Buckwheat Browning and Color Assessment

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ABSTRACT

A modified procedure for measuring nonenzymatic browning of buckwheat groats was developed. The procedure is based on extraction of soluble colored materials, clarification of the resultant extracts, and spectrophotometric evaluation of the extracted color. Using buckwheat groats subjected to high storage temperatures, browning results obtained by this procedure were compared to surface color of the groats determined with a Hunterlab tristimulus colorimeter. The correlation coefficients between absorbance of the extracted color of 420 nm and CIE tristimulus values, X, Y, and Z, were −0.966, −0.914, and −0.947, and those between absorbance and Hunter L, a, and b values were −0.974, 0.970, and −0.901, respectively. When the modified procedure was used to investigate the influence of water activity on nonenzymatic browning of buckwheat groats, it was found that minimum production of pigments occurred at water activities corresponding to the monolayer moisture content. The correlations between absorbance of the extracted color and Hunter color values of samples stored at 0.11–0.67 water activities were lower than those obtained with samples subjected to high storage temperatures; however, they were still sufficiently high to be useful for predicting color changes in buckwheat groats and could be used commercially for routine quality-control purposes.

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Key words: Color assessment, *Fagopyrum esculentum*, storage temperature, storage water activity

Buckwheat (*Fagopyrum esculentum* Moench) is a cool climate dicotyledonous plant adapted to a short growing season and high elevations. It is of economic importance in Nepal, India, Pakistan, Afghanistan, Iran, China, Japan, Korea, Russia, Poland, Hungary, Yugoslavia, Canada, the United States, and Brazil. Some buckwheat is also grown in Czechoslovakia, Austria, Switzerland, Italy, France, South Africa, Great Britain, and Australia. In eastern Europe, buckwheat is a basic food item in porridges and soups. In North America, it is marketed primarily as pancake mixes. These prepared mixes may contain buckwheat mixed with wheat, corn, rice, or oat flours, and a leavening agent. Buckwheat is also used in mixtures with wheat flour for bread, noodles, spaghetti, macaroni, ready-to-eat breakfast flakes, health foods, and ethnic dishes. In Japan, buckwheat is marketed primarily as flour for manufacturing a variety of noodles (soba) and as groats. Groats, that part of the grain left after the hull is removed from the seed, and farina made from groats are used for breakfast food, porridge, and thickening materials in soups, gravies, and dressings (Taira 1974, Marshall and Pomeranz 1982). Most of the buckwheat grown in Canada and the United States is exported to Japan.

The most important quality attributes of buckwheat are groat color and flavor. The color is light green in freshly harvested seed but gradually changes to reddish brown during storage. The color change is accompanied by loss of desirable flavor and nutrients, and formation of brown pigments. Because of these changes, Japanese buckwheat millers import only new buckwheat crop, and marketing of grain older than one year is a problem for the industry. Although this problem has received industry-wide attention in recent years, there has been little research aimed at developing improved storage methods and objective quality standards for buckwheat.

Recently, however, Mazza and Campbell (1985) reported on the influence of water activity and temperature on dehulling and color of buckwheat seed stored for less than two months. In that study a Hunterlab colorimeter was used for the measurement of buckwheat color. The applicability of tristimulus color measurement for pigment concentration appeared limited, however, because the tristimulus coordinates varied over a relatively narrow range. Attempts to determine brown pigments in buckwheat using methods reported in the literature for browning determination in dehydrated vegetables (Hendel et al 1950) and in citrus products (Karel and Nickerson 1964, Meydav et al 1977) were unsuccessful. Present clarification procedures suffer from serious accuracy drawbacks, especially when the measurement of small differences in browning is required. This investigation was undertaken with the aim of developing a method for browning determination in buckwheat. The relationship between brown pigment concentration and surface color of buckwheat groats subjected to different storage regimes was also determined.

MATERIALS AND METHODS

Buckwheat

Mancan buckwheat, grown commercially during 1983 and 1984 near Morden, Manitoba, was used. The buckwheat was dehulled at a commercial buckwheat processing plant within one month after harvest, and the dehulled material was stored at −25 ± 1° C for two weeks before being subjected to a variety of storage regimes and analyses.

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Instrumental Color Measurements

Color measurements were made using a Hunterlab tristimulus colorimeter model D25L-9 (Hunter Associates Laboratory, Reston, VA) equipped to display color values in CIE tristimulus values (*Y, X,* and *Z*), CIE chromaticity coordinates (*Y, x,* and *y*), Hunter color values (*L, a,* and *b*), and CIELAB values (*L*, a*,* and *b**).

A 25-g sample was used for all measurements. The results are the mean values of these readings of each parameter taken after thoroughly mixing the sample in the sample holder each time.

Browning Determination

Browning was determined by measurement of the absorbance of clarified buckwheat extracts prepared by the following modified procedure: 1) whole groats equivalent to 5 g of dry solids were shaken with 25 ml of 50% aqueous ethanol in a wrist shaker for 30 min at room temperature; 2) the decanted solution was centrifuged at 18,000 rpm (39,100 × *g*) for 10 min at 2° C in a Sorval RCZ-B automatic refrigerated centrifuge and filtered through filter paper (Whatman No. 42), to obtain a fully clarified extract; 3) the absorbance of the clarified extracts was measured at 350–700 nm in a Beckman DU-50 spectrophotometer with 50% ethanol as the blank reference.

Storage Treatments

Browning determinations and instrumental color measurements were made on buckwheat groats stored at −25° C for 2–4 weeks; on samples kept in a forced-air oven at 60, 80, and 100° C for 0, 3, 6, 12, 24, 48, and 96 hr; and on samples stored for 19 months at 25° C in vacuum desiccators containing saturated salt solutions, which gave relative humidities of 11–67% (Greenspan 1977).

RESULTS AND DISCUSSION

Absorbance spectra of fresh, slightly, moderately, and severely browned buckwheat extracts are given in Figure 1. With increased browning of the buckwheat samples the spectra shifted to much higher absorption values in the wavelengths between 390 and 500 nm. Increase in absorbance in this wavelength range is the most frequently used variable to measure progress in nonenzymatic browning reactions on foods and model systems (Ellis 1959, Lee et al 1979, Reyes et al 1982) and indicates that the extraction and clarification procedures used in this work are suitable for buckwheat groats.

The results of the browning determinations, taken as the absorbance of the clarified extracts at 420 nm, and the tristimulus and Hunter color values of buckwheat groats stored at 60, 80, and 100° C for 0–96 hr are presented in Table I. As expected, the browning of the samples increased with heating time and temperature. In Figure 2, the rate of browning, calculated from graphs of browning values (A_{420}) versus time, is shown to increase sharply at temperatures above 70–75° C. This indicates that the

TABLE I
Absorbance of Extracted Color and Color Values of Whole Buckwheat Groats After Storage at 60, 80, and 100° C

Storage			Tristimulus Values			Hunter Color Values		
Temp. (° C)	Time (hr)	Absorbance (A_{420})	*X*	*Y*	*Z*	*L*	*a*	*b*
60	0	0.138	38.0	39.0	26.8	62.9	−2.2	18.6
	3	0.140	36.4	37.7	24.4	61.4	−1.2	19.4
	6	0.153	36.2	37.5	24.1	61.3	−1.8	19.6
	12	0.150	36.2	37.4	24.6	61.1	−1.4	18.9
	24	0.151	36.5	37.7	24.6	61.4	−1.5	19.3
	48	0.156	35.9	36.9	24.4	60.8	−0.9	18.8
	96	0.182	34.5	35.3	22.4	59.4	−0.4	19.2
80	0	0.139	37.9	38.9	26.9	62.9	−2.2	18.6
	3	0.152	36.6	37.9	25.4	61.6	−1.5	18.6
	6	0.157	36.0	37.2	24.1	61.0	−1.5	19.3
	24	0.197	34.6	32.2	23.6	59.4	0.2	18.0
	48	0.255	32.9	33.0	22.0	57.4	1.9	17.4
	72	0.279	30.9	30.5	19.8	55.3	3.2	17.4
100	0	0.137	38.1	39.7	27.1	63.0	−2.3	18.6
	3	0.168	37.9	39.2	26.4	62.6	−1.5	18.8
	6	0.208	35.4	36.0	23.7	60.0	0.2	18.6
	12	0.246	33.5	33.6	21.9	58.0	1.6	18.2
	24	0.364	29.1	28.4	18.4	53.3	4.2	16.8
	48	0.537	25.8	24.4	15.5	49.4	6.9	15.9

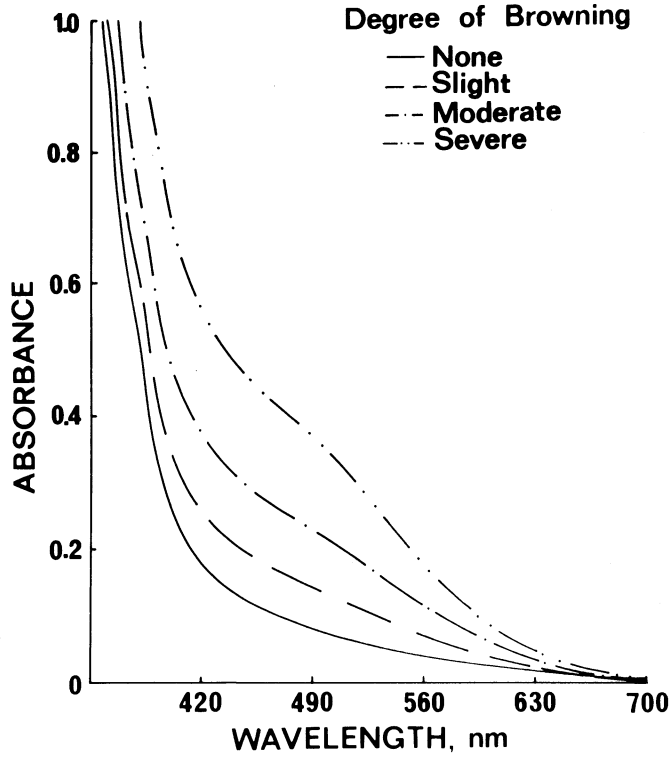

Fig. 1. Influence of degree of browning on absorbance spectra of buckwheat extracts.

TABLE II
Correlation Coefficients[a] for Color Values and Browning Index

Parameters	*X*	*Y*	*Z*	*L*	*a*	*b*	A_{420}	A_{440}	A_{460}
$(a^2 + b^2)^{1/2}$	0.788	0.786	0.786	0.803	−0.856	0.957	−0.775	−0.771	−0.785
$(\tan^{-1} b/a)$	0.972	0.926	0.926	0.981	−0.995	0.935	−0.974	−0.969	−0.977
X		0.939	0.991	0.999	−0.976	0.885	−0.966	−0.962	−0.969
Y			0.921	0.941	−0.929	0.867	−0.914	−0.908	−0.915
Z				0.986	−0.956	0.818	−0.947	−0.943	−0.948
L					−0.984	0.901	−0.974	−0.970	−0.977
a						−0.932	0.970	0.964	0.974
b							−0.901	−0.896	−0.908
A_{420}								0.999	0.999
A_{440}									0.992

[a] All coefficients ≥0.406 significant at $P \leq 0.001$; 55 df.

sample temperature is very important in determining its browning behavior. The calculated rate of browning was plotted on an Arrhenius-type plot versus 1/T (Fig. 3) and used to calculate the energy of activation of the browning reactions. This energy was found to be 80 J/kmol and comparable to that reported for other foods and model systems (Flink et al 1974, Petriella et al 1985).

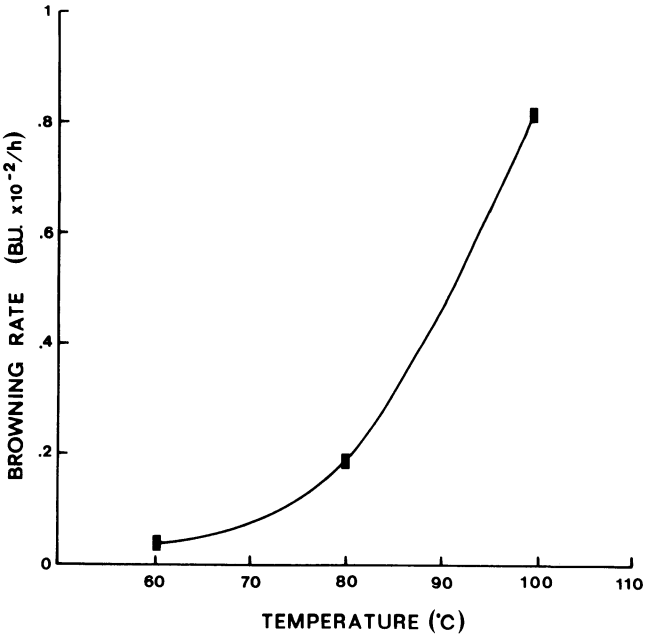

Fig. 2. Rate of browning of buckwheat groats.

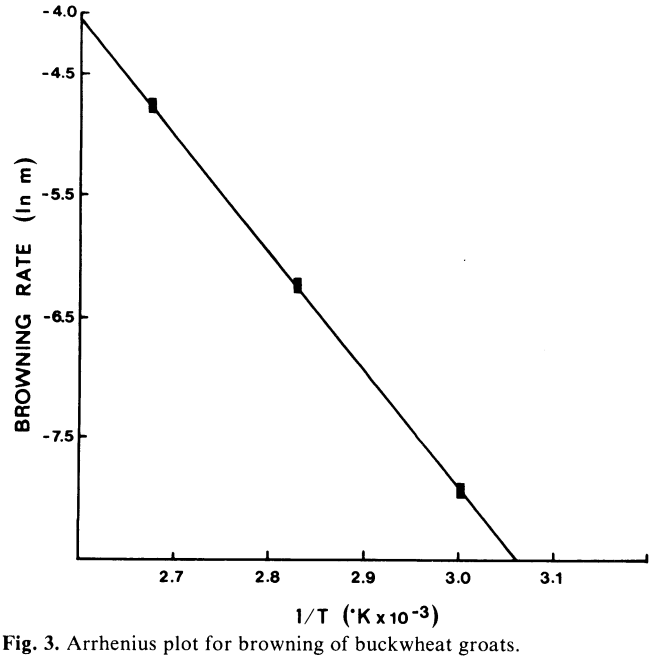

Fig. 3. Arrhenius plot for browning of buckwheat groats.

All tristimulus and Hunter color values were highly correlated with absorbance of the clarified extracts at 420, 440, and 460 nm and with each other (Table II). The regression equation of Y and X, for instance, was: $Y = -6.92 + 1.21\,X$ ($r = 0.939$; $P \leq 0.001$; 55 df).

Multiple regression analysis for the absorbance of the extracted color at 420 nm, based on the values of X and Y gave an estimating equation: $A_{420} = 1.28 - 0.029\,X - 0.0014\,Y$ ($r = 0.966$; $P \leq 0.001$; 53 df). However, this was only a marginal improvement in fit over the linear equations based on Y only: $A_{420} = 1.01 - 0.023\,Y$ ($r = -0.914$; $P \leq 0.001$; 55 df).

In light of the results obtained with buckwheat samples stored at 60, 80, and 100° C for 0–96 hr, it was deemed desirable to determine if the outlined method for browning determination could be used

TABLE III
Absorbance of Extracted Color and Tristimulus Values of Buckwheat Samples Stored at 25° C and Five Water Activities for 19 Months

Water Activity	Moisture Content (% db)	Absorbance Index (A_{420})	Tristimulus Values		
			X	Y	Z
0.11	4.1	0.257 b[a]	26.3 c	26.2 c	15.1 b
0.23	6.7	0.233 c	26.7 b	26.5 b	15.1 b
0.31	8.7	0.241 c	27.1 a	27.0 a	15.3 a
0.51	13.0	0.290 a	25.3 d	24.7 d	13.4 d
0.67	13.8	0.238 c	26.4 bc	25.9 c	14.2 c

[a] Means separated by Duncan's multiple range test, 0.01 level of probability.

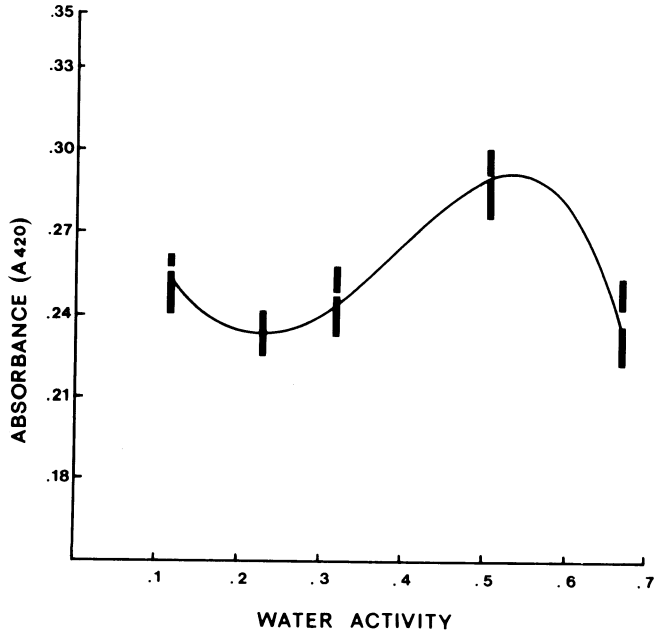

Fig. 4. Color change of buckwheat groats stored at 25° C for 19 months as a function of water activity

TABLE IV
Correlation Coefficients[a] for Absorbance of Extracted Color and Surface Color of Buckwheat Samples Stored at 25° C and Five Water Activities for 19 Months

Parameters	Y	Z	L	a	b	A_{420}	A_{440}	A_{460}
X	0.979	0.870	0.189	−0.642	0.312	−0.802	−0.789	−0.821
Y		0.933	0.142	−0.785	0.202	−0.780	−0.771	−0.816
Z			0.123	−0.858	−0.165	−0.598	−0.596	−0.664
L				0.044	0.512	−0.201	−0.195	−0.177
a					0.181	0.499	0.505	0.579
b						−0.503	−0.486	−0.427
A_{420}							0.999	0.998
A_{440}								0.998

[a] All coefficients ≥0.480 significant at $P \leq 0.001$; 43 df.

to investigate the effect of water activity on browning of buckwheat groats.

Table III gives the absorbance of the extracted color and tristimulus color values of buckwheat samples stored at 25° C and 0.11–0.67 water activity for 19 months. As can be seen, the maximum concentration of browning pigments occurred at intermediate water activities. Figure 4 more clearly shows that maximum browning pigment production occurs at 0.45–0.55 water activity. This behavior is consistent with the notion that water activity influences browning.

The calculated BET monolayer for the material stored for 19 months was 7.4 g H_2O/100 g of solids. This corresponded to a water activity of 0.275. Dry foods are usually considered to be most stable to chemical reactions if their moisture content is at or near the BET monolayer (Labuza et al 1970). The results presented in Table III and Figure 4 clearly show that color degradation is minimized when buckwheat groats are stored at the relative humidity corresponding to the monolayer moisture content. Therefore, storing buckwheat at 6–8% moisture content rather than at the traditional 12–16% may reduce degradation of its color. The correlations between absorbance of the extracted color and surface color values of buckwheat groats stored at 25° C and 0.11–0.67 water activity (Table IV) were lower than those obtained with samples stored at 60–100° C for 0–96 hr. However, they were still sufficiently high to be used for predicting changes in surface color of buckwheat groats. Therefore, on the basis of the data presented, it may be suggested that either the absorbance of the extracted color or tristimulus color values could be useful commercially for routine quality control instead of subjective, visual assessment of buckwheat groats.

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