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Effects of Seeding Time on Lipid Content and Fatty Acid Composition of Buckwheat Grains

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The effects of cropping season on lipid content and fatty acid composition of buckwheat grains were investigated on five cultivars by two seeding times. The early-seeding culture, as compared with the late-seeding culture, gave significantly higher lipid content and arachidic, behenic, oleic, and eicosenoic acid contents and lower linoleic and linolenic acid contents. The daily mean temperature during ripening showed significant positive correlations with lipid content and oleic acid content and negative correlations with linoleic and linolenic acid contents. As to the fatty acid composition, oleic and linoleic acids were main acids, and the dominant fatty acid was oleic acid in early-seeding culture and was linoleic acid in late-seeding culture. There was a highly negative correlation between oleic and linoleic acid contents.

Buckwheat grain is used as human food and also livestock and poultry feed. As for food, most of buckwheat is marketed in the form of flour. The flour is used primarily for making griddle cakes and is more commonly marketed in the form of pancake mixes than as pure buckwheat flour in U.S. (Marshall and Pomeranz, 1982). In Japan, however, buckwheat flour is mostly used for Soba, or Sobakiri (buckwheat noodle), which is prepared at Soba shops and at home from a mixture with 30–70% wheat flour. Japanese market for Soba making requires new crop seed because of the retention of greenish color of the testa and the fresh flavor of the grain. For Soba

making, it is known that buckwheat flour must not be stored over 1 week after purchase because of the deterioration of its palatability. As one of the reasons for the deterioration during storage of the grain and after milling, it may be pointed out that lipid in the grain and flour is broken down by lipases into free fatty acids. The deterioration of buckwheat flour is faster than that of wheat flour because buckwheat flour contains embryo part, which is high in lipid content (Dorrell, 1971) and also lipase content. In the previous study on rice grain, it was shown that the temperature during ripening correlated with the lipid content and fatty acid composition (Taira et al., 1979). The seeding time of buckwheat is April to September in the south area and July to August in the north area in Japan. Accordingly, it was suggested that the seeding time or cropping season may affect lipid content and fatty acid composition of buckwheat grain. Little information is available on the influence of seeding time on lipid content and fatty acid composition of buckwheat grain. Therefore,

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Table I. Flowering and Maturing Stages (1981) and Daily Mean Temperature during Ripening

cultivar	flowering stage early seeding[a]	flowering stage late seeding[a]	maturing stage early seeding	maturing stage late seeding	daily mean temp during ripening, °C early seeding	daily mean temp during ripening, °C late seeding
Botansoba	Jul 15	Aug 28	Aug 26	Oct 24	19.9	17.4
Hashigamiwase	Jul 14	Aug 27	Aug 24	Oct 22	20.3	17.6
Inazairai	Jul 25	Sep 2	Sep 5	Oct 27	19.9	17.9
Shinano No. 1	Jul 20	Aug 30	Sep 1	Oct 27	19.6	17.4
Kyuushuuakisoba	Jul 25	Sep 3	Sep 12	Oct 27	19.7	17.2

[a] Seeding time of early-seeding culture, Jun 14; late-seeding culture, Aug 1.

Table II. Whole and Dehulled Buckwheat Grains 1000-Kernel Weight and Lipid Content of Dehulled Buckwheat Grains

cultivar	1000-kernel weight, g whole grain early seeding	late seeding	mean	1000-kernel weight, g dehulled grain early seeding	late seeding	mean	lipid, % on dry basis early seeding	late seeding	mean
Botansoba	32.8	37.2	35.00	26.9	31.5	29.20	3.04	2.93	2.99
Hashigamiwase	32.2	35.8	34.00	25.1	30.0	27.55	3.27	2.97	3.12
Inazairai	34.8	32.4	33.60	27.4	27.5	27.45	3.16	2.71	2.94
Shinano No. 1	33.6	36.2	34.90	27.5	27.9	27.70	3.13	2.70	2.92
Kyuushuuakisoba	30.4	31.3	30.85	23.3	25.1	24.20	3.14	2.96	3.05
mean	32.76	34.58		26.04	28.40		3.15	2.85	
LSD (5%)									
cultivar									
seeding time								0.19	

Table III. Saturated Fatty Acid Composition[a] (Weight Percent of Total Acids) of Dehulled Buckwheat Grains

cultivar	14:0 early seeding	late seeding	mean	16:0 early seeding	late seeding	mean	18:0 early seeding	late seeding	mean	20:0 early seeding	late seeding	mean	22:0 early seeding	late seeding	mean
Botansoba	0.2	0.2	0.20	16.0	15.9	15.95	2.1	1.9	2.00	1.9	1.7	1.80	2.3	2.0	2.15
Hashigamiwase	0.2	0.1	0.15	15.8	15.7	15.75	2.0	1.7	1.85	2.1	1.8	1.95	2.1	2.0	2.05
Inazairai	0.1	0.1	0.10	15.4	16.3	15.85	1.8	1.8	1.80	2.2	2.2	2.20	2.5	2.3	2.40
Shinano No. 1	0.2	0.2	0.20	15.7	15.8	15.75	1.8	1.8	1.80	2.4	2.2	2.30	2.1	2.0	2.05
Kyuushuuaki-soba	0.1	0.1	0.10	15.3	15.8	15.55	1.9	1.7	1.80	1.7	1.6	1.65	2.1	1.8	1.95
mean	0.16	0.14		15.64	15.90		1.92	1.78		2.06	1.90		2.22	2.02	
LSD (5%)															
cultivar											0.22			0.20	
seeding time											0.14			0.12	

[a] Fatty acids are expressed as the ratio of number of carbons to the number of double bonds.

Table IV. Unsaturated Fatty Acid Composition[a] (Weight Percent of Total Acids) of Dehulled Buckwheat Grains

cultivar	16:1 early seeding	late seeding	mean	18:1 early seeding	late seeding	mean	18:2 early seeding	late seeding	mean	18:3 early seeding	late seeding	mean	20:1 early seeding	late seeding	mean
Botansoba	0.3	0.3	0.30	38.5	35.3	36.90	32.9	36.9	34.90	2.1	2.2	2.15	3.7	3.6	3.65
Hashigamiwase	0.3	0.3	0.30	38.0	35.7	36.85	33.9	36.8	35.35	1.9	2.5	2.20	3.6	3.5	3.55
Inazairai	0.2	0.2	0.20	39.4	34.6	37.00	32.5	36.0	34.25	1.8	2.4	2.10	4.2	4.0	4.10
Shinano No. 1	0.3	0.3	0.30	38.7	34.4	36.55	33.3	37.0	35.15	1.8	2.4	2.10	3.8	3.8	3.80
Kyuushuuaki-soba	0.2	0.3	0.25	39.4	35.5	37.45	33.5	36.8	35.15	1.9	2.5	2.20	3.8	3.7	3.75
mean	0.26	0.28		38.80	35.10		33.22	36.70		1.90	2.40		3.82	3.72	
LSD (5%)															
cultivar														0.14	
seeding time					1.21			0.51			0.28			0.09	

[a] Fatty acids are expressed as the ratio of number of carbons to the number of double bonds.

investigations were undertaken to study lipid content and fatty acid composition of buckwheat grain by two seeding time cultures.

MATERIALS AND METHODS

Buckwheat grains of five cultivars by early- and late-seeding cultures were collected from a field experiment conducted by the Tohoku National Agricultural Experiment Station, Japan, in 1980. The seeding time, flowering and maturing stages, and daily mean temperature during ripening are shown in Table I. The hulls (pericarps) were removed by hand, and the kernels were ground to pass a 30-mesh sieve. Lipid was extracted from 10-g ground samples on a Butt type extractor by using diethyl ether as a solvent. Fatty acids in the lipid were determined by gas chromatography after transesterification to their methyl ester by the boron trifluoride method as outlined by the Association of Official Analytical Chemists (1975). Esters were separated by using a Shimadzu GC-6APF chromatograph equipped with a FID by using a 3 mm × 3 m glass column packed with Unisol 3000 Uniport C, 80–100 mesh (Gasukurokogyo Co., Ltd.). The column temperature was 240 °C, and the carrier gas was nitrogen at a flow rate of 40 mL/min. Compound retention times

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Table V. Correlation Coefficients of Lipid Content with Fatty Acid Content, Fatty Acid Content Pair, and Lipid and Fatty Acid Contents with 1000-Kernel Weight and Daily Mean Temperature during Ripening

	14:0	16:0	18:0	20:0	22:0	16:1	18:1	18:2	18:3	20:1	1000-kernel wt[a]	daily mean temp during ripening[b]
lipid	0.073	-0.601	0.370	-0.021	0.196	-0.009	0.865**	-0.739*	-0.784**	-0.071	-0.410	0.802**
14:0		0.261	0.581	0.308	-0.106	0.655*	0.016	-0.089	-0.256	-0.359	0.248	0.190
16:0			0.139	0.135	-0.028	0.252	-0.636*	0.415	0.525	-0.151	0.343	-0.385
18:0				0.000	0.352	0.091	0.443	-0.533	-0.472	-0.149	-0.202	0.626
20:0					0.518	-0.134	0.150	-0.362	-0.395	0.520	0.058	0.357
22:0						-0.625	0.496	-0.687*	-0.524	0.722*	-0.017	0.604
16:1							-0.289	0.351	0.280	-0.771**	0.334	-0.257
18:1								-0.947**	-0.891**	0.265	-0.489	0.917**
18:2									0.886**	-0.424	0.467	-0.960**
18:3										-0.347	0.332	-0.889**
20:1											-0.203	0.260

[a] Dehulled grain. [b] Key: *, significant at the 5% level; **, significant at the 1% level.

and areas were automatically recorded by means of a Shimadzu Chromatopac C-R2A. Standard methyl ester fatty acid mixtures were separated under identical conditions to identify the compounds and to calculate the response factors of the acids. Moisture content was determined by heating the samples for 1 h at 135 °C, and lipid contents were reported on a dry basis of grain samples.

RESULTS AND DISCUSSION

As the mean values of duplicated data, Table II shows the 1000-kernel weight of whole and dehulled grains and lipid content of dehulled grains, and Tables III and IV show the saturated and unsaturated fatty acid compositions of dehulled grains, respectively. Analysis of variance for two-way layout for 1000-kernel weight and lipid and fatty acid contents have been carried out. The results of significance at the 1 and 5% levels by the F value are also shown as least significant difference (LSD) at the 5% level in Tables II–IV.

The early-seeding culture, as compared with the late-seeding culture, gave higher lipid content. The range and mean value of early-seeding culture/late-seeding culture ratio (E/L ratio) were 1.04 (Botansoba)–1.17 (Inazairai) and 1.11. As to the 1000-kernel weight, the late-seeding culture had heavier tendency in whole and dehulled grains, but the difference between both cultures was not significant (Table II).

There were significant differences between the early- and late-seeding cultures in arachidic and behenic acid contents on saturated fatty acid composition (Table III) and in oleic, linoleic, linolenic, and eicosenoic acid contents on unsaturated fatty acid composition (Table IV). Compared with the late-seeding culture, the early-seeding culture gave high arachidic, behenic, oleic, and eicosenoic acid contents and low linoleic and linolenic acid contents. The range and mean values of E/L ratio were 1.00 (Inazairai) to 1.17 (Hashigamiwase) and 1.09 in arachidic acid, 1.05 (Hashigamiwase and Shinano No. 1) to 1.17 (Kyuushuuakisoba) and 1.10 in behenic acid, 1.06 (Hasigamiwase) to 1.14 (Inazairai) and 1.11 in oleic acid, 1.00 (Shinano No. 1) to 1.05 (Inazairai) and 1.03 in eicosenoic acid, 0.89 (Botansoba) to 0.92 (Hashigamiwase) and 0.90 in linoleic acid, and 0.75 (Inazairai and Shinano No. 1) to 0.95 (Botansoba) and 0.79 in linolenic acid, respectively (Tables III and IV).

There were significant differences among the cultivars in arachidic and behenic acid contents on saturated fatty acid composition and eicosenoic acid content on unsaturated fatty acid composition. The highest mean value/the lowest mean values of two seeding cultures on the cultivar in arachidic, behenic, and eicosenoic acids were 1.39, 1.23,

and 1.15, respectively (Tables III and IV). The results of the fatty acid composition show that there was neither seeding time difference nor cultivar difference for the lower carbon saturated fatty acids (myristic, palmitic, stearic acids) (Table III) and that there was no cultivar difference for C_{16} and C_{18} unsaturated fatty acids (palmitoleic, oleic, linoleic, linolenic acids) (Table IV).

Correlation coefficients of lipid content with fatty acid content, fatty acid content pair, and lipid and fatty acid contents with 1000-kernel weight of dehulled grain and daily mean temperature during ripening on all samples of the early- and late-seeding cultures are shown in Table V. The lipid content showed significant positive correlation with daily mean temperature during ripening. Taira et al. (1979) reported that lipid content of brown rice also correlated positively with daily mean temperature during ripening. The daily mean temperature during ripening showed significant positive correlation with oleic acid content and significant negative correlations with linoleic and linolenic acid contents. The same tendency was observed in the correlations between fatty acid content and daily mean temperature during ripening in the previous study of brown rice (Taira et al., 1979). The lipid content showed significant positive correlation with oleic acid content and significant negative correlations with linoleic and linolenic acid contents. From the relationship between fatty acid contents, there were significant positive correlations between myristic acid–palmitoleic acid, behenic acid–eicosenoic acid, and linoleic acid–linolenic acid and significant negative correlations between palmitic acid–oleic acid, behenic acid–linoleic acid, oleic acid–linoleic acid, oleic acid–linolenic acid, and palmitoleic acid–eicosenoic acid. The highest value showed between oleic and linoleic acid contents. As to the relationship between fatty acid contents in cereals, it was reported that there was also the highest and negative correlation between oleic and linoleic acid contents in rice (Taira et al., 1979), Japanese barnyard millet (Taira, 1983), foxtail millet (Taira, 1984), pearl millet (Jellum and Powell, 1971), Job's tears (Taira et al., 1985), and corn (Jellum, 1970).

The main fatty acids of buckwheat grain were oleic and linoleic acids, and both the acids comprised about 70% of total acids. The dominant fatty acid, however, varied from oleic acid in early-seeding culture to linoleic acid in late-seeding culture. The relations of oleic acid content ($X\%$) with linoleic acid content ($Y\%$) and of oleic and linoleic acid contents with daily mean temperature during ripening (Z °C) were expressed by the following regression equations: $Y = -0.88X + 67.56$, $X = 1.45Z + 9.80$, and $Y = -1.42Z + 61.43$. From the regression equations, an equal value of both the fatty acids gave 35.94%, and its daily mean temperature during ripening gave 18.03 °C from oleic

acid content and 17.95 °C from linoleic acid content.

As to the variation of fatty acid composition of seed lipid, it was known that some plants produce more highly unsaturated lipid when grown at lower temperature. The effect, however, appeared to be limited to certain species (Canvin, 1965). Our results show that buckwheat is temperature-sensitive plant for variation in fatty acid composition and lipid content of the grain. On the basis of this work, the early-seeding culture may be less desirable than the late-seeding culture for the storage because of higher lipid content and also higher temperature after harvest. However, the late-seeding buckwheat may be easily oxidized during storage period, especially for the ground flour, because of higher linoleic and linolenic acids. Increasing those essential fatty acids by the late-seeding time may be of nutritional importance.

Registry No. Arachidic acid, 506-30-9; behenic acid, 112-85-6; oleic acid, 112-80-1; linoleic acid, 60-33-3; linolenic acid, 463-40-1; eicosenoic acid, 28933-89-3; myristic acid, 544-63-8; palmitic acid, 57-10-3; stearic acid, 57-11-4; palmitoleic acid, 373-49-9.

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Mobility of Water in Wheat Flour Suspensions as Studied by Proton and Oxygen-17 Nuclear Magnetic Resonance

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The mobility of water in wheat flour suspensions and doughs (30–95% moisture) was investigated by nuclear magnetic resonance (NMR), in water and deuterium oxide. Two frequencies (20, 360 MHz) and two pulse sequences were employed for the proton (^1H) data; the standard 34 MHz and single pulse were used for the oxygen-17 (^{17}O) NMR data. The standard isotropic two-state model with fast exchange was used to interpret these data by means of the Derbyshire and Kumosinski models. The correlation time for the water "bound" by wheat flour was calculated to be 16.7 ps. The results suggested that the best NMR methodology for the investigation of water mobility in wheat flour suspensions was provided by ^{17}O NMR in deuterium oxide. However, both ^{17}O and ^1H NMR results showed the same trend in the dependence of the transverse relaxation rate on flour concentration in both water and deuterium oxide.

INTRODUCTION

In recent years one of the most successful techniques employed to investigate water binding and water mobility in biological systems is nuclear magnetic resonance (NMR) spectroscopy (Fuller and Brey, 1968; Steinberg and Leung, 1975; Hansen, 1976; Woessner, 1977; Ulmius et al., 1977; Eisenstadt and Fabry, 1978; Leung et al., 1979; Leung et al., 1983; Lang and Steinberg, 1983; Baianu et al., 1985). NMR spectroscopy provides a rapid, sensitive, noninvasive, and nondestructive determination of the molecular mobility of water in complex systems such as foods. Two NMR relaxation parameters, T_1 (spin–lattice or longitudinal relaxation) and T_2 (spin–spin or transverse relaxation) (Deslauriers and Smith, 1980), monitor a wide range of molecular mobilities of water in a macromolecular system. The complexity of such a system produces two major concerns: (1) the nucleus to be probed and (2) the model to be adopted for data interpretation.

First, the majority of NMR studies of food systems have been carried out by probing the proton (^1H) nucleus. Recently, however, difficult problems with the interpretation of ^1H NMR relaxation data in macromolecular systems were pointed out; the major concern is with the relative influence of the various relaxation mechanisms that contribute to the line width of the water peak in the ^1H NMR spectra of such complex systems (Kalk and Berendsen, 1976; Edzes and Samulski, 1978; Koenig et al., 1978). These references stated that two relaxation mechanisms that contribute significantly to the water proton line broadening are (1) the cross-relaxation between the bulk of the water protons and protons of the macromolecule and (2) the proton exchange between distinct states of water, i.e. "bound" and "free" water.

Therefore, recent interest in measuring water binding and hydration of macromolecules has been directed to oxygen-17 (^{17}O) NMR (Halle and Wennerstrom, 1981; Halle et al., 1981; Laszlo, 1983; Lioutas, 1984; Lioutas et al., 1985b). The advantages of measuring ^{17}O are discussed by Halle et al. (1981); of major consequence is that "except for a narrow pH range around neutral, the ^{17}O relaxation is not influenced by proton (deuterium) exchange with prototropic residues on the protein". Therefore, the ^{17}O

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