiber contents (32-07), and protein (46-12). Alkaline extract viscosity was determined according to Ullrich et al (1981). Samples (0.5 g) were extracted with 10 mL of sodium carbonate-bicarbonate buffer (pH 10.0) and measured by cone-plate viscometry (Wells-Brookfield LV, Brookfield Engineering Laboratories, Stoughton, MA). Free fatty acid concentration was determined from a chloroform-methanol extract (colorimetric copper soap method) (Shipe 1980). MDA concentrations were determined by the TBA-MDA method (Draper et al 1993) using an HPLC system (Waters, Milford, MA) with a C18 μ Bondapak column and a 5 mM phosphate buffer (pH 7.0) with 15% (v/v) acetonitrile and 8% (v/v) tetrahydrofuran mobile phase. The TBA-MDA complex was detected at 546 nm.

Statistics

Data were analyzed using data analysis software (SAS Institute, Cary, NC). Analysis of variance, Duncan's multiple range test ($P = 0.05$) and t -testing were used to determine differences between treatments.

RESULTS AND DISCUSSION

Chemical Components

There were no significant differences in the chemical composition of the WB and FL (Table I). However, the viscosity of an alkaline extract from the FL was higher than the WB. The pearling and sieving processes were selected to produce flours with varying lipid and fiber concentrations. The PL had the highest

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lipid and insoluble fiber concentration and the lowest starch, soluble fiber, and β -glucan concentration. The PG had lower lipid and insoluble fiber than the WB but higher starch, soluble fiber, and β -glucan. Upon sieving the PG, two very different flours were produced. The HF had lower lipid and starch concentration than the PG but higher fiber and extract viscosity. The LF had a lipid concentration similar to the PG, but higher starch and lower fiber and extract viscosity than the PG.

Free Fatty Acids

The PL had the highest overall concentration of free fatty acids (FFA) before storage and during all storage periods at all three storage temperatures (Fig. 2). This is partly explained by the high lipid concentration (12.8%) and the fact that lipase is found in the outer layers of the barley grain (Kaukovirta-Norja et al 1998).

An increase in FFA was observed during storage for all treatments at each of the three storage temperatures (Fig. 2). Samples stored at 25°C had the greatest increase and those stored at 4°C had the lowest increase. At all three temperatures, the greatest increase was in the PL and WB treatments and the lowest increase was observed in the FL.

Free fatty acid concentration on a mg/g of sample basis was converted to mg/g of lipid basis to remove the confounding effect of lipid concentration. Before storage, the LF had the highest level of FFA/g of lipid (85.3) and the FL (27.7) had the lowest. After 12 weeks of storage at 37°C and 52 weeks at 4 and 25°C, the PL had the highest level of FFA/g of lipid increasing from 63.8 to 111.7, 109.2, and 199.2, respectively. In the final storage period at all temperatures, the FL still had the lowest concentration of FFA (36.3mg/g of lipid).

Malondialdehyde

The increase in MDA concentration observed in all samples at 4 and 25°C was similar (Fig. 3). MDA increased at each storage period up to 44 weeks and then decreased at 52 weeks. Most of the samples stored at 37°C increased in MDA during the first two-week period and then decreased or were unchanged. MDA concentration has decreased with time in stored meat and fowl (Igene et al 1979; Farouk and Wieliczko 2003) and this decrease has been attributed to the reactivity of MDA with free amino groups resulting in MDA complexes (Esterbauer et al 1991).

The increases at 37°C were significantly less than the increases observed at 4 and 25°C. The PL consistently had the lowest concentration of MDA at all storage periods and temperatures, even though the PL had the largest concentration of FFA at all storage times and temperatures. The outer layers of barley contain the majority of the phenolics (Zielinski and Kozłowska 2000) including high levels of hydroxycinnamic and ferulic acid (Hernanz et al 2001). These phenolics, along with vitamin E, may have a greater inhibitory effect on oxidation of unsaturated lipids found in the pearlins, resulting in a lower MDA concentration than found in the other treatments. In addition, barley peroxidase, a class III peroxidase (Howes et al 1999), uses lipid hydroperoxides as a substrate (Kvaratskhelia et al 1997) and may be removing hydroperoxides before they have a chance to decompose, producing MDA.

All of the treatments stored at 25°C, except the PL, had a detectable rancid odor (informal sensory) after 44 weeks of storage. The odor was stronger after 52 weeks of storage. This corresponds to the storage periods in which MDA concentration peaked and subsequently decreased. However, this was not observed in the samples stored at 4°C.

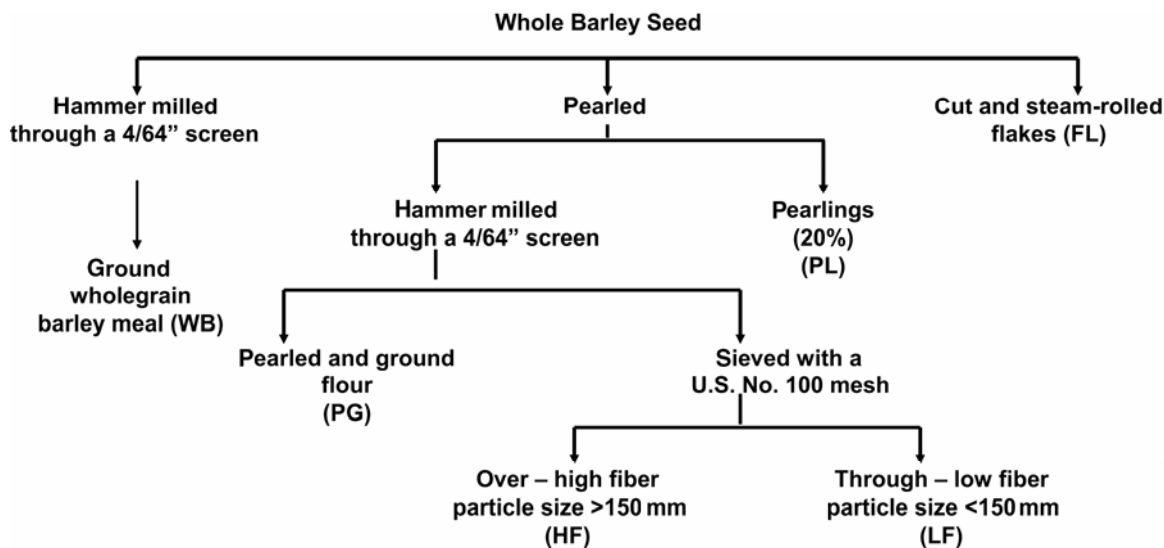


Fig. 1. Commercial milling procedures used to produce five barley flours and the flakes.

TABLE I
Chemical Characteristics of Hulless Barley (cv. Merlin) Milled Flours and Flakes^a

	Whole Grain Barley Meal (WB)	Pearled Flour (PG)	Sieved Flour >150 mm (HF)	Sieved Flour <150 mm (LF)	Pearlings (PL)	Flakes (FL)
Moisture (%)	8.3a ^a	7.7b	7.8b	7.4c	6.6d	7.5c
Protein (% dwb)	14.9b	12.7c	12.3d	12.1e	23.9a	14.8b
Lipid (% dwb)	3.8b	1.8c	1.3d	1.6c	12.8a	3.9b
Starch (% dwb)	51.1d	58.5b	54.9c	60.8a	11.2e	52.4d
Insoluble fiber (% dwb)	9.8b	7.3c	7.8b	4.9d	27.3a	9.6b
Soluble fiber (% dwb)	6.2b	6.6b	9.8a	5.2c	4.4c	6.3b
Total fiber (% dwb)	16.0b	13.9c	17.6b	10.1d	31.7a	15.9b
β -glucan (% dwb)	6.1b	6.4b	8.9a	4.8c	2.8d	6.2b
Alkaline extract viscosity (cP)	19.7c	31.6b	51.7a	16.1d	4.8e	30.5b

^a Means in a row followed by the same letter are not significantly different ($P = 0.05$).

CONCLUSIONS

Changes in FFA and MDA in samples stored at 37°C did not correspond to the changes observed in samples stored at 4 and 25°C. Storage at 37°C was chosen to accelerate lipid degradation to predict the stability of these barley samples under normal conditions. Accelerated shelf life testing uses increased temperatures and sampling frequency to obtain data on storage stability of products in a relatively short period of time (Ragnarsson and Labuza 1977).

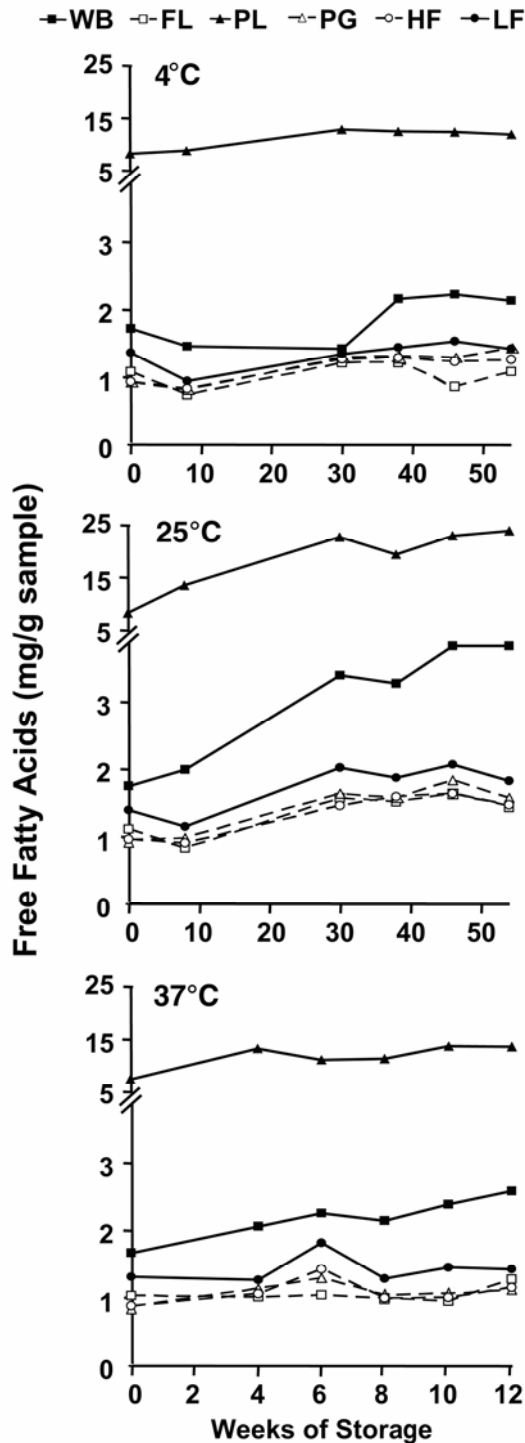


Fig. 2. Free fatty acid content of treatments stored at 4, 25, and 37°C. WB, whole grain meal; PG, pearled and ground flour; PL, pearlings; HF, pearled and ground flour sieved with a U.S. No. 100 mesh, particle size > 150 mm; LF, pearled and ground flour sieved with a U.S. No. 100 mesh, particle size < 150 mm; FL, whole grain, cut and steam-rolled flakes.

With increasing temperatures, reactions that may not occur readily at lower temperatures may arise. Thus, the FFA released may decompose more rapidly, resulting in lower concentrations. At elevated temperatures, FFA may also undergo reactions that are not normally present at lower temperatures, leading to different products and a reduction in the concentration of MDA. Furthermore, MDA is very reactive, and the elevated temperatures may have resulted in reaction of MDA, making it undetectable in the method used for its quantification.

After 12 weeks, FFA levels of all samples were significantly below the FFA levels observed in the samples stored at 25°C for 30 weeks or more. This suggests that the accelerated storage conditions and sampling frequency require modification if the results of accelerated storage conditions are to mimic lipid deterioration that occurs during normal storage.

MDA levels increased only slightly in the samples stored at 37°C compared with the other storage temperatures. A significant increase in MDA was observed in samples stored at 25°C for 44 weeks or longer. This may be related to the rancid odor detected in these samples.

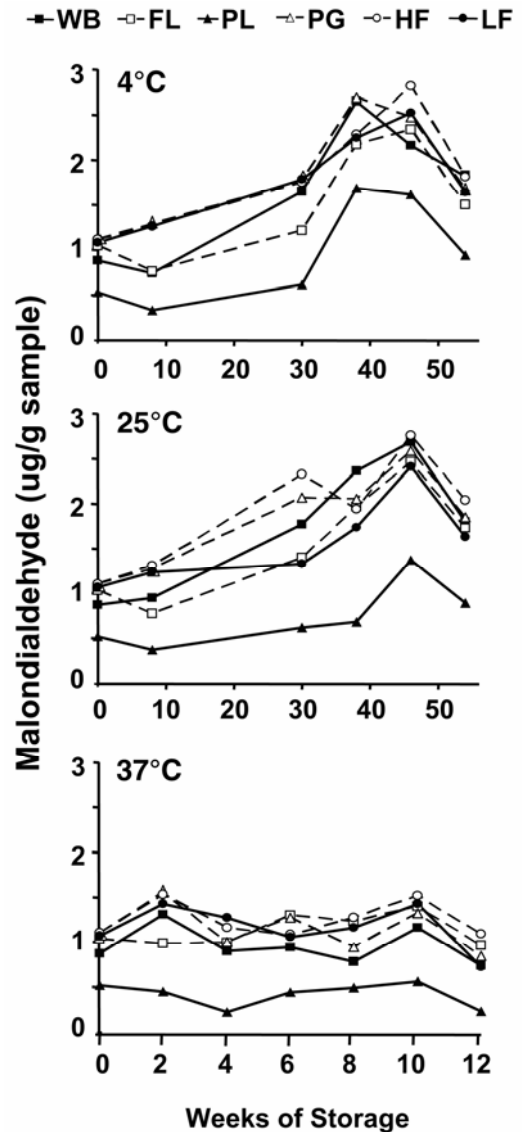


Fig. 3. Malondialdehyde content of treatments stored at 4, 25, and 37°C. WB, whole grain meal; PG, pearled and ground flour; PL, pearlings; HF, pearled and ground flour sieved with a U.S. No. 100 mesh, particle size > 150 mm; LF, pearled and ground flour sieved with a U.S. No. 100 mesh, particle size < 150 mm; FL, whole grain, cut and steam-rolled flakes.

A rancid odor was not detected in the pearlings (PL) after 52 weeks of storage, even though this treatment had the highest level of free fatty acids and the lowest level of malondialdehyde at all storage temperatures.

The processing may have inactivated lipase in the flakes (FL), which had a lower concentration of free fatty acids and malondialdehyde compared with whole grain barley meal (WB) which had a similar lipid concentration.

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