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Physicochemical Assessment of Quality Characteristics of Extruded Barley under Varied Storage Conditions

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상이한 조건하에서 저장한 압출보리의 품질특성에 관한 이화학적 평가

제 1 보 : 지방질 산화

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Abstract

Raw and extruded barleys prepared by three different conditions were powdered and stored for four months at ambient (25 °C) and accelerated temperatures (40 °C) with A_w of 0.31 and 0.71, respectively. The stability of the these samples with respect to lipid oxidation was studied. The lipid oxidation of all samples, as measured by the lipid diene conjugation of the extracted oil, increased with increased A_w and temperature and with the storage time elapsed. The ratio of unsaturated to saturated fatty acids (U/S ratio) tended to decreased as the A_w and temperature were increased. The raw sample had a greater increase in lipid conjugation diene but a decrease in U/S ratio than the extruded samples. The extruded sample containing the added sucrose had greater lipid stability than the other extruded samples. Lipid free-amino group content in all samples decreased with increased A_w and temperature.

Introduction

One of the major chemical reactions that takes place during food processing and storage is deterioation caused by lipid oxidation and non-enzymatic browning. These reactions, during storage, are dependent on such factors as moisture content, storage temperature and storage atmosphere. The effects of these factors on the quality of dry foods has been investigated by many authors, including studies of lipid oxidation and non-enzymatic browning of navy bean powder[1] during storage at accelerated temperature, storage stability studies of whole milk powder under different oxygen concentration[2,3], changes in lipid oxidation and nitrogenous compounds on freeze-dried turkey muscle during storage[4], lipid oxidation and nutritional changes in stored herring meal for a year at 20 °C and with a moisture content of about 6%[5], and studies of browning caused by the interaction between oxidized oil and protein in dried-frozen tofu[6].

The effect of water activity or equilibrium relative humidity on the rate of oxygen uptake of dry foods and model systems was studied by Labuza *et al.*[7,8] and Heidelbaugh *et al.*[9] The results indicate that in general the rate of oxidation increased with water activity at higher water activities. At very low water activity the rate of oxidation decreased with water activity until it reaches a minimum.

At present, very little of the literature deals with the effect of temperature and water activity on the lipid oxidation of breakfast cereals during storage. In this studies, extruded barley prepared under three different conditions were stored at ambient (25°C) and accelerated temperatures (40°C) with the water activities of 0.31 and 0.75, respectively. The purpose of this research was to study the stability of extruded barley with respect to lipid oxidation under varied conditions of temperature and water activity.

Materials and Methods

Preparation of extruded barley

Extruded barley was obtained from the Kellogg Company (Battle Creek, MI 49016, U.S.A.). The extruder used is a co-rating double screw Creusot-Loire apparatus of about 20 Kg dry matter output per hour. Three experimental runs were made by the following characteristics: run 1, without water addition; run 2, the water content of the feed in the extruder is about 14% by weight; run 3, the sucrose content of the feed in the extruder is about 5% by weight. The extrusion-cooking time is, a residence time of the feed in the apparatus, 60 sec at 210°C, and the rotation of the screw is 120 rpm.

The extruded and raw barley were ground in a Fitzmill (Model D, Fitzpatrick Company, Chicago) to pass through No. 1 standard sieve with Tyler equivalent of 16 mesh.

Storage conditions

Powders obtained as described above were employed in the storage studies. Three hundred gram samples were weighed into beakers and stored in desicators where water activities of 0.31 and 0.75, which obtained according to the method of saturated salt solutions[10] and at a uniform temperatures of 25°C and 40°C, respectively. Samples were stored for four months and analyzed at one month interval for the various physical and chemical parameters of quality. Initial quality parameters were measured on the freshly prepared products.

Lipid extraction and analyses of lipid oxidation

Total lipids were extracted by homogenizing in Waring blender with a mixture of chloroform-methanol-water (1.0:1.0:0.9, v/v) as described by Bligh and Dyer[11]. The lipid extracts were evaporated to dryness under vacuum, redissolved in diethyl ether, and transferred to vials and stored under nitrogen at -15°C until analysis.

The conjugated dienoic acid of unsaturated linkages present in the extracted lipids were measured according to AOCS method[12]. Fatty acid composition were determined by gas-liquid chromatography as described in the previous paper[13]. From the data of GLC analysis, the ratios of the unsaturated fatty acids to the saturated fatty acids were calculated. The content of lipids containing free-amino groups were determined spectrophotometrically at 340 nm by the procedure of Siakotos[14].

Results and Discussion

Lipid oxidation as measured by diene conjugation

Fig. 1 shows the effects of varying the water activities, temperatures, and the storage time on lipid oxidation as measured by lipid diene conjugation absorbance at 233 nm, for the raw and extruded barley powders.

From the data, it was found that as the water activity increased from 0.31 to 0.75 there was a resultant increase in the lipid oxidation of each of the samples. This means that there was a multistage trend in the relationship of lipid oxidation to changes in the A_w of the system. This trend is in agreement with many authors described in the literature[15-17]. The recorded increase in lipid oxidation, when A_w was increased from 0.31 to 0.75 may also be explained according to Labuza[18] who speculated that such high A_w water may be promoting catalyst mobility and /or new catalyst surface exposure.

In all of the samples tested, an increase in temperature from 25°C to 40°C led to an increase in lipid oxidation. Chemical reactions generally are accelerated when temperatures are increased. This is

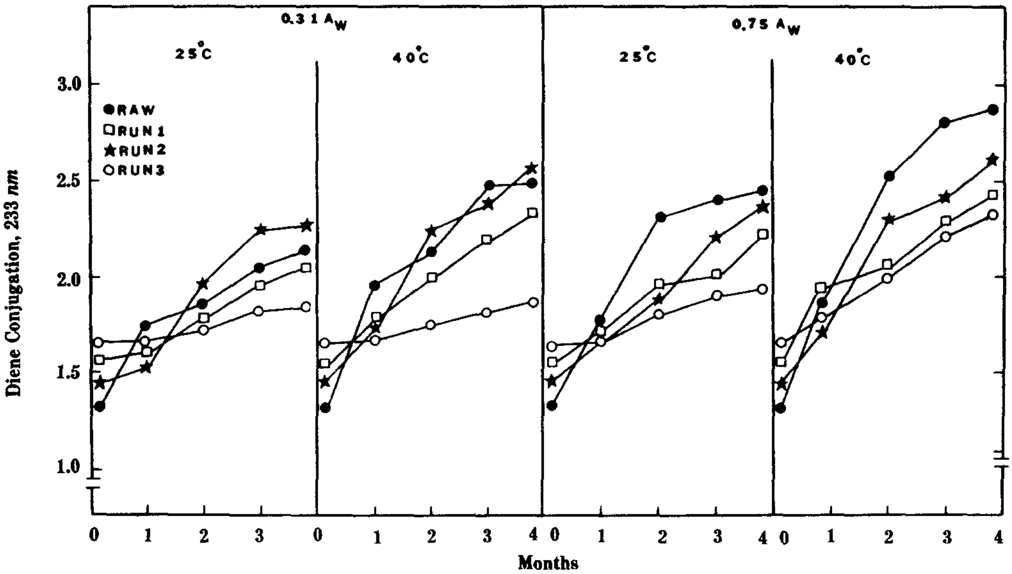

Fig. 1. Effects of water activities, temperatures and storage time on the lipid conjugation diene value of raw and extruded barley powders

even more evident for the initiation process of lipid autoxidation. Accordingly, any input of thermal energy is likely to increase oxidation as is demonstrated graphically in the Fig. 1. Apart from supplying greater energy for the oxidation processes, the high storage temperature of 40 °C may also have acted to increase the rate of oxygen diffusion into the system therefore promoting increased lipid oxidation. This would have been particularly important in view of the raw and extruded barleys during processing and storage.

Table 1 shows the rate of oxidation (the increase in lipid conjugated diene absorbance per one month interval) for the raw and extruded barley powders. The raw sample had lower oxidation status than the extruded samples at the initial stage. But the raw sample had a higher rate of oxidation than the extruded samples at all the A_w s and temperatures. The treatment temperature of the extrusion process may have caused some initial oxidation of the extruded barley's lipids which may accounts for its higher oxidation status. The higher oxidation status of the raw samples may have been due to the fact that both autoxidation and lipoxygenase catalyzed oxidation were occurring in these samples. Lipoxygenase, which is principally a plant enzyme, is known to be distributed widely in cereals and legumes. Graveland *et al.*[19] reported that lipoxygenase in suspension of barley flour in water forms mainly mono and trihydroxy acids, and small amounts of dihydroxy and ketodihydroxy acids. These compounds may be concerned in the development of an oxidized off-flavor in barley during storage.

Table 1. Calculated rates* of lipid oxidation in stored raw and extruded barley powders

Sample	0.31 A_w		0.75 A_w	
	25°C	40°C	25°C	40°C
Raw	0.203	0.293	0.289	0.404
Run 1	0.118	0.213	0.169	0.220
Run 2	0.194	0.254	0.233	0.289
Run 3	0.041	0.070	0.069	0.178

* The rates are changes in oxidation, over the storage period (increase in lipid conjugation diene absorbance per one month interval).

The extruded sample containing the added sucrose had higher stability than the other extruded samples. This stability may be due to the caramelization-type browning compounds formed as a result of the extrusion process upon the added sucrose. Griffith and Johnson[20] reported that sugar cookies with produced a marked browning, exhibited greater stability to oxidative rancidity than cookies in which no browning ocurred. Recently, Rhee and Kim[21] reported that almost colorless intermediate compounds such as reductones and dehydroreductones produced by the caramelization-type browning reaction had antioxidant activity.

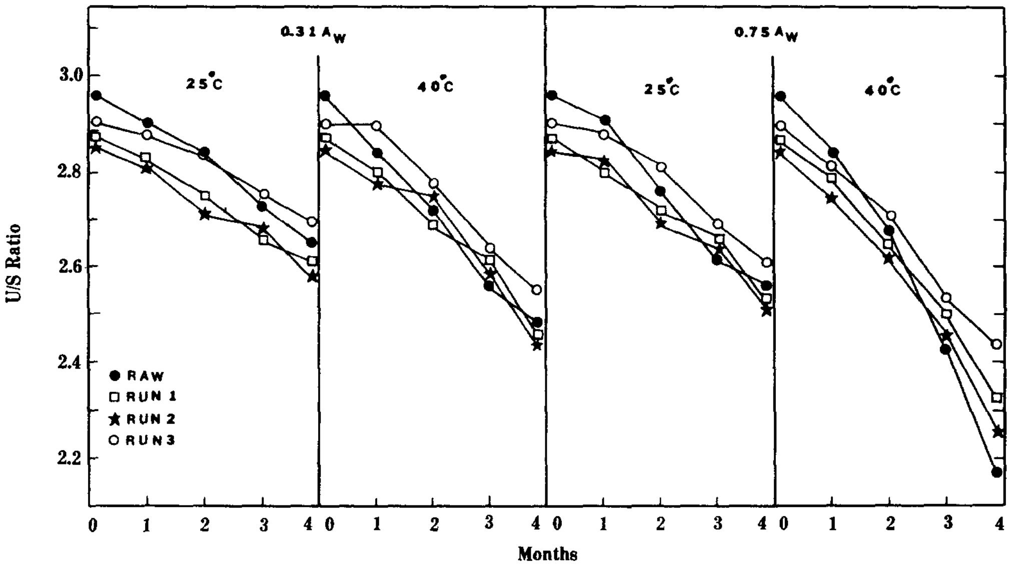

Fig. 2. Effects of water activities, temperatures and storage time on the U/S ratios of fatty acids of raw and extruded barley powders

Changes in fatty acid compoisition

Changes in the ratio of unsaturated to saturated fatty acids (U/S ratio) were used as a measure of changes in lipid composition of stored products. The changes U/S ratios at various stage of this experiment are shwon in Fig. 2. Since lipid oxidation is associated almost exclusively with unsaturated fatty acids, it can be expected that the U/S ratio decreases as a result of lipid oxidation during storage.

The U/S ratios in this study tended to decrease when the A_w was increased from 0.31 to 0.75. An A_w of about 0.33 has been found to be the most protective against lipid oxidation for dehydrated intermediated moisture foods[18]. An increase in temperature from 25 °C to 40 °C led to corresponding decreases in the U/S ratio. The results are as expected since lipid oxidation would proceed faster at higher temperature. These results were in agreement with the oxidation measurements obtained by lipid diene conjugation analysis.

The raw sample had higher percentage changes of U/S ratio than extruded samples (Table 2). Again, a combination of lipoxygenase catalyzed autoxidation and autoxidation is inferred. As shown in the Table 2, the extruded sample with containing sucrose had a lower U/S ratio change than obtained from the other extrusion methods. Again, this was in agreement with lipid oxidation measurement data. In this study, changes of U/S ratio during barley storage were lower than those of

Table 2. Calculated percentage changes* of U/S ratios in stored raw and extruded barley powders**

Sample	0.31 A_w		0.75 A_w	
	25°C	40°C	25°C	40°C
Raw	10.47	16.22	13.51	26.69
Run 1	9.38	14.58	11.81	19.44
Run 2	9.12	14.03	11.93	20.70
Run 3	7.24	12.41	10.00	15.86

* Percentage decrease between initial and final values.

** Ratio of unsaturated fatty acids to saturated fatty acids $(C_{16:1} + C_{18:2} + C_{18:3}) / (C_{14:0} + C_{16:0} + C_{18:0})$.

dried soybean curds during storage[22]. It may be due to the fact that soybean has a higher linolenic acid content than barley.

Changes in lipid free-amino groups

Fig. 3 shows the effects of changing the water activities and the temperatures on the lipid free-amino groups of the stored raw and extruded barley samples.

As shown in Fig. 3, incrase in temperature and A_w decreases the lipid free-amino group contents in all samples. The reason probably lies in the fact that increasing A_w and increasing temperature promoted increased carbonyl-amino reactions. Indeed, the literature indicates that phospholipid which contain amino groups such as phosphatidyl ethanolamine and

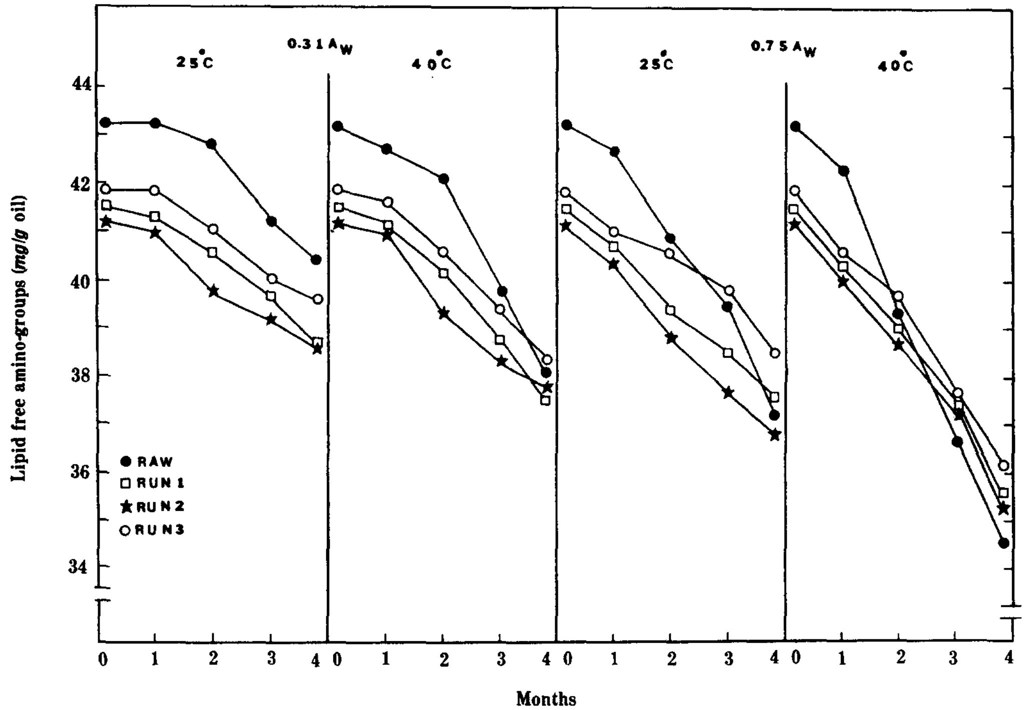

Fig. 3. Effects of water activities, temperatures and storage time on the lipid free-amino groups content (*mg/g* oil) of raw and extruded barley powders.

phosphatidyl serine are capable of contributing to the browning observed in foods. For example, Lea[23] noted that glucose in dried egg yolk was able to enter into Maillard type browning reactions with the amino-phospholipids of dried eggs. Similarly, Folch[24] reported that phosphatidyl ethanolamines isolated from brain changed color from white to a tan brown color only after two weeks of stoage in a vacuum descicator implicating Maillard reactions as the occurring phenomenon in the browning process. Ukhum[25] indicated that lipid free-amino groups decreased with increased in A_w and temperature in storage of processed cowpea powders.

The raw sample again had higher rates of losses than extruded samples (Table 3). This was probably because the enzyme systems were left intact in the raw sample therefore more oxidation products capable of reacting with the amino groups were formed. Even the so-called non-enzymatic Maillard browning may also have been accelerated by these intact enzyme systems such as glycosyl hydraolase enzymes capable of releasing glucose from complex polymer[26]. As shown in the Table 3, the extruded sample with containing sucrose had lower rates of losses than the other extruded samples. This was agreement with lipid oxidation data obtained by diene conjugation and U/S ratios. It is quite obvious, as a result of this study, that a combination of the browning phenomenon and lipid oxidation account for the loss of the lipid free-amino groups in these powders during storage.

Table 3. Calculated rates* of lipid free-amino groups content in stored raw and extruded barley powders

Sample	0.31 A_w		0.75 A_w	
	25°C	40°C	25°C	40°C
Raw	0.708	1.275	1.493	2.193
Run 1	0.748	1.008	1.048	1.508
Run 2	0.693	0.940	1.278	1.523
Run 3	0.555	0.880	0.823	1.433

* The rates are decrease in lipid free-amino groups content (*mg/g* oil) per one month interval.

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요 약

3가지 다른 조건하에서 제조된 압출보리와 생보리를 0.31 및 0.71의 수분활성과 25℃ 및 40℃의 온도에서 각각 4개월 저장하면서 지방질의 산화에 대한 수분활성과 온도의 영향에 대하여 연구하였다. 모든 시료로부터 컨출한 지방질중의 Conjugated diene의 함량은 저장기간의 경과와 함께 수분활성과 온도가 증가함에 따라 증가하였고, 지방산의 U/S비는 감소하는 경향이었다. 생보리는 압출보리보다 저장중 Conjugated diene함량의 증가와 U/S비의 감소가 더 심하였으며, 설탕을 첨가하여 제조한 압출보리는 다른 압출보리보다 저장중 산화에 대한 지방질의 안정성이 양호하였다. 모든 시료에서 추출한 지방질중 유리 아미노기를 함유하는 지방질의 함량은 저장중 수분활성과 온도가 증가함에 따라 감소하였다.

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